Low-cost sorption technologies for large-tonnage wastewater treatment in mining industries

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Abstract. The current state of water bodies in the zone of influence of the largest mining complexes in Russia – JSC "Apatit" and JSC "Kovdorsky GOK" was assessed on the basis of the conducted monitoring studies. The review of the natural and artificial materials with the high sorption capacity was carried out on the purpose of elimination of the revealed sources of hydrochemical anomalies. The paper presents the laboratory test results of sorbents depending on the methods of their modification, composition and properties of purified water. The introduction of developed sorbents into the wastewater treatment systems will significantly reduce the negative impact of the mining enterprises on surface waters, thus it will improve the environmental situation in the studied areas and the life quality of the local community.

1. Introduction
The development of human activity is accompanied by the involvement of new materials in the production process. In turn, to obtain them, it is necessary to increase the mining and processing volume of minerals, which is leads to the expansion of search geography and to the alienation of new territories. As a result, today there are several serious problems, including environmental ones, in the mining and processing industries. Modern mining and processing technologies of minerals are still remaining multi-waste in some cases, which leads to contamination of all components of the environment. The annual extraction of all kinds of raw materials in the world is about 25 billion tons; overall, less than 1.5 billion tons of them are used as finished products. The remaining part is stored in the waste, to accommodate those more than 10 thousand hectares of land are annually alienated [1, 2].

As a result of long-term waste storage, not only soils but also natural waters and the atmosphere are polluted, which adversely affects on humans health. The negative impact persists for 150 - 200 years or more even after the termination of field development and conservation of mine workings, due to the hypogene transformation of rock formations.

Anthropogenic waters are one of the most dangerous types of mining waste due to their high migration capacity. Mine waters and sewage from the tailings of processing plants pose a greater threat to water resources, located in the areas of mining and processing enterprises. A huge amount of pure water, which is taken from surface water bodies, is used at each technological process to obtain marketable products from ores of various metals. Processed water is saturated with various pollutants, including dangerous synthetic reagents and components of the extracted ore, during ore processing. Significant volumes of waste waters, which are generated as a result of minerals extraction and processing, their multicomponent composition and the uneven inflow, currently make it impossible to solve the problem of sewage treatment using standard methods at the majority of mining enterprises. This fact is confirmed by the increasing total amount of sewage discharge. Thus, according to the Federal Agency for water resources, as a result of mining, the total volume of sewage in 2018 in the Russian Federation was 1394 million m³, including 996 million m³ of polluted wastewater.

The long-term irrational use of mineral resources has led to a shortage of drinking water in a number of mining regions.

The zones of influence of such enterprises as JSC "Apatit" and JSC "Kovdorsky GOK" are vivid
examples of mining areas with unfavorable ecological situation connected with the formation of extensive hydrochemical halos and streams of heavy metals pollution. The first of them is JSC "Apatit" - the world's largest manufacturer of high-grade phosphate raw materials and nepheline concentrate. The activity of this enterprise is annually accompanied by a discharge of 50 million m³ of mine waters. As a result, a high-contrast hydrochemical anomaly in the basin of the lake Imandra was formed, in which the molybdenum content is 100 times exceeds the maximum allowable concentration for fishery waters (MAC) [3, 4].

The second of them is JSC "Kovdorsky GOK" - manufacturer of iron ore, apatite and baddeleyite concentrates. Water pollution in the Kovdor river basin is caused by the annual discharge of 50 million m³ of insufficiently treated industrial wastewater into water bodies. 20 million m³ of sewage, in which a manganese (II) concentration 90 times exceeds the MAC, are come from the tailing pond [5].

The studied objects - mining and processing plants - are located on the territory of the Kola Peninsula in the Northern part of the Russian Federation, which aggravates the environmental problem due to poor stability and low self-cleaning ability of the investigated ecosystems. At the same time, the main pollutants of wastewater belong to heavy metals and have a toxic effect on hydrobionts and the ecosystem as a whole. In addition, these pollutants can accumulate in sediments, becoming a source of secondary pollution.

Taking into account the above, the search for effective and safe sewage purification technologies from heavy metal is one of the priority areas in the field of environmental protection. The choice of the optimal sewage treatment method is determined by many factors, including the concentration and form of the element in the wastewater. The selection of the sewage treatment scheme depends on the amount and composition of wastewater, the possibility and economic feasibility of extracting impurities, the requirements for the quality of purified water and so on. Nowadays, combined treatment methods based on mechanical, chemical, physico-chemical and biological methods are used for large-tonnage sewage purification from heavy metals.

