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ASSESSMENT OF POSSIBILITY OF OBTAINING ALLOYING COMPONENTS IN THE PROCESS OF DESALTING OF HEAVY HYDROCARBON RAW MATERIALS. Part 1

B. Issa[1], V. Yu. Bazhin[1], T. A. Aleksandrova[1], V. G. Povarov[1]

[1] *St. Petersburg Mining University (St. Petersburg, Russia)*

E-mail: ***basharissashtain@gmail.com; basharissa3@gmail.com; bazhin-alfoil@mail.ru; alexandrova_tatyana@mail.ru; povarov_vg@pers.spmi.ru***

AUTHOR'S INFO

B. Issa, Post-graduate, Dept. of Metallurgy,
V. Yu. Bazhin, Dr. Eng., Associate Prof., Head of the Department of Automation of Technological Processes and Production,
T. A. Aleksandrova, Cand. Eng., Leading engineer of the Quality Control Dept.,
V. G. Povarov, Dr. Chem., Head of the Dept. of Analytical Research of Core Facilities Center

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ABSTRACT

In the current situation of the mineral resources with a general depletion of ferrous and non-ferrous ores, it becomes necessary to search for new and alternative resources for obtaining metals and their compounds from available resources. Taking into account that ferrous and non-ferrous ores are practically lacking in some foreign countries, especially in Central Asiaб this problem becomes more actual. Thus, a high share of exports of ferrous and non-ferrous metals products remains due to lack of self resources, which increases the additional load on the countries, especially that suffer from wars like Syria.
There is a wide range of hydrocarbon metal-containing raw materials (metal-bearing oils, oil sands, coal ash, shale, etc.) in Syrian resources, which may become an alternative source for production of ferrous and non-ferrous metals and their alloys; they also have a strategic interest for the Russian and foreign metallurgical industry.
The concentration of impurities of ferrous and non-ferrous metals (such as Fe, Mn, Cr, V and Ni) in heavy crude oil is quite high, what in its turn leads to negative effects on operation of some equipment components, resulting in the need for emergency stops and downtimes of equipment and consequent repairs and technical maintenance.
Development of alternative technologies for extraction of these metals at the desalination's process of metal-bearing heavy crude oils can be characterized by interdisciplinary character, which simultaneously solves the problem of extracting ferrous and non-ferrous metal components in order to improve the properties of heavy oil as well as the oil products quality.
Extraction of ferrous and heavy non-ferrous metals (iron, manganese, chromium, vanadium and nickel, copper) from the heavy metal-bearing Syrian crude oils makes a great interest, due to deteriorating economic situation in this country and lack of mineral ores.
This study describes the hydrometallurgical technology based on combination of extraction-sorption processes for ferrous and non-ferrous metal extraction from heavy crude oil. The extraction is based on processing the emulsion of crude oil with aqueous solution of naphthenic acid, followed by centrifugal separation; them hydrocarbon metal-containing concentrate (acidified by HCl) is subjected to sorption process using a mixture of two Syrian natural sorbents, The following desorption process allows to recover vanadium and nickel from sorbent and to regenerate the sorbents with desorption efficiency 89.6 and 95.8% consecutively.

1. Introduction

Desalination of oil is one of the most common processes associated with the oil's preliminary processing. The presence of ferrous and non-ferrous trace metals (like Fe, Mn, Cr, V and Ni, Cu) in the alternative resources of raw materials make them very attractive for recycling [1]. There is an urgent task for producing high-grade metal-containing concentrates from the secondary resources [2, 3], like crude oil and followed by purification and circulating of the waste water [4, 5] by using hydrometallurgical, pyrometallurgical and electrometallurgical processes [6, 7].

Currently, the problems of rational use of Syrian natural resources (crude oil in our case), recycling of industrial waste water (by excluding waste water discharge in the surrounding environment) and environmental pollution (resulting from burning the oil products with a relatively high metal content) are considered very challenging issues [8]. Our work can contribute to providing a comprehensive and integrated approach to solve these problems or at least to reduce their negative impacts.

