

# Processing of fuel oil ash from thermal power plant with extraction of vanadium and nickel

**K. V. Goncharov**, Senior Researcher<sup>1</sup>, e-mail: goncharov-imet@mail.ru

**D. Yu. Kashekov**, Research Assistant<sup>1</sup>, Postgraduate, e-mail: deniskashekov@mail.ru

**G. B. Sadykhov**, Head of Laboratory<sup>1</sup>, Chief Researcher, e-mail: guseyn.sadykhov@gmail.com

**T. V. Olyunina**, Senior Researcher<sup>1</sup>, e-mail: toliun@yandex.ru

<sup>1</sup> A. A. Baikov Institute of Metallurgy and Materials Science (Russian Academy of Sciences), Moscow, Russia.

The article presents results of research on extraction of vanadium and nickel from fuel oil ash. The studied ash contains a significant amount of valuable components (7.82% of  $V_2O_5$  and 0.74% of NiO), which makes it a promising raw material for processing. We researched the influence of oxidizing roasting and its duration, the type of charge mixing and the amount of sodium carbonate addition on the level of extraction of vanadium and nickel through consecutive water and sulphuric acid leaching. The article also presents the chemical processes that occur during oxidizing roasting of ash with different amounts of sodium carbonate additions and their influence on the results of extraction of vanadium and nickel. We established that vanadium is generally extracted at the water leaching stage, whilst nickel is extracted only at the sulphuric acid leaching stage this allows for a selective separation of vanadium from nickel. The extraction level of nickel can reach 56.7%, yet it may decrease considerably due to the formation of insoluble nickel ferrite through maximum extraction of vanadium. In the article we offer a schematic diagram of ash processing, where ash is introduced at the wet briquetting stage with addition of 50% of soda. After drying, the obtained briquettes go through 60 minutes of oxidizing roasting at the temperature of 500 °C. We then leach the roasted product in water at the temperature of 80 °C for 60 minutes. During this process nearly 82.0% of  $V_2O_5$  goes into the solution, whilst almost all of nickel remains in the solid residue. After that, we extract vanadium from the vanadate solution by sedimentation of ammonium vanadates to obtain a marketable high-purity vanadium pentoxide. Afterwards, we leach the solid residue with a 3% sulphuric acid for 60 minutes to extract nickel. The solid residue, whose mass equals 42.4% of the mass of the initial ash, contains 56.9% of  $Fe_2O_3$ , 2.1% of  $V_2O_5$ , 1.4% of NiO etc. It poses no harm to the environment and may be further processed as iron-ore or titanomagnetite raw materials at the existing enterprises with extraction of iron, vanadium and, perhaps, nickel.

**Key words:** vanadium, nickel, ash, utilization, processing, fuel oil, leaching, roasting, extraction.

**DOI:** 10.17580/nfm.2020.01.01

## Introduction

During oil processing, vanadium and nickel cumulate in heavy fractions, especially in fuel oil [1]. When fuel oil is burned at a thermal power plant, a significant amount of technogenic wastes (ash) is formed. Nowadays, there are more than 110 thousand tons of such ashes on the territory of Russia, and the number continues to grow. For example, the Murmansk thermal power plant alone currently produces more than 1000 tons of ash per year [2]. These ashes contain up to 20% of  $V_2O_5$ , whilst traditional vanadium raw materials (titanomagnetites) have to contain only 1.5–2% of  $V_2O_5$  for profitable processing. Furthermore, vanadium in the ashes is partially present in a soluble form, which poses a serious environmental threat to ground waters and basins [3–5]. Subsequently, developing a technology for utilization and neutralization of vanadium-containing fuel oil burning wastes is important from both economic and ecological point of view. The problem of extraction of vanadium and other valuable components has been widely considered in several scientific articles [6–8]. However, due to highly heterogeneous composition of ashes and ash slimes

no universally efficient technology for their processing has yet been designed. Hence, further research in this field is required.