2. Materials and methods

Nowadays, several methods for purification of manganese-containing wastewater have been developed and are actively implemented at industrial facilities. The five main methods of wastewater treatment from manganese are ion-exchange, reagent methods, oxidizing filters, aeration under pressure with subsequent filtration, chemical oxidation with subsequent deposition and filtration, sorption.

Numerous works and developments are devoted to solving the problem of molybdenum-containing wastewater treatment. The main methods of wastewater treatment from molybdenum ions are ultrafiltration, electrodialysis, reagent methods, sorption and ion exchange.

Taking into account the specifics of the sewage formation at the mining enterprises, typical methods are required a significant refinement and additional field and laboratory studies.

A detailed literature review showed that nowadays methods of waste water purification from molybdenum and manganese based on sorption are most widespread. Their application is characterized by high productivity, as well as the possibility of selective treatment of multicomponent wastewater.

Sorbents are divided into carbon and non-carbon. The first are active coals, peat and other materials, those are obtaining mainly by the processing of various organic materials. At the same time, non-carbon sorbents prepared from natural and artificial materials (clay rocks, zeolites and etc.) are increasingly used. The wide using of such sorbents is due to their selectivity, relatively low cost, availability and cation exchange properties of some of them. The relevant trend is using production waste as cheap raw materials to obtain sorbents and, at the same time, recycling of accumulating by-products.

Despite this, the widespread use of sorption methods for industrial wastewater treatment from heavy metals is limited for a number of reasons. The most important of them is insufficient sorption capacity of the material in its original form in relation to heavy metals and lack of reliable regeneration methods of sorbents [6, 7].

Among the materials with high sorption activity in relation to manganese are montmorillonite, limestone and dolomite [8, 9]. However, these sorption materials are not in demand for the industrial sewage purification for the following reasons: insufficient cleaning efficiency, lack of selective extraction of heavy metals, limited raw material base for the sorbents production.

The review of sorption materials providing sewages purification from molybdenum showed that their effective work is observed in the pH range from 1 to 7 pH units. In addition, the existing sorbents are practically not used on an industrial scale due to the high cost and limited amount of feedstock, which includes bentonite clay, activated bone charcoal, aluminum oxide, bean skin, peat and others [10].
Thus, the search and study of sorbents on the basis of natural materials and production waste, capable to provide an increase of industrial wastewater treatment efficiency, is an urgent problem.

In order to solve the current environmental problem related to wastewater treatment from manganese and molybdenum, the sorption activity of natural materials and industrial waste was assessed in the laboratory.

Vermiculite from Kovdor Deposit, located in close proximity to sources of formation of hydrochemical anomalies, was chosen as a potential sorbent for treatment of the considered sewage. It has a high selectivity to large cations of alkaline, alkaline earth and heavy metals, which indicated the prospects of its application in wastewater treatment of manganese and molybdenum. The study of vermiculite as a sorbent began with the analysis of its composition and properties. The chemical composition of Kovdorsky vermiculite was determined by the method of atomic emission spectrometry with inductively coupled plasma on the analyzer ICPE-9000. The results of the analysis are presented in table 1.

Table 1. Chemical composition of Kovdor vermiculite concentrate

| Components | Content, % |
|------------|------------|
| SiO₂       | 40.0       |
| Fe₂O₃      | 12.5       |
| Al₂O₃      | 12.1       |
| MgO        | 29.7       |
| TiO₂       | 0.9        |
| CaO        | 2.3        |
| K₂O        | 1.8        |

As it can be seen from table 1, the main components of vermiculite are Si, Fe, Al, Mg. Data of x-ray structural analysis showed that vermiculite belongs to water aluminosilicates of complex chemical composition.

The parameters of the porous structure of vermiculite were studied using the method of mercury penetration porosimetry, which allowed obtaining a qualitative and quantitative assessment of the vermiculite pores, as well as calculating the specific surface area (table 2). The value of the specific surface of vermiculite studied samples amounted to 700-800 m²/g.

