

Recovery of non-ferrous metals from sulfide ores by the method of heap bioleaching on the example of Allarechensk technogenic deposit

Elena Latyuk^{1*}, Sergey Potapov², Alena Kompanchenko³, and Andrey Goryachev¹

¹ Institute of North Industrial Ecology Problems – Separate subdivision of the Federal State Budgetary Institution of Science of the Federal Research Center «Kola Science Center», 184209, 14A, Akademgorodok, Apatity, Russian Federation

² Federal State Budgetary Institution of Science South Urals Research Center of Mineralogy and Geoecology of the Urals Branch of the Russian Academy of Sciences, 456317, Miass, Ilmsky reserve territory, Russian Federation

³ Geological Institute – Separate subdivision of the Federal State Budgetary Institution of Science of the Federal Research Center «Kola Science Center», 184209, Fersmana st., 14 Apatity, Russian Federation

Abstract. On the example of the Allarechensk technogenic deposit ore, the heap bioleaching method feasibility for the copper-nickel ores processing and non-ferrous metals recovery was considered. The content of metals in the initial ore sample was following: nickel – 2.42 %, copper – 0.75 %. The ore grinded to a size of -5+3 mm was irrigated with a solution containing a strain of *Acidithiobacillus ferrivorans*. The S:L ratio was 4:1, the flow rate was 0.1 mL/min. In pregnant solutions, the pH and ORP values were controlled, and the concentrations of ferrous and ferric iron, copper, and nickel ions were also measured. The experiment duration was 330 days, 8.9 % nickel and 6.1 % copper were recovered. The pathways for the metals extraction from pregnant solutions, as well as the utilization of bioleaching residue were considered.

1 Introduction

Non-ferrous metals such as copper and nickel are mainly deposited in sulfide ores. These ores are processed all over the world, primarily in the Chile, Canada, China, Russia, USA, Australia. The world reserves of rich polymetallic sulfide ores deposits are gradually depleted, including in the Murmansk region of Russia. Therefore, the involvement of refractory and low-grade ores in processing is a topical issue for the mining industry.

Every year, the world industry extracts about 10 billion tons of solid substances from the bowels, 70 % of which subsequently becomes an industrial waste. Huge areas with valuable lands are being alienated for dumps and tailings. Waste from the mining and industrial complex causes soil and water pollution [1, 2].

* Corresponding author: latyuk.es@gmail.com

There is a constant search for the new technologies and improvement of the existing pathways for the deposit development, as well as the ores beneficiation. Involvement in the processing of deposits that were previously considered unprofitable becomes economically attractive. In this regard, attention is drawn to the dumps of depleted deposits, namely technogenic formations, and ultimately to technogenic deposits [3].

Technogenic formation – accumulation on the surface or in the mine workings, in bowels, hydrosphere or atmosphere of products created by man, as well as mineral substances artificially separated from the natural massif or subjected to change directly in the massif as a result of human activities, which are waste. A technogenic deposit is a technogenic formation, which, in terms of the quantity and quality of the contained mineral raw materials, is suitable for effective use in the field of material production at the present time or in the future (as science and technology develop) [3].

The possibility of processing sulfide copper-nickel raw materials by the heap leaching method due to the environmental attractiveness of this pathway is becoming an increasingly important topic for mining and processing industry [4]. Heap leaching method is used mainly for low-grade and secondary raw materials. Increased attention to secondary raw materials is due to a decrease the copper-nickel ores quality, which are currently processed by the traditional enrichment methods. Particular attention is paid to the possibility of involving technogenic raw materials in the beneficiation process. In general, that is due to the fact that there are no more costs for the deposit development, which leads to an additional economic incentive [5].

However, previous studies of the mineral and phase composition of copper-nickel ore enrichment wastes were shown that during its storage, irreversible transformation occur due to oxidation and natural leaching, resulting in the migration of valuable components into surrounding ecosystems. Therefore, the loss of target metals in technogenic formation should be considered as a profit lost, as well as the cause of a long-term negative environmental impact.