## Materials and research methods

For our research we used a sample of ash from the state district power plant (GRES) in the town of Konakovo. The sample has the following composition, % :  $Fe_{total}$  (45.0), FeO (57.86),  $SiO_2$  (9.05),  $V_2O_5$  (7.82), CaO (3.40),  $Al_2O_3$  (2.72), NiO (0.74), MnO (0.04), MgO (0.70),  $Na_2O$  (0.36),  $Cr_2O_3$  (0.01),  $SO_3$  (5.94), C (4.23), LOI (6.3).

Sodium carbonate (coarseness: –0.1 mm, grade: CP) was added as an additional reaction ingredient for sintering. Sulphuric acid (grade: CP) was used for leaching.

Here we will describe the preparation of samples, roasting and leaching. First of all, the initial ash was mixed with sodium carbonate, and both dry and wet mixing were applied as well as the subsequent briquetting and drying. The obtained charge samples (or briquettes) were roasted in a muffle furnace at the temperature of 300–500 °C in an air atmosphere. After that, the samples were consecutively leached in water and acid.

The water leaching lasted one hour at the temperature of 70–80 °C and the ratio of S:L = 1:20. After the leaching we filtered the solution and determined the level of  $V_2O_5$  in it, whilst the solid residue was acid-leached for one hour in a 3% sulphuric acid at a room temperature and the ratio of S:L = 1:20. After the leaching we filtered the solution and analysed it for the presence of  $V_2O_5$  and Ni. We used the Mohr salt titration method to estimate the vanadium content in the solutions [9]. The content of nickel in the solutions was estimated by the atomic absorption spectrophotometry method by using the Thermo scientific Ice 3000 series instrument.

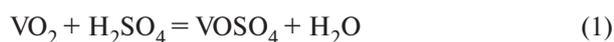
We used the FACT software package to perform the thermodynamic calculations [10].

The X-ray phase analysis of the samples was carried out with the DRON-3M diffractometer with  $CuK\alpha$ -radiation.

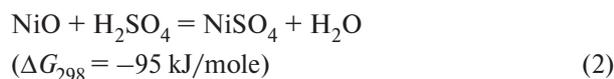
### Results and discussion

According to the X-ray phase analysis data, the main phase of the ash is goethite  $FeOOH$ . Vanadium in the ash is distributed between  $VO_2 \cdot V_2O_3$ , spinel  $FeO \cdot V_2O_3$  and vanadium bronze  $NaV_6O_{15}$ . The ash also contains calcium sulphite  $CaSO_3$ , calcium aluminosilicate  $CaAl_2Si_2O_8$ , quartz and soot carbon.

As the oxidation level of vanadium in the initial ash is  $V^{3+}$  and  $V^{4+}$  and vanadium practically does not dissolve in water, only 1.9% of vanadium is extracted by water leaching. However, even such a low level of extraction is rather harmful for environment as the maximum permissible concentration of  $V_2O_5$  in water should not exceed 0.1  $g/m^3$  [7]. To estimate the possibility of direct extraction of valuable components, we performed ash leaching in a 3% sulphuric acid. Under these conditions, the extraction level of vanadium was 55.1% thanks to a good solubility of  $V^{4+}$  compounds [11]:



The ash contains 0.74% of NiO which, possibly, does not form independent compounds and is present mainly in an oxide form together with FeO. Nickel is almost unextractable by water leaching (the extraction level is only 0.5%). The level of extraction by acid leaching equals 57.0% thanks to the formation of a very soluble nickel sulphate according to the reaction:



To increase the level of extraction of vanadium from ashes, we must oxidize vanadium to  $V^{5+}$  and bind it into soluble compounds. Oxidizing roasting with addition of  $Na_2CO_3$  allows us to obtain soluble sodium vanadates, suitable for further extraction.

Fig. 1 shows the results of the research on the influence of the duration of oxidizing roasting on the total extraction levels of vanadium and nickel after consecutive water and

sulphuric acid leaching. We established that 60 minutes of oxidizing roasting allows us to increase the extraction level of vanadium to 66.5%, whilst the extraction level of nickel was 53.5%. Extending the duration does not increase the extraction levels.