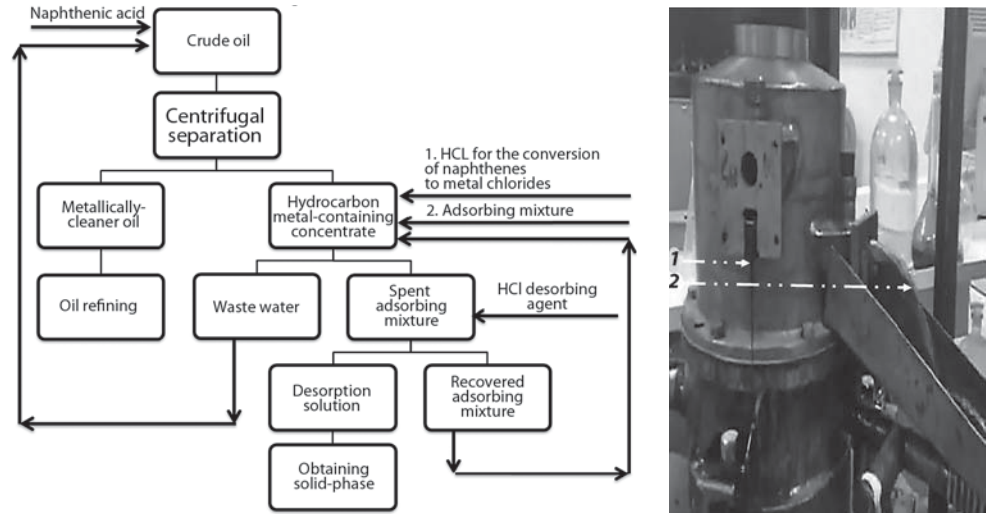
Without preliminary extraction of ferrous and non-ferrous metals (like Fe, Mn, Cr, V and Ni, Cu) from the crude oil to make the crude oil more metallically clean, these metals can easily and accumulatively cause many serious problems to oil refineries, such as aggressive corrosion, catalyst poisoning, plugging by deposits, catalyzing undesired side reaction. These problems are apart from their harmful effect on the environment, which can lead to premature failure of equipments and installations and, thus can cause huge economic losses [9–11].

Syrian oil and Russian oil have different types (low-viscosity and high-viscosity oils), in general, in terms of composition we can say that West Siberian oil is relatively similar to the heavy Syrian crude oil, so we can use it as a model object.

The main aim of the work is to assess possibility of the associated extraction of non-ferrous metals (nickel, vanadium, etc.) in the desalination process of heavy oil (pre-purification from metals).

2. Research methods

During the scientific research, the following methods and research devices were used: an XRF-1800 X-ray fluorescence spectrometer to determine the chemical composition of crude oil; an atomic emission spectrom-



a *b*

Fig. 1. Schematic diagram of the developed hydrometallurgical technology (*a*) and installation for the extraction of metal-containing components from a crude oil by centrifugal separation (*b*)

eter with inductively-coupled plasma ICPE 9000 for determining the metal content and composition of the compounds passing into the aqueous phases after centrifugal separation from the organic phase; a complex of combined thermogravimetric analysis and differential scanning calorimetry TGA / DSC1 NT MX1 for continuous record of the kinetic dependence of mass change on time and temperature (where the mass and heat are measured sequentially in relation to temperature changes to study the thermal stability and the changes that can occur to the components); LECO-CHN628 analyzer to determine the elemental composition of the sorbents; a gas chromatography mass spectrometer GCMS-QP2010 SE for thermogravimetric analysis of impurity detection.

A conical plate centrifuge with rotor and inlet pipe was used for feeding and the same with outlet pipes was used for oil and water; this equipment is devoted for centrifugal separation of a water-oil mixture containing mechanical impurities characterized by vertically-located shaft. A set of conical plates which are parallel to each other are arranged coaxially around the rotation axis with a constant distance between them by means of bar-shaped spacers, equally distributed over the top surface of each plates in the rotor.