Biohydrometallurgical technologies were used on an industrial scale for the production of non-ferrous and precious metals from sulfide ores processing wastes, as well as from low-grade ores and concentrates [6-8]. This technology is based on the processes of sulfide minerals oxidation by the microorganisms, that use ferrous iron, sulfur, and sulfide minerals as an energy substrate [8]. Previously, we have conducted the studies that showed high and stable metal contents in the pregnant solutions during bacterial leaching of poor ores and industrial wastes, comparing parallel experiment with a weakly (low-concentrated) sulfuric acid solution [9]. The results obtained have showed that the search and selection of the effective conditions for experiments with the use of microorganisms can give higher metals recovery.

The objective of this research was to determine the kinetics of copper and nickel recovery from the Allarechensk technogenic deposit (Allarechensk TD) ore using bioleaching.

2 Experimental

For the research, Allarechensk technogenic deposit ore was used. Ore sampling was performed in 2021. This object is a rock dump formed as a result of the development of the primary Allarechensk deposit. During the primary deposit excavation, overburden and host rocks were stockpiled into the dump, the volume of rocks in which reached 6.700 thousand m³ (Fig. 1a). Previously, the dump was comprehensively studied, the consequences of the sulfide minerals hypergenesis were considered [10, 11].

It has been established that the concentration of non-ferrous metals in the flooded quarry water (Fig. 1b), is many times higher than the MPC, while the surrounding ecosystems are in a depressed state and are a technogenic wasteland (Fig. 1c). It is typical for the dump that

almost all the main minerals groups and types of the primary Allarechensk deposit are represented among the ores. All types of ores are characterized by approximately the same composition of ore minerals and differ only by its quantitative ratio [10]. The main ore-forming minerals are: pyrrhotite, pentlandite, chalcopyrite and magnetite. The metals content in the initial Allarechensk TD ore sample: Ni – 2.42 %, Cu – 0.75 %.



Fig. 1. Landscapes of the area the Allarechensk technogenic deposit: a – dump surface, b – flooded quarry of deposit development, c – technogenic wasteland type ecosystem at the bottom of the dump.

During the research the Allarechensk TD ore was grinded to a fraction $-5+3$ mm, and then placed in the glass percolators. Experiment was performed in two replications. The loading weight of each percolator was 4 kg. The ore layer was irrigated by the feeding solution using peristaltic pump (Shenchen Precision Pump Co., Ltd, China). Feeding solution was prepared using mineral medium of Silverman and Lundgren 9K, containing nitrogen and phosphorous salts, also inoculated by the strain *Acidithiobacillus ferrivorans* with initial population of the microorganisms 3×10^8 cell/mL. The S:L ratio was 4:1, consumption – 0.1 mg/L. The pregnant solution was acidified by a 10% sulfuric acid solution, and fed to the ore layer again. The duration of the experiment was 330 days.

Determination of the pH values and the redox potential (ORP) of pregnant solutions was carried out using the I-160MI ion meter (Izmeritelnaya Tekhnika LLC, Moscow, Russia). The concentrations of Fe^{2+} and Fe^{3+} ions were determined by trilonometric titration. The concentrations of nickel and copper in the pregnant solutions were determined by atomic absorption spectroscopy (Shimadzu-AA7000G, Shimadzu Corp., Kyoto, Japan) with electrothermal atomization (PND F 14.1:2:4.140-98). The copper and nickel recovery rate were calculated on a base of the concentration of metals in the liquid phase.

XRD analysis was carried out on a Shimadzu XRD-6000 diffractometer, Cu-anode, graphite monochromator. Interpretation of X-ray patterns was performed using the reference X-ray patterns of minerals in the Mincrust electronic X-ray database (<http://mincryst.iem.ac.ru/rus/>).

For visualization, study of the morphology and elemental composition of mineral formations, a scanning electron microscope TESCAN Vega 3 with an energy dispersive spectrometer (EDS) X-ACT (Oxford Instruments) at the Institute for Problems of Superplasticity of Metals of the Russian Academy of Sciences, Ufa was used. The study was carried out with Au-Pd sputtering in the back-scattered electron (BSE) mode.

3 Results and discussion

Throughout the experiment, the pH values of the pregnant solutions were higher compared to the initial solution fed to the top of the ore layer. This is due to the predominant dissolution of oxide minerals, which are present in a significant amount in the ore.