We studied the possibility of increasing the extraction level of vanadium through wet mixing of ash with soda. Wet mixing should enable a better contact between reagents and fuller transfer of vanadium into water-soluble sodium vanadates. If the amount of added sodium carbonate is increased to 50%, almost all of vanadium transfers into soluble forms. Table 1 shows the results of the study on the influence of the charge mixing type on the extraction levels of vanadium and nickel.

Wet mixing at the water leaching stage increases the extraction level from 27.4% to 41.1% and the total extraction level from 63.9% to 78.5%. This is conditioned by two factors. Firstly, wet mixing enables a more even distribution of soda in the ash mass and significantly increases the contact surface, which accelerates diffusion processes when roasting is performed without a liquid phase. Secondly, this type of mixing is accompanied by partial alkaline leaching, which also leads to the growth of extraction level of vanadium through dissolution of vanadium bronze  $NaV_6O_{15}$  [11].

Also, by applying wet mixing we increase the extraction level of nickel from 42.8% to 56.8%, which is slightly lower than by applying direct sulphuric acid leaching (57.0%). This may be related to the formation of nickel ferrite poorly soluble in a 3% sulphuric acid solution during roasting – according to the reaction (3):

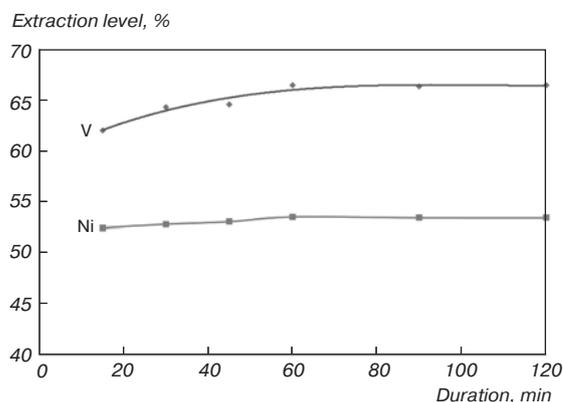
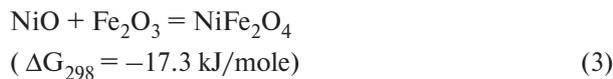


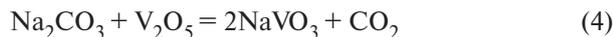
Fig. 1. Dependence of the extraction level of elements on the duration of oxidizing roasting of ash at the temperature of 350 °C with addition of 20% of  $Na_2CO_3$  and dry mixing

Table 1. Influence of charge mixing type on the extraction levels of vanadium and nickel

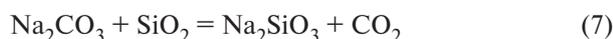
Type of mixing	Extraction of $V_2O_5$ , %			Extraction of Ni, %
	Water	3% $H_2SO_4$	Overall	
Dry	27.4	36.5	63.9	42.8
Wet	41.1	37.4	78.5	56.8



We studied the influence of the added amount of sodium carbonate on the extraction of vanadium and nickel into solutions after water and the subsequent sulphuric acid leaching of the charge, roasted at different temperatures (Fig. 2). We established that by increasing the temperature of oxidizing roasting from 300 °C to 400 °C and the amount of soda in the charge from 4.5 to 50%, we increase the extraction level of vanadium from 59.7 to 80.5% through the growth in formation of water-soluble meta-, ortho- and pyrovanadates of sodium, according to the reactions (4)–(6):



However, when roasting at the temperature of 500 °C by adding 4.5–20% of soda, we observed that the total extraction level of vanadium decreased to 50.1%–54.8%, mostly due to decrease at the water leaching stage. The most probable explanation is that this temperature initiates the process of formation of sodium silicate with interaction of sodium carbonate and quartz according to the reaction (7), which causes deficiency of sodium cations, required for formation of soluble vanadates. This is confirmed by thermodynamic calculations (Fig. 3) which show that the process of formation of sodium silicate develops in the temperature range of 400–500 °C (673–773 K):