3. Research results and discussion

3.1. Metals extraction from West-Siberian crude oil using naphthenic acid

The most promising method for ferrous and non-ferrous metals extraction (like Fe, Mn, Cr, V–Ni, Cu) from organometallic compounds of the crude oil is, from our point of view, their selective extraction by naphthenic acid, in spite of its negative role in corrosion and plugging [12, 13] as well as on reproductive health [14]. Naphthenic acid as a surface-active material can play a vital role in the equilibrium partition and distribution processes [15–17]. The extracted non-ferrous metals and components from the obtained hydrocarbon metal-containing concentrate can be used as alloying components in steelmaking.

As shown in **Fig. 1**, the emulsion of West-Siberian crude oil (formation with water-oil correlation 1:1) is processed with 3% naphthenic acid (pH 5) under continuous stirring during 1 hour, followed by centrifugal separation into two phases: metallically cleaner oil phase (*1* in Fig. 1, *b*) and aqueous phase (hydrocarbon metal-containing concentrate) *2* in Fig.1, *b*).

Naphthenic acid molecules ″RCOOH react with the atoms of Fe, Mn, Cr, V – Ni, Cu metals and extract them from their organometallic compounds $'R_nM$ (metal-containing hydrocarbon chains RH, cyclometallic compounds and metal complexes) of the oil-phase in the form of metal naphthenates $(''RCOO)_nM$ as surface-active materials are centrifugally-separated to the aqueous-phase (hydrocarbon metal-containing concentrate). Extraction occurs on the basis of acid-base mechanism, where the ′R-carbanion is the stronger base, the proton can be removed from the carboxyl group of the stronger acid (naphthenic acid), which leads to the formation of a weaker conjugated base (metal naphthenate) and a weaker conjugated acid (hydrocarbon) ′RH. It is following by treatment with hydrochloric acid 0.1M (5% of the concentrate) to convert naphthenates of all ferrous and non-ferrous metals into chloride metals (M^{n+}) and naphthenic acid again (for the subsequent recycling of the waste water after sorption to reduce the amount of consumed naphthenic acid) and in addition to prevent dissociation of the unreacted part of naphthenic acid according to the following reactions:

$$'R_nM + n''RCOOH \rightarrow n\,'RH + (''RCOO)_nM$$

$$(''RCOO)_nM + n\,HCl \rightarrow n''RCOOH + MCl_n$$

Results of XRF (X-ray fluorescence) analysis of the crude oil by analyzing the carbon residues obtained from burning the crude oil (column $(M)_1$, g/t in **Table 1**) show that West-Siberian crude oil contains 1,721.5 g/t; 31.3 g/t; 217.6 g/t; 25.1 g/t and 82.5 g/t of Fe, Mn, Cr, V and Ni sequentially, while these metals are absent in formation water. It is concluded based on the result of atomic emission spectrometer with inductively-coupled plasma ICPE 9000 to the formation water, separated from the

Table 1. **Metal concentration in crude oil, formation water and concentrate with extraction efficiency**

M	$(M)_1$, g/t	$(M)_2$, mg/dm³	Extraction efficiency, %	Concentrate, mg/dm³
Al	842.9	—	72.4	610
Fe	1721.5	0.055	85.9	1479.2
Ca	521.6	13.9	44	229.8
V	25.1	—	43.5	10.93
Co	—	0.093	–	–
Ba	—	0.23	–	–
Na	—	7.3	–	–
Ni	82.5	—	83.3	68.71
Cu	52.6	0.46	89.9	47.3
K	782.4	2.7	75.8	593.4
Mg	389.7	3.6	82.8	322.7
Mn	31.3	0.95	86.6	27.1
Zn	86	9.7	75.4	64.81
Cr	217.6	–	75.7	164.7
Ti	86.8	–	71.9	62.4
Sr	–	0.078	–	–
Zr	–	–	–	–

crude oil without any treatment (column $(M)_2$, mg/dm³ in **Table 1**.

As it is seen from the table 1, simultaneously extracting of non-ferrous metal compounds occurs in desalination process of heavy oil.