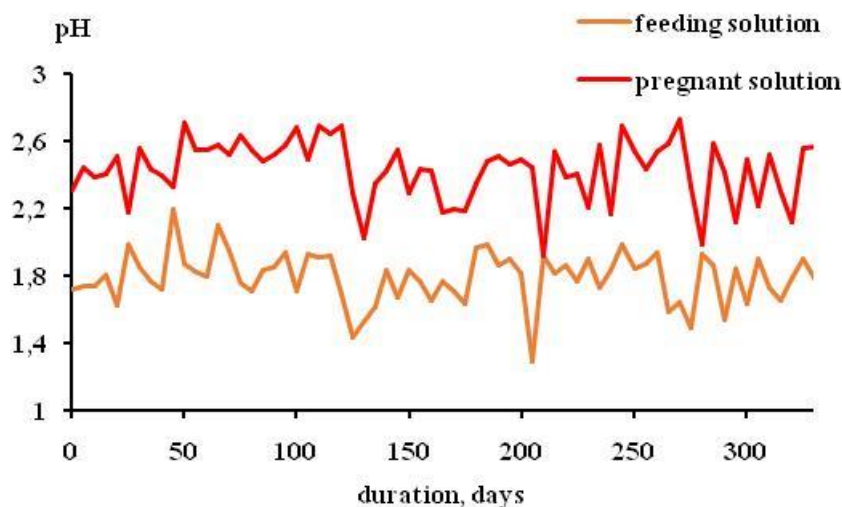


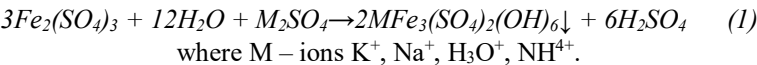
Fig. 2. The pH values prior to and after leaching.

The Figure 2 shows the dynamics of the pregnant solution pH values during the experiment. To maintain the pH in the range optimal for the functioning of microorganisms, the pregnant solution was acidified, so the average pH value during the experiment was ~1.9. Sulfuric acid consumption was 33 kg/t. During the experiment the ORP values varied in the range of 500-652 mV, the average value was 564.8 mV.

Table 1. Iron concentrations and oxidation-reduction potential of productive solutions

	Fe ³⁺ , g/L	Fe ²⁺ , g/L	ORP, mV
1 column	1,54 - 14,20	0,15 - 2,44	496 - 635
2 column	0,9 - 15,25	1,15 - 2,05	504 - 670
Average value	1,22 - 14,75	0,65 - 2,25	500 - 652

There was a decrease in the concentration of ferrous and ferric iron (Table 1). The initial content of ferric iron was 9 g/L. The concentration of Fe³⁺ was increased to 14 g/L for the first 10 days, and for the next 60 days it was remained in the range of 12-13 g/L. Starting from the 80th day, a gradual decrease iron ions in solution was noted, the concentration of ferric iron reached about 1.5 g/L at the end of the experiment. The concentration of ferrous iron was about 1.5 g/L throughout the experiment. The decrease of the iron concentration in the solution is probably due to the formation of jarosite, which leads to the secondary precipitation of iron:



The concentrations of copper and nickel was gradually increased (Fig. 3), nickel was recovered into the solution more intensively than copper. This is due to the inclusion of copper in the chalcopyrite, which is more resistant to biooxidation than nickel minerals.

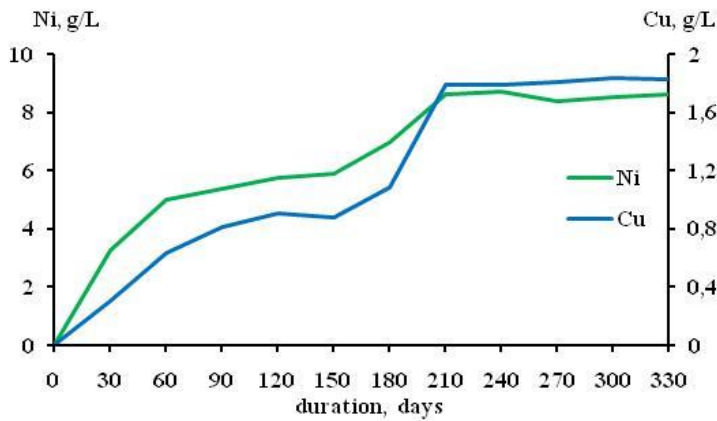


Fig. 3. The nickel and copper concentrations in the pregnant solution throughout the experiment.