According to our calculations, binding the whole  $\text{SiO}_2$  (9.1%) into sodium silicate requires the addition of nearly 16% of  $\text{Na}_2\text{CO}_3$ . Subsequently, when increasing the amount of soda to 30% and higher, we observed a considerable growth of the total extraction level of vanadium to 81.4–89.2% due to formation of water-soluble sodium vanadates. Most probably, the growth of extraction is caused by extraction of vanadium, connected with silicates, and by more complete decomposition of spinel  $\text{FeO} \cdot \text{V}_2\text{O}_3$  according to the Reaction (8):



We must note that in the case of deficiency of sodium cations the products of oxidation of spinel  $\text{FeO} \cdot \text{V}_2\text{O}_3$  at the temperatures over 450 °C interact immediately with formation of iron pyrovanadate  $\text{FeVO}_4$ , which is partially soluble in sulphuric acid solution (Reaction (9)). At the same time, this leads to a slight decrease in extraction of vanadium [11].

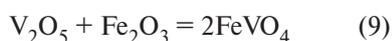


Fig. 4 shows extraction of nickel from solution after sulphuric acid leaching, depending on the temperature of roasting and the amount of soda. The extraction levels of nickel at the temperatures of 300 °C and 350 °C are almost the same. They grow from 47.4–48.3% to 55.2–56.7% when adding higher amounts of sodium carbonate. When roasting at the temperature of 400 °C the results slightly

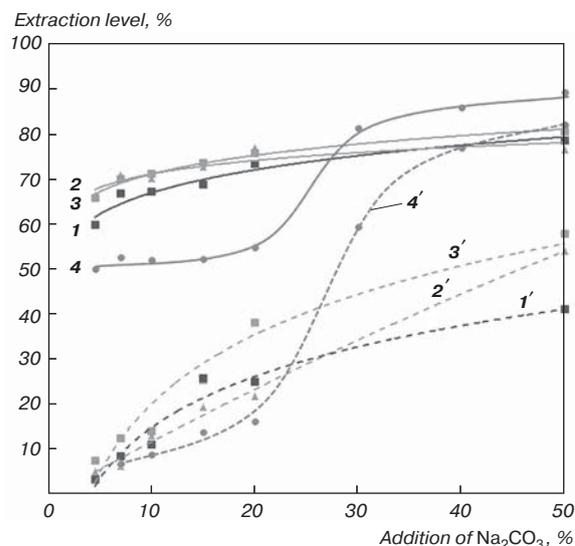


Fig. 2. Dependence of the extraction level of vanadium on the addition of  $\text{Na}_2\text{CO}_3$  at different temperatures: 1 – 300 °C; 2 – 350 °C; 3 – 400 °C; 4 – 500 °C, where 1'–4' is the extraction as a result of water leaching, whilst 1–4 is the total extraction

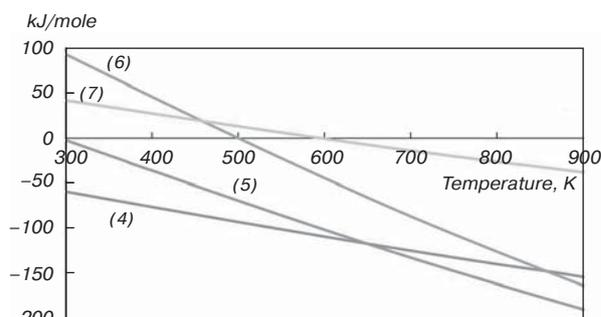


Fig. 3. Dependence of  $\Delta G$  reactions (4)–(7) on the temperature of oxidizing roasting