It should be noted that we have converted the percentages of metals in carbon residues to the percentages of metals in crude oil using the following equation:

$$(M)_0,\% = (m_c, g/m_0, g)*(M)_c,\%,$$

and then we have converted the percentages of metals in crude oil into grams per ton by multiplying by 10^4, where $(M)_0$, % and $(M)_c$, % — percentages of metals in crude oil and carbon residues subsequently; m_c, *g* and m_0, *g* — mass of the obtained carbon residues and mass of the burned crude oil subsequently.

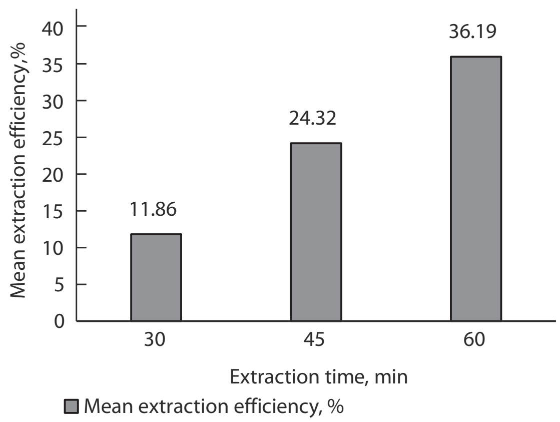


Fig. 2. Effect of processing time on the extraction efficiency

The effects of processing time, mixing ratio and naphthenic acid concentrate on extraction efficiency are shown in the **Fig. 2, 3** and **4**.

The effect of processing time on the extraction efficiency was studied at 1% naphthenic acid concentration and a 50% : 50% mixing ratio, while the effect of mixing ratio on extraction efficiency on the same naphthenic acid concentration was studied at 60 min processing time.

We can conclude from these figures that, the higher is the processing time, the more effective is the extraction. The optimum mixing ratio for extraction is 50 : 50%, as mentioned above; the reason for the lower extraction efficiency at a greater amount of oil in comparison to the water amount can be explained by the difficulty of the mixing process. The naphthenic acid molecules were not able to interact freely as they should be. By increasing of naphthenic acid concentration, the extraction efficiency increases initially significantly up to 3%, but afterwards increase in the extraction efficiency is very weak and is not proportional to increase of naphthenic acid concentration.

The data about the maximum efficiency of extraction of the main studied metals from the oil fraction under optimal process conditions (see Fig. 2–4) are presented in Table 1.

3.2. Metal sorption from the obtained concentrate

Two Syrian sorbents have been selected (Syrian church resin (incense) and Syrian clay) to make a mixture of them in equal amounts without any activation.

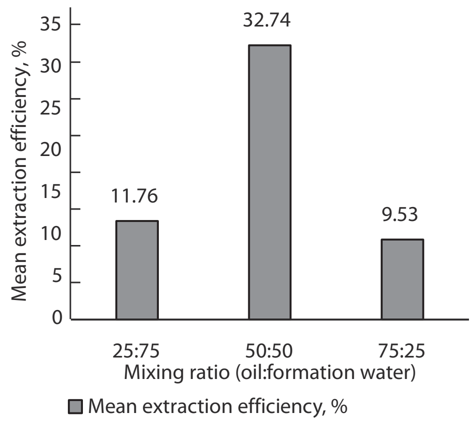


Fig. 3. Effect of mixing ratio on extraction efficiency

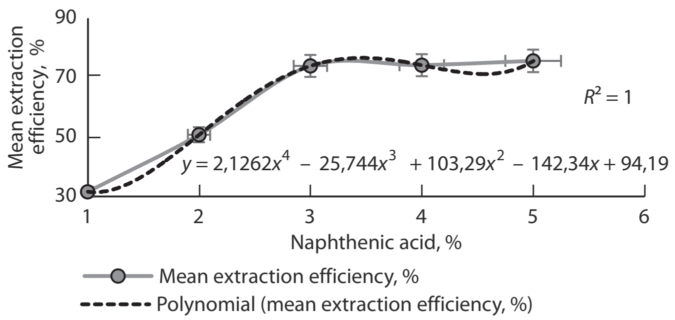


Fig. 4. Effect of naphthenic acid concentration on extraction efficiency

Table 2. **Elemental composition of the Syrian church resinby XRF analysis**

Composition	Ca	Fe	Si	K	Cl	S	Al	P	Cu	C
Content,%	0.07362	0.06501	0.05988	0.03704	0.02652	0.01098	0.00956	0.00388	0.0033	100-∑

Syrian church resin (incense) — characteristics and preparation

Firstly, we made XRF analysis for our resin, the results which are shown in Table 2 and they testify that the resin is represented only by the organic component.