The figure 4 shows X-ray diffraction patterns of the initial ore sample and residue after bioleaching. It was found that the sulfide copper-nickel ore from the Allarechensk technogenic deposit has a complex sulfide composition, represented by chalcopyrite CuFeS_2 , magnetite Fe_3O_4 , pyrrhotite $\text{Fe}_{(1-x)}\text{S}$, pentlandite $(\text{Fe}, \text{Ni})_9\text{S}_8$, quartz SiO_2 . A decrease of the sulfide minerals reflections, as well as the appearance of reflections of clinocllore and magnesium sulfate were noted in the residue after bioleaching sample.

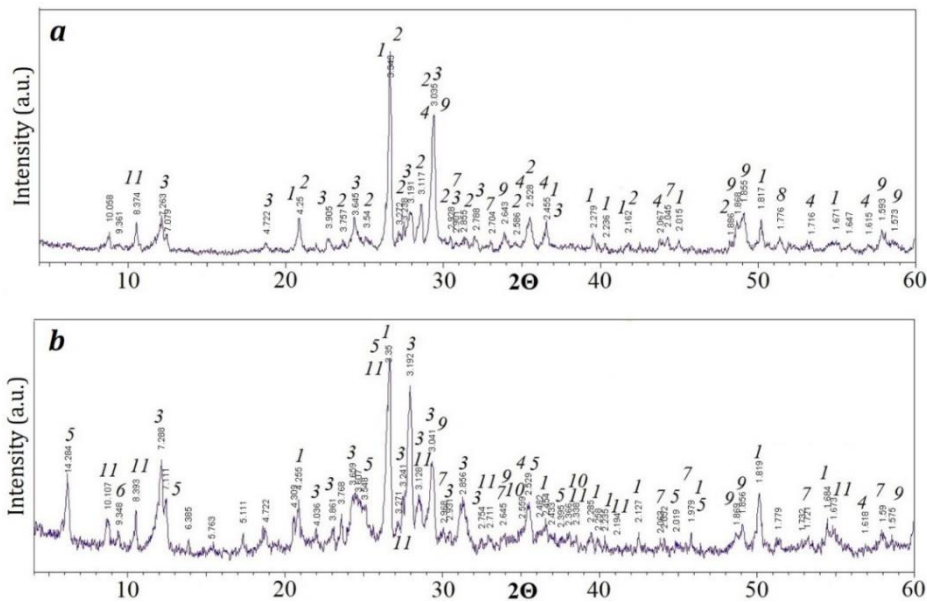


Fig.4. X-ray diffraction patterns of the sulfide ore prior to (a) and after (b) interaction with a bacterial solution: 1 – quartz (SiO_2), 2 – microcline (KAlSi_3O_8), 3 – manaksite ($\text{KNaMnSi}_4\text{O}_{10}$), 4 – magnetite Fe_3O_4 , 5 –clinocllore ($(\text{Mg})_5\text{Al}[\text{Si}_3\text{AlO}_{10}](\text{OH})_8$), 6 – phlogopite ($\text{KMg}_3(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_2$), 7 – pyrrhotite ($\text{Fe}_{(1-x)}\text{S}$), 8 – pentlandite ($(\text{Fe}, \text{Ni})_9\text{S}_8$), 9 – chalcopyrite (CuFeS_2), 10 – magnesium sulfate (MgSO_4), 11 –hastingsite ($\text{NaCa}_2\text{Mg}_4\text{Fe}^{3+}(\text{Si}_6\text{Al}_2)\text{O}_{22}(\text{OH})_2$).

The surface of the particles after grinding was characterized by a splintered shape, that is favorable for ensuring the contact with the reagent (Fig. 5a, 5b). After interaction with the bacterial solution, the surface of the particles was characterized by the appearance of cracking, that indicates a high degree of opening of sulfide grains by the leaching solution (Fig. 5c, 5d). That is especially important when leaching chalcopyrite, since this mineral is resistant to opening by various chemical reagents.