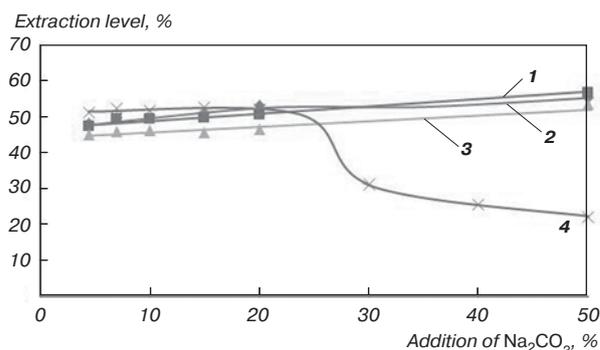


Fig. 4. Dependence of the extraction level of nickel on the amount of the added soda at different temperatures: 1 – 300 °C; 2 – 350 °C; 3 – 400 °C; 4 – 500 °C

decrease to 45.0–53.7% as the process of decomposition of spinel  $\text{FeO}\cdot\text{V}_2\text{O}_3$  (Reaction 9) with formation of  $\text{Fe}_2\text{O}_3$  starts in these conditions, which is followed by formation of poorly soluble nickel ferrite  $\text{NiFe}_2\text{O}_4$ . When increasing the temperature to 500 °C and adding 4.5–20% of soda, we observed that the extraction level of nickel increased to 51.4–52.2%. This is a result of a limited formation of nickel ferrite due to binding of  $\text{Fe}_2\text{O}_3$  into iron pyrovanadate (Reaction (9)).

When the amount of added soda is 30% or higher, the extraction level of nickel decreases considerably to 21.2–31.0%. The analysis of solutions after water leaching in the case of samples, roasted at the temperature of 500 °C, showed almost no extraction of nickel into the solution, which excludes the formation of a water-soluble nickel sulphate. According to the results of our analysis, the residue has the following composition after sulphuric acid leaching, %:  $\text{Fe}_2\text{O}_3$  (56.9),  $\text{SiO}_2$  (18.0),  $\text{V}_2\text{O}_5$  (2.1),  $\text{Al}_2\text{O}_3$  (2.1),  $\text{NiO}$  (1.4), (K, Na) $_2\text{O}$  (1.1),  $\text{SO}_3$  (1.5),  $\text{P}_2\text{O}_5$  (0.07), LOI (15.6) etc. Subsequently, under the above mentioned conditions, nickel remains in the solid phase. The decreasing extraction level of nickel is thus related to formation of a poorly soluble nickel ferrite according to the Reaction (3) which is intensified through oxidation of spinel  $(\text{Fe, Ni})\text{O}\cdot\text{V}_2\text{O}_3$  (Reaction (8)) and interaction of  $\text{V}_2\text{O}_3$  with  $\text{Na}_2\text{O}$ , where a considerable amount of  $\text{Fe}_2\text{O}_3$  and  $\text{NiO}$  is released.

Therefore, at oxidizing roasting at the temperature of 500 °C with addition of 30–50% of soda, we noticed a considerable growth of the extraction level of vanadium and more than a doubled decrease in extraction of nickel. As the total value of vanadium in ash is ten times higher than the value of nickel, we chose a maxim extraction of vanadium as our priority task. The question of increasing the extraction level of nickel remains open. However, taking into account our experience and positive results of our research on sulphuric acid leaching of nickel from ferrous raw materials (lateritic ores) [12–13], we can assume a considerable improvement of this parameter in our further research.