Then the elemental analysis of the resin was made by LECO analyzer CHN628 to determine its real elemental composition; the obtained results show that in addition to carbon, hydrogen and nitrogen, there is also oxygen content (42.3, 6.83, 0.12 and 50.75% sequentially).

To confirm this fact, a thermal analysis was carried out with a combined thermogravimetric analysis and differential scanning calorimetry TGA / DSC1 NT MX1. TGA results (**Fig. 5**) show that the components of the resin are non-volatile because the volatile organic compounds are really small less than 1%, as the temperature rises, and the components undergo to decomposition processes due to decreased weight loss. The derivative weight loss curve shows the point at which the weight loss is most apparent at 340 °C. At the end of heating at 600 °C, only about 3% of the sample mass remains.

Impurity detection which is made by GC-MS chromatogram using a GCMS-QP 2010 S gas chromato-graph-mass spectrometer (**Fig. 6**) shows that there are three main impurities: two of them are alkyl phthalates (diethyl and diisooctyl with peaks 6 and 28 sequentially), they are usually taken from plastic materials or products, and the third is amber synthetic musk (peak 14).

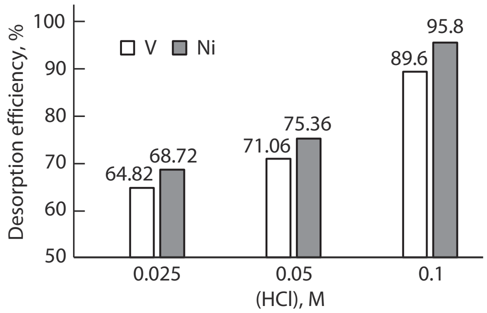


Fig. 5. Thermal analysis spectrum of Syrian church resin (incense)

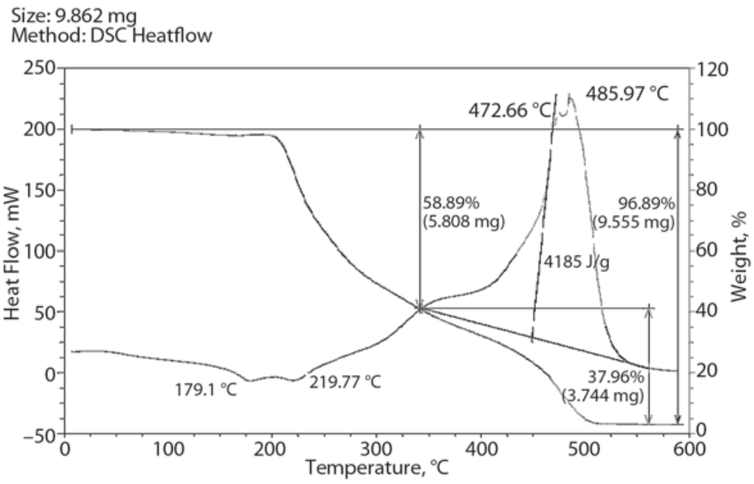


Fig. 6. Gas chromate-mass spectrometer

4. Syrian clay — characteristics and preparation

The Syrian natural clay has a silicate-silicate structure, exists only in Aleppo Governorate, has high surface area ~ 750 m²/g, it can sorb up to 100% of water and up to 75% of oil, meaning its dry weight. We can testify that we have a calcium-type clay (hydrated calcium-magnesium-aluminum silicate) due to the high calcium content (**Table 3**).

Table 4 shows concentration of metals in the aqueous phase (concentrate) before and after sorption, by using 1 g of a mixture (Syrian clay / Syrian resin = 1 : 1) under the following conditions: 25 °C and 50 rpm for 1 hour and 7 pH.