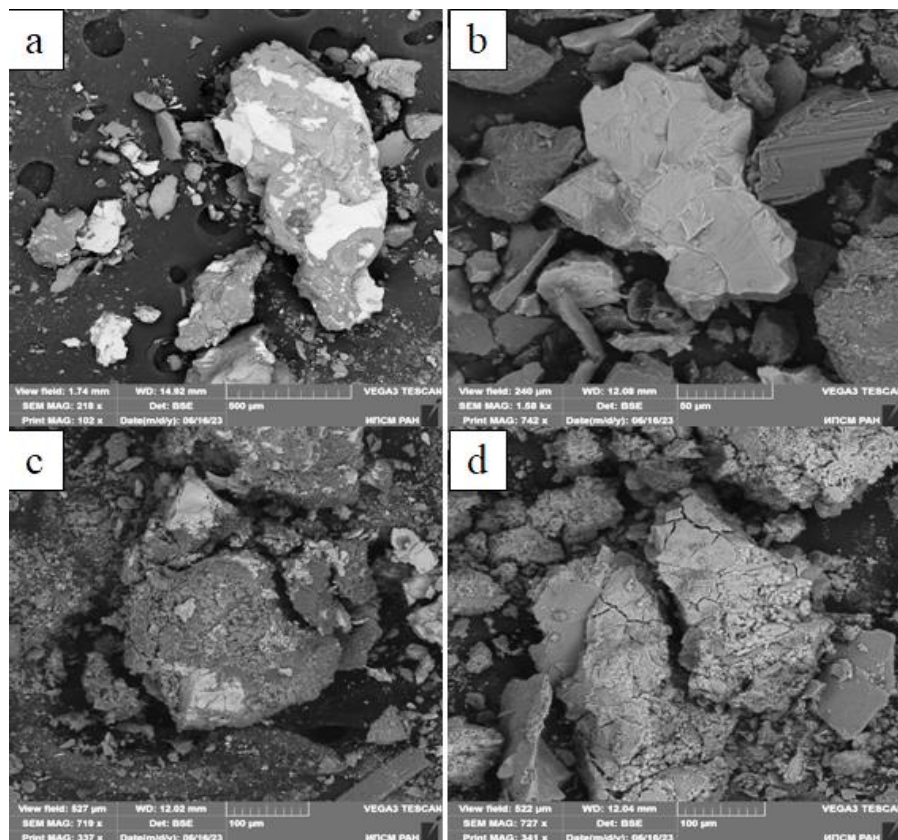
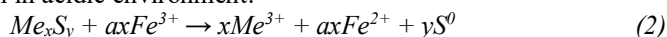


Fig. 5. The SEM-images of sulfide ore particles surface prior to (a, b) and after (c, d) bioleaching.

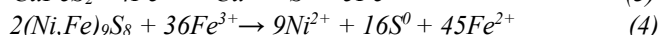
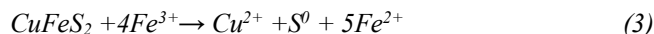
The destruction of the crystal lattice of sulfide minerals occurs due to their interaction with ferric iron in acidic environment:



where «a» is the valence of the metal, «x» and «y» are the stoichiometric coefficients for the metal and sulfur.

Thus, in the presence of Fe^{3+} , the role of bacteria in the process of sulfide minerals oxidation, as a rule, consists in the regeneration of the oxidizer, that is, in the oxidation of Fe^{2+} .

The leaching of chalcopyrite and pentlandite can be represented as the following formulas:



Taking into account the kinetics of metals recovery into the solution, after 150 days of leaching, the solution was diluted, that was resulted in a sharp increase of the metals recovery,

especially copper (Fig. 3). By the end of the experiment, 8.9 % nickel and 6.1 % copper were recovered from the ore. The most intense leaching process occurred within 210 days from the beginning of the experiment, after that the recovery of metals into the solution slowed down significantly. This indicates the need to mix the ore layer, that will probably promote the contact of the solution with minerals in those parts of the ore pile where the solution was difficult to get.

For the processing of pregnant solutions, a scheme is proposed for the sequential extraction of metals, in which at the first stage, copper is precipitated by cementation, at the second stage, the pH is increased to a value that contributes to the precipitation of iron, at the third stage, by further increasing the pH value, commercial nickel hydroxide is extracted from the solution.

According to the authors [12], the theoretical calculated consumption of iron for the copper (Cu^{2+}) cementation process is 0.867 weight units per unit of copper. In fact, the iron consumption becomes higher, since the active surface area of the precipitator is reduced during the cementation process. The use of the cementation method is especially important for small-scale production (up to 5 thousand tons/year) [13], when the use of extraction methods for pregnant solutions is not economically feasible. With full mechanization of the cementing plant, the solution is sent for further processing, and cement copper is sent to a vacuum filter or filter press. In this case, the final product is obtained in the form of cement copper powder.