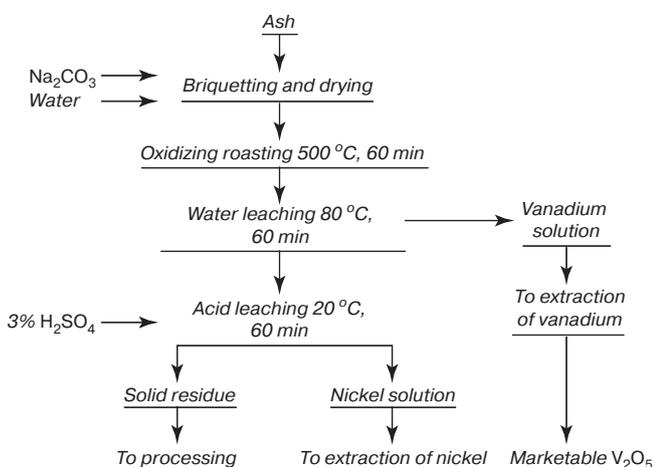


Fig. 5. Schematic diagram of ash processing

Based on the obtained data, we offer a schematic diagram of fuel oil ash processing (Fig. 5). This diagram shows the introduction of ash at the wet briquetting stage with addition of 50% of soda. After drying, the obtained briquettes go through 60 minutes of oxidizing roasting at the temperature of 500 °C. We then leach the roasted product in water at the temperature of 80 °C for 60 minutes. During this process nearly 82.0% of  $\text{V}_2\text{O}_5$  goes into the solution, whilst almost all of nickel remains in the solid residue. After filtration, the solution is returned to the water leaching stage in order for the concentration of vanadium to exceed 20 g/l of  $\text{V}_2\text{O}_5$ . Vanadium is then extracted from the vanadate solution by sedimentation of ammonium vanadates and their subsequent drying and calcination [14–15]. We thus obtain a marketable high-purity vanadium pentoxide. To extract nickel, we leach the solid residue with a 3% sulphuric acid for 60 minutes. We applied well-known methods to extract nickel from a sulphuric acid solution [16]. The solid residue, whose mass equals 42.4% of the mass of the initial ash, contains 56.9% of  $\text{Fe}_2\text{O}_3$ , 2.1% of  $\text{V}_2\text{O}_5$ , 1.4% of  $\text{NiO}$  etc. It poses no harm to the environment and may be further processed as iron-ore or titanomagnetite raw materials at the existing enterprises with extraction of iron, vanadium and, perhaps, nickel.

### Conclusion

Based on the performed research, we established the chemical and phase compositions of fuel oil ash. Thanks to oxidizing roasting and the subsequent water leaching we managed to selectively release vanadium and nickel. Furthermore, we applied wet mixing with soda, which significantly improved the extraction levels of vanadium and nickel.

We also studied the influence of  $\text{Na}_2\text{CO}_3$  additives, the temperature and the duration of roasting on extraction of vanadium and nickel. We established that when roasting at the temperature of 500 °C for 60 minutes and adding 50% of  $\text{Na}_2\text{CO}_3$ , the level of extraction of vanadium into a water solution equals 80.5%, whilst the level of extraction of nickel into a sulphuric acid solution equals 21.2%.

Based on our research, we offer a schematic diagram of ash processing with extraction of vanadium and nickel.

***Our research was carried out with the support of a program of Presidium of RAS (Filing number of Research, Development and Technological Work: AAAA-A18-118032690052-5).***

### References

1. Lur'e M. A. Metal Content of Oils, a Genetic Aspect. *Otechestvennaya Geologiya*. 2017. No. 4. pp. 109–114.
2. Annual Report of Murmansk Thermal Power Plant for 2019. Available at: [https://www.murmantec.com/storage/app/media/reports/GBO\\_AZ%20%20za%202019.pdf](https://www.murmantec.com/storage/app/media/reports/GBO_AZ%20%20za%202019.pdf) (accessed: 30.04.2020).
3. Pastrana-Corral M. A., Wakida F. T., Temores-Peña J., Rodríguez-Mendivil D. D., García-Flores E., Piñon-Colin T. D. J.,