The effect of hydrochloric acid (HCl) concentration on the desorption efficiency of vanadium and nickel is shown in the **Fig. 7**. Increase of HCl concentration leads to elevation of desorption efficiency for both vanadium and nickel.

Conclusions

Nickel and vanadium are the most important metals for their subsequent extraction from the obtained concentrate as an alloying component in steelmaking.

Processing of desalination oil with naphthenic acid is followed by centrifugal separation to obtain hydrocarbon-metal containing concentrate, in order to be acidified with hydrochloric acid and to undergo later to sorption-desorption process. It leads finally to recovery of vanadium and nickel and regeneration of the sorbents with desorption efficiency 89.6% and 95.8% consecutively.

Obtaining ferrous and non-ferrous metal concentrates from crude oils makes it possible to organize their own local production facilities on the territory of Syria, combined with

Table 3.**The chemical composition of the Syrian natural clay by XRF analysis**

Composition	Content, %	Composition	Content, %
SiO_2	58.0039	MnO	0.1003
Al_2O_3	12.2513	SO_3	0.0937
CaO	10.8561	Cl	0.0446
MgO	9.1789	SrO	0.0257
Fe_2O_3	8.1432	ZrO_2	0.0122
K_2O	0.9662	Y_2O_3	0.0090
Na_2O	0.1585	Rb_2O	0.0031
P_2O_5	0.1062	C	100-∑

Table 4. **Sorption efficiency,%**

Metals	Concentrate, mg/dm3	Concentrate after sorption, mg/dm3	Sorption efficiency,%
Al	610	116,5	80.9
Fe	1479,2	468,17	68.3
Ca	229,8	48,42	78.9
V	10,93	3,3	69.8
Co	–	–	–
Ba	–	–	–
Na	–	–	–
Ni	68,71	16,46	76
Cu	47,3	19,35	59.1
K	593,4	213,6	64
Mg	322,7	73,25	77.3
Mn	27,1	13,29	50.9
Zn	64,81	52,89	18.4
Cr	164,7	61,27	62.8
Ti	62,4	18,53	70.3
Sr	–	–	–
Zr	–	–	–

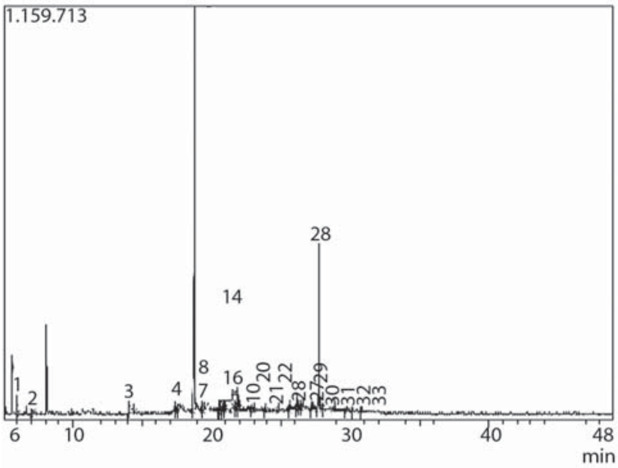


Fig. 7. Effect of HCl acid concentration on the desorption efficiency of vanadium and nickel

the recycling of metallurgical wastes and scraps, in order to reduce the share of imports.

The heavier is the crude oil, the better it is for its processing by naphthenic acid, the more metallically rich is obtained hydrocarbon metal-containing concentration and the more metallically clean is the centrifugal-separated oil. It allows to reduce the industrial problems in oil refineries (due to the aggressive corrosion, catalyst poisoning, plugging by deposits, catalyzing undesired side reaction), as well as to reduce environment problems.