Table 2. Parameters of the porous structure of Kovdor Deposit vermiculite

| Sorbent       | Vₙ, cm³/g | Vᵣ, cm³/g | Sₙ, m²/g | Rᵣ, Å  | Vᵣ,m, cm³/g | τ, Å   | Vᵣ/m/Vₙ |
|---------------|-----------|-----------|----------|--------|-------------|--------|---------|
| Kovdor Deposit vermiculite | 0.18       | 0.03      | 12       | 90     | 0.15        | 5.6    | 0.83    |

*Note: Vₙ is the limiting adsorption volume; Vᵣ is the volume of transitional pores; Sₙ is the specific surface area of transient pores; Rᵣ is the radius of the transitional pores; Vᵣ,m is the volume of micropores; τ is the thickness of the micropores.

The results of the comprehensive analysis showed that the vermiculite refers to a microporous adsorbent with changing pore sizes in the process of adsorption. In addition to the primary microporosity, due to the crystalline structure, vermiculite has secondary, mainly, transitional pores formed by gaps between the contacting particles. At the same time, the surface and volume of secondary pores in vermiculite is much smaller than the surface and volume of primary pores.

The evaluation of sorption properties of vermiculite in relation to the studied cations was carried out on model solutions under laboratory conditions using high-tech equipment of the Environmental laboratory of the Mining University. The analysis of metals residual concentrations in solutions by atomic absorption method on Shimadzu AA-7000 spectrometer showed that after contact with a potential sorbent under static conditions the degree of manganese (II) extraction was 51 %, molybdenum sorption from the solution was not observed. In this regard, there was a need to develop and evaluate possible methods of vermiculite modification in order to increase its sorption capacity with respect to manganese (II), as well as to continue the search for a sorbent capable of extracting molybdenum ions from aqueous solutions.

To solve the problem of surface water protection in Apatitsky district, a detailed study of the mineral resource base of the Kola Peninsula was carried out. Clays were chosen among the available and common...
natural sorbents. During the laboratory experiment, the maximum efficiency of model solution purification equal to 69% was achieved with Pechenga Deposit clay. A characteristic feature of this clay is an increased iron content, which according to chemical analysis reaches 22% in terms of Fe₂O₃.

It was established, due to the applying of modern instrumental methods of research, that the chemisorption process, based on the formation of chemical compounds FeMoO₄ and Fe₂(MoO₄)₃ and their subsequent sorption on developed surfaces, is an essential factor in the purification of molybdenum-containing wastewaters. However, using clays did not allow achieving the required standard values of molybdenum concentrations in purified solutions. In this regard, the next stage of laboratory research was the study of sorption abilities of iron-containing waste, which included sulfuric acid production slag and metalworking waste. The degree of molybdenum extraction from the model solution reached 98-99 % in case of using each of the waste types. Despite this, further work with slag was impractical due to desorption of a number of toxic components (Zn, Mn, Fe, Cu) from the waste during the purification process. Thus, the sewage treatment using metal processing waste (steel chips), providing efficiency up to 99 % has become the most promising method.

The development of the preparation technology of the adsorbent and assessment of its work depending on the composition and properties of the treated water has become the main objectives of further laboratory research.

3. Results

Given that the properties of vermiculite predetermine its possible grinding by impact and cutting, at the initial stage, the method of mechanical activation of vermiculite was chosen, which will allow showing the maximum sorption activity of the sorbent with respect to the extracted manganese ions. To grind the material by impact, jaw and hammer crushers were used; layer-by-layer disintegration was carried out in a rotary crusher with a cutting-grinding nozzle. In order to increase the specific surface area of vermiculite concentrate, heat treatment was also used, after which vermiculite is able to swell. Based on the above, parts of the vermiculite test portions were incubated in a muffle furnace at temperatures of 300 °C and 600 °C for two hours. Laboratory tests showed that high efficiency of purification of manganese-containing water, reaching 88 %, was observed in the vermiculite disintegration with the predominant use of cutting and shear forces without additional heat treatment. However, the results were obtained using samples of size 1-2 mm. It is known that the grinding of the sorption material leads to an increase in the contact area with the purified water and, as a result, significantly increases the amount of adsorption of pollutants from the solution. The study of the influence of the vermiculite samples size on the purification efficiency showed that the maximum permissible concentration (0.01 mg/dm³) in the model solution with the initial manganese content of 1 mg/dm³ can be achieved in the case of using a layer-by-layer crushed sorbent with a size of 0.5-1.0 mm and less. Further, the adsorption values of the solutes on the solid sorbent were obtained experimentally. The adsorption value was 2.1 mg/g for vermiculite with a size of 0.5-1 mm. In General, the results of laboratory tests showed that for a smaller fraction the adsorption value is much higher than the adsorption value for large fractions at the same equilibrium concentrations. This is due to an increase in the specific surface area of the sorbent and, possibly, opening more micropores. The study of sorption kinetics showed that the rate of sorption of manganese on vermiculite is maximum in the first minutes of contact. First of all, the equilibrium was occurred in the system with the participation of vermiculite with a size of 0.125-0.315 mm and amounted to 20 minutes, with the participation of vermiculite with a size of 0.315-0.5 mm and 0.5-1 mm – 30 minutes.