For the subsequent extraction of metals, it is advisable to precipitate iron from the solution by increasing the pH. To increase the pH value of the solution, it is proposed to use quicklime (CaO), as a result of interaction with the solution, an iron-gypsum cake will be formed, containing the following main phases – gypsum, portlandite and iron hydroxides. The sediment can be used as a component in the production of building industry mixtures. After the precipitation of iron, the extraction of nickel is proposed to be carried out using brucite $\text{Mg}(\text{OH})_2$ to obtain commercial nickel hydroxide.

4 Conclusion

The obtained results showed the prospective of the heap bioleaching technology for processing of the Allarechensk technogenic deposit ore using the *Acidithiobacillus ferrivorans* strain. The selected temperature regime and the use of a circulating solution made it possible to recover 8.9 % nickel and 6.1 % copper over 330 days of the experiment. The high concentrations of copper and nickel in the pregnant solutions have been reached in a relatively short period, the solution became suitable for the extraction of non-ferrous metals from it.

Many impurities, such as iron, aluminium and magnesium, which are part of copper-nickel ores, are simultaneously leached into the pregnant solution with valuable components. In the hydrometallurgical process, a cleaning step can be required after the leaching process due to the presence of these impurities [14].

The existing method for removing ferric iron is the precipitation method. Precipitation of ferric iron from an acidic production solution is carried out by neutralizing the solution with various available and inexpensive neutralizing materials, such as limestone or slaked lime in the form of milk of lime. Neutralization to $\text{pH}=5.0$ leads to the hydrolysis of ferric iron and its precipitation in the form of hydroxide $\text{Fe}(\text{OH})_3$ [14].

According to the literature [15], a lot of experience has been accumulated on the extraction of nickel, cobalt and copper from multicomponent solutions, as well as the methods for removing impurities.

In work [16], as a result of bioleaching of non-ferrous metals for 300 days, the recovery of nickel into solution was 65 %, copper – 30 %. In addition to the main elements, the solution

contained ferric iron and ferrous iron. The iron was precipitated with calcium carbonate (16 g/L). All dissolved iron precipitated when pH=3.0 was reached, while the entire bulk of non-ferrous metals remained in solution. Copper and nickel were precipitated from purified solutions with sodium carbonate, magnesium oxide, calcium oxide, and sodium sulfide.

The authors [15] considered a sorption method for extracting nickel from pregnant solutions of bacterial-chemical leaching using the universal cationite KU-2-8. The contact duration between the sorbent and the pregnant solution was 1 hour. Then the sorbent was separated from the suspension, replacing with a new portion of the sorbent. For 3 cycles of sorption, up to 90% of nickel is extracted by Na-form KU-2-8.

The authors have noted that chelating resins are more selective for certain metals, making them more effective than cationic resins. The main advantage of using chelating resins is the selective extraction of metals from a solution with many other metals present.

The use of ion-exchange technology for the extraction of nickel and cobalt from a multicomponent sulfate solution of bioleaching was considered in [17]. The ion-exchange chelating resins were: Dowex M4195 (bispicolylamine functionality), Dowex XUS43605 (hydroxypropylpolyolamine functionality), and Amberlite IRC748 (IDA functionality). Dowex M4195 has been shown to have the highest selectivity for nickel and cobalt over other dissolved metals (iron, zinc, manganese and aluminium) at all tested pH values (2.0–4.0). This resin is less iron ion selective than IDA type resins.

There are many different ways to extract nickel, cobalt, copper from solutions of various compositions. One of the most important and promising methods of separation and concentration is the sorption method [14]. It has a number of advantages over other methods, these are high efficiency, availability and low cost of raw materials. The literature data [17–20] considers the strong base universal cation exchange resin KU-2-8 and ion-exchange chelating resins: Dowex M4195, DOW XUS43605, Purolite S 930, Amberlite IRC 748, Lewatit TP 207, Lewatit TP 208, Lewatit TP 207 Monoplus, Ionac SR-5. It was noted that ion-exchange resins have high selectivity with respect to nickel, cobalt, and copper ions.