REFERENCES

1. Issa B., Aleksandrova T. A. Processes of Extraction of Non-Ferrous and Precious Metals from Alternative Sources of Raw Materials. *IOP Conference Series Materials Science and Engineering*. 2019. Vol. 582. pp. 234–243.
2. Kuzin E. N., Kruchinina N. E. Purification of circulating and waste water in metallurgical industry using complex coagulants. *CIS Iron and Steel Review*. 2019. Vol. 18. pp. 72–75. DOI : 10.17580/cisisr.2019.02.15.
3. Kolokoltsev V. M., Vdovin K. N., Mayorova T. V., Ponomareva O. S. Ecological indicators in the system of non-financial reporting at industrial enterprises. *CIS Iron and Steel Review*. 2017. Vol. 13. pp. 4-10. DOI : 10.17580/cisisr.2017.01.01.
4. Kumolo S. T., Yulizar Y., Haerudin H., Kurniawaty I., Apriandanu D. O. B. Identification of metal porphyrins in Duri crude oil. *IOP Conference Series Materials Science and Engineering*, 2019. Vol. 496. pp. 1-6. DOI: 10.1088/1757-899X/496/1/012038.
5. Kondrasheva N. K., Povarov V. G., Rudko V. A. Determination of Sulfur and Trace Elements in Petroleum Coke by X-Ray Fluorescent Spectrometry. *Coke and Chemistry*. 2017. Vol. 60. No. 6. pp. 247–253.
6. Vzorodov S. A., Klyushnikov A. M. Development of technology for processing of copper wastes that contain precious metals. *Tsvetnye metally*. 2019. No. 8. pp. 90-96. DOI: 10.17580/tsm.2019.08.10.
7. Sayadova Yu. B., Chernousov P. I., Golubev O. V. Econometric modeling of secondary resources of iron. *CIS Iron and Steel Review*. 2019. Vol. 18. pp. 69-71. DOI: 10.17580/cisisr.2019.02.14.
8. Molchanov A. A., Ageev P. G. Implementation of new technology is a reliable method of extracting reserves remaining in hydrocarbon deposits. *Zapiski gornogo instituta*. 2017. Vol. 227. pp. 530–539.
9. Kondrasheva N. K., Anchita J. Effect of chemical composition and quality of heavy yarega oil on selection of appropriate Processing Technology. *Zapiski gornogo instituta*. 2016. Vol. 222. p. 833–838.
10. Yang Ch., Zhang G., Serhan M., Koivu G., Yang Z., Hollebone B., Lambert P., Brown C. E. Characterization of naphthenic acids in crude oils and refined petroleum products. *Fuel*. 2019. Vol. 255. pp. 833–838.
11. Shadrunova I. V., Gorlova O. E., Kolodezhnaya E. V. Technology for producing high-grade concentrates from waste metallurgical slags. *Obogashchenie rud*. 2019. Vol. 4. pp. 54–60. DOI: 10.17580/or.2019.04.10.
12. Qundan Zh., Jiliang W., Songbai T., Chunsheng Xu. Naphthenic acid distribution and transmission in acidic crude processing. *Petroleum processing and petrochemicals*. 2016. Vol. 12. pp. 97–102.
13. Bertheussen Ar., Simon S., Sjöblom J. Equilibrium partitioning of naphthenic acid mixture, Part 1: commercial naphthenic acid mixture. *Energy & Fuels*. 2018. Vol. 32. pp. 32–35. DOI: 10.1021/acs.energyfuels.8b01494.
14. Bertheussen Ar., Simon S., Sjöblom J. Equilibrium partitioning of naphthenic acid mixture Part 2: crude oil-extracted naphthenic acids: commercial naphthenic acid mixture. *Energy & Fuels*. 2018. Vol. 32. pp. 65–71. DOI: 10.1021/acs.energyfuels.8b01870.
15. Raez-Villanueva S., Jamshed L., Ratnayake G., Cheng L., Thomas Ph. J., Holloway A. Adverse effects of naphthenic acids on reproductive health: A focus on placental trophoblast cells. *Reproductive toxicology*. 2019. Vol. 90. pp. 126–133.
16. Samanipour S., Hooshyari M., Lomba J. A., Reid M., Casale M., Thomas K.V. The effect of extraction methodology on the recovery and distribution of naphthenic acids of oilfield produced water. *Science of the total environment*. 2019. Vol. 652. pp. 1416–1423.
17. Peng Hu, Guozhong Wu, Mucong Zi, Lei Li, Daoyi Chen. Corrigendum to “Effects of modified metal surface on the formation of methane hydrate”. Elsevier. 2019. Vol. 225. p. 263.