Further, the influence of the composition and properties of the purified solution on the vermiculite sorption properties was studied. The limiting parameters of the solution were: the concentration of manganese in the solution, the temperature of the solution and the value of the hydrogen index.

Model solutions with concentrations ranging from 0.5 to 5 mg/dm³ were prepared to assess the degree of manganese extraction by vermiculite depending on the initial concentration. Contact of the sorbent with the solution was carried out under static conditions in the mode of mixing at a constant temperature of 20 °C. The obtained experimental data showed that the degree of manganese cations extraction with an increase in the concentration of solutions decreases. This is due to the fact that the ion strength of the solutions increases with the increase in the concentration of the initial solution and the activity of manganese cations decreases. Consequently, the number of free manganese ions in the solution becomes smaller, and therefore the degree of cation extraction is reduced.

The effect of temperature on sorption from aqueous solutions is far from clear. It is known that the penetration of substances into the pores depends on their kinetic energy in case of the sorption of these
substances on microporous sorbents, the size of which is close to the effective size of the pores. At a sufficient temperature, the sorbate molecules penetrate into the pore and are sorbed; otherwise, there is only a slight absorption on the surface of the meso- and macropores. In other words, the sorption capacity increases with temperature. This phenomenon is called "activated adsorption". At the same time, physical sorption, like any exothermic process, generally deteriorates with increasing temperature. Therefore, the total externally recorded manifestation of these two phenomena can have a maximum at a certain temperature. The experiment was conducted to confirm the proposed assumptions. The results of the research allow making a clear conclusion that with the decrease in temperature by 5 °C, the degree of manganese extraction from the model solution falls by 3 %. The peak of sorption on the selected temperature range of the model solution 5-20 °C was not recorded.

One of the most important factors in the sorption extraction of ions from the solution is the value of the acidity of the medium, which affects both the form in which the ion under study is in the solution and the state of the ionogenic groups. In most cases, the decrease in acidity causes an increase in the adsorption of pollutants from wastewater. However, it was found that acidic solutions destroy the crystal lattice of vermiculite. The destruction of the lattice occurs unevenly and leads to a decrease in the exchange capacity of vermiculite. The study of the influence of pH on the processes of manganese cation sorption was carried out in the range from 3 to 10 units. At pH = 3, there was a sharp decrease in the degree of manganese extraction from the solution, by almost 30 %, due to the partial destruction of vermiculite in an acidic medium. In all other solutions, the purification efficiency was not less than 95%. As a result of studies purification efficiency up to 95-99% of manganese-containing waters of the Kovdor Deposit by the using of the modified vermiculite has been proven.

As it was noted earlier, the waste, represented by metal chips, has proven to be available for use as a sorbent for the molybdenum extraction from wastewater. Due to the fact that the main role in the purification process is played by iron oxides, which have a developed specific surface area and increased reactivity, chip samples were treated with distilled water and kept in the air for 24 hours for the intensification of the corrosion processes. Further, the analyses were carried out on a Mossbauer spectrometer MC1104Em with the 57Co (Cr) source in order to determine the exact composition of corrosion products of iron-containing metal waste.

According to the results of Mossbauer spectrometry the content of Fe₂O₃ is 32.2 %, and Fe₃O₄ - 67.8 %. At the same time, the assessment of the efficiency of model solutions purification with each of the corrosion products separately showed that the main role in the molybdenum-containing waters treatment belongs to Fe₂O₃.

It should be noted that the intensification of the corrosion process, which is directly related to the subsequent rate of molybdenum extraction from the solution, is influenced by such parameters as the temperature of the purified solution, its acidity level, and the content of dissolved oxygen. A series of experimental studies have shown that:

- with an increase in temperature by 5 0°C, in the studied temperature range (5 0°C – 25 0°C), the efficiency of model solutions purification from molybdenum increases