Thus, the use of ion exchange resins for the extraction of metals has a great advantage and can be further introduced into the technological scheme for processing this type of raw material.

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References

1. Bloshenko, T. A., Pozdnyaev, A.S. Economy. Taxes. Law, 2015;**3**, 87-93
2. Osipov, V. I. Bulletin of the Russian Academy of Sciences, 2016;**86(8)**, 675-684
3. Eremicheva, E. V., Ashikhmin, A. A. Scientific Bulletin of the Moscow State Mining University, 2012, **5**, 28-35.

4. Sun, J. Z., Chen, B. W., Wen, J. K., Wang, D. Z. The Chinese Journal of Nonferrous Metals, 2018, **28(2)**, 356-364. DOI:10.19476/j.ysxb.1004.0609.2018.02.18
5. Masloboev, V. A., Seleznev, S. G., Svetlov, A. V., Makarov, D. V. Minerals, 2018, **8(10)**. DOI: <https://doi.org/10.3390/min8100436>.
6. Johnson, D. B. 2014. Current Opinion in Biotechnology, **30**, pp. 24–31. DOI: <https://doi.org/10.1016/j.copbio.2014.04.008>.
7. Bulaev, A. G. MIAB. Mining Inf. Anal. Bull. 2021;**(3-1)**, 56—87. DOI: 10.25018/0236_1493_2021_31_0_56.
8. Roberto, F. F., Schippers, A. Applied Microbiology and Biotechnology, 2022; **106(18)**, 5913-5928. <https://doi.org/10.1007/s00253-022-12085-9>.
9. Fokina, N. V., Yanishevskaya, E. S., Svetlov, A. V., Goryachev, A. A. Vestnik of MSTU, 2018, **21(1)**, 109–116. DOI: <https://doi.org/10.21443/1560-9278-2018-21-1-109-116>.
10. Seleznev, S. G., Boltyrov, V. B. News of higher educational institutions. Mining Journal, **(7)**, 57-64.
11. Seleznev, S. G., Svetlov, A. V., Menshikov, Yu. P., Nesterov, D. P., Makarov, D. V. Mineralogy of technogenesis, 2013,**14**, 177-190.
12. Scorcelletti, V. V.. Theoretical bases of corrosion of metals. (Leningrad. 1973)
13. Khalezov, B. D., Vatolin, N. A., Makurin, Yu. N., Bykov, N. A. Mining Informational and Analytical Bulletin (scientific and technical journal), 2005, **5**, 302–311.
14. Avfukova, L. S. Bulletin of the Tver State University. Series: Chemistry, 2021,**1**, 45-52. DOI 10.26456/vtchem2021.1.6
15. Belova, T. P., Ershova, L. S., Ratchina, T. I. Mining information and analytical bulletin (scientific and technical journal), 2017, **S32**, 210-215. DOI: 10.25018/0236-1493-2017-12-32-210-215
16. Seleznev A.N., Balikov S.V., Emelyanov Yu.E., Shketova L.E., Kopylova N.V. *Evaluation of the possibility of extracting copper and nickel from sulfide products by heap bacterial leaching*. Proceedings of the IV All-Russian Scientific and Practical Conference with International Participation. Prospects for the development of technology for processing hydrocarbon, plant and mineral resources. Irkutsk, April 24–25, 2014. Publishing house: IRGTU, 2014. 295 p
17. Liebenberg, C. J., Dorfling, C., Bradshaw, S. M., Akdogan, G. A., Eksteen, J. J. *The recovery of nickel and cobalt from a sulphate bioleach solution using Dow M4195*. In The Southern African Institute of Mining and Metallurgy Base Metals Conference, 2013, 269-282.
18. Koliehova, A., Trokhymenko, G., Magas, N. Technology audit and production reserves, 2019, **5(3 (49))**, 22-27. <https://doi.org/10.15587/2312-8372.2019.181411>
19. Zainol, Z., Nicol, M. J. Hydrometallurgy, 2009, **96(4)**, 283-287. <https://doi.org/10.1016/j.hydromet.2008.11.005>
20. Mendes, F. D., Martins, A. H. International Journal of Mineral Processing, 2004, **74(1-4)**, 359-371. <https://doi.org/10.1016/j.minpro.2004.04.003>