- Quiñonez-Plaza A. Heavy Metal Pollution in the Soil Surrounding a Thermal Power Plant in Playas de Rosarito, Mexico. *Environmental Earth Sciences*. 2017. Vol. 76, Iss. 16. DOI: 10.1007/s12665-017-6928-7
4. Zubcova E. I., Protasov A. A., Biletski L. I., Zubcova N. N., Ungureanu L. N., Tihonenkova L. N., Philipenko E. N., Silaeva A. A. Migration of Vanadium in the Ecosystem of Kuchurgan Cooling Reservoir of the Moldovan Thermal Power Plant. *Journal of Siberian Federal University. Biology*. 2017. Vol. 10, Iss. 4. pp. 446–458.
5. Issa M. J., Hussain H. M., Shaker I. H. Assessment of the Toxic Elements Resulting from the Manufacture of bricks on Air and Soil at Abu Smeache Area – Southwest Babylon Governorate – Iraq. *Iraqi Journal of Science*. 2019. Vol. 60, Iss. 11. pp. 2443–2456.
6. Tsygankova M. V., Bukin V. I., Lysakova E. I., Smirnova A. G., Reznik A. M. Vanadium recovery from ash produced in oil burning at thermal power plants. *Izvestiya Vuzov. Tsvetnaya Metallurgiya*. 2011. No. 1. pp. 21–26.
7. Sirina T. P., Mizin V. G., Rabinovitch E. M., Slobodin B. V., Krasnenko T. I. Recovery of Vanadium and Nickel from Waste of Thermal Power Plants. Ekaterinburg: Rossiyskaya Akademiya Nauk. Uralskoe Otdelenie, 2001. 234 p.
8. Rahimi G., Rastegar S. O., Rahmani Chianeh F., Gu T. Ultrasound-Assisted Leaching of Vanadium from Fly Ash Using Lemon Juice Organic Acids. *RSC Advances*. 2020. Vol. 10, Iss. 3. pp. 1685–1696.
9. Ponomarev A. I. Methods of Chemical Analysis of Iron, Titanium-Magnesium and Chromium Ores. Moscow : Nauka, 1966. 406 p.
10. Facility for the Analysis of Chemical Thermodynamics (FACT). Available at: <http://www.crct.polymtl.ca/fact/> (accessed: 30.04.2020).
11. Mizin V. G., Rabinovitch E. M., Sirina T. P., Drobov V. G., Rabinovitch M. E., Krasnenko T. I. Complex Processing of Vanadium Raw Materials: Chemistry and Technology. Ekaterinburg: Rossiyskaya Akademiya Nauk. Uralskoe Otdelenie, 2005. 415 p.
12. Sadykhov G. B., Zablotskaya Yu. V., Anisonyan K. G., Khasanov M. Sh., Olyunina T. V., Goncharov K. V., Kopev D. Yu. Development of a New Combined Process for Nickel and Cobalt Recovery from Ferriferous Laterite Ores. *Metally*. 2019. No. 2. pp. 3–10.
13. Zablotskaya Yu. V., Sadykhov G. B., Khasanov M. Sh., Smirnova V. B. Kinetics of Sulphuric Acid Leaching of Nickel from Reduced Limonite Ore of the Buruktal Deposit. *Tsvetnye Metally*. 2018. No. 12. pp. 27–31. DOI: 10.17580/tsm.2018.12.04
14. Goncharov K. V., Anisonyan K. G., Kopjov D. Yu., Sadykhov G. B. Investigation of The Process of Purification of Sulfuric Acid Vanadate Solutions from Manganese and Other Impurities. *Tsvetnye Metally*. 2017. No. 2. pp. 62–67. DOI: 10.17580/tsm.2017.02.10
15. Goncharov G. V., Kashekov D. Yu., Atmadzhidi A. S., Olyunina T. V., Sadykhov G. B. Obtaining of Pure Vanadium Pentoxide During the Processing of Slimes of Vanadium Production. *International Scientific Conference “Physical and Chemical Bases of Metallurgical Processes” (Moscow, November 25–28, 2019)*. Collection of Reports. Moscow : IMET RAN, 2019. p. 118.
16. Reznik I. D., Ermakov G. P., Shneerson Ya. M. Nickel. Vol. 2. Moscow : Nauka i Tekhnologii, 2004. 468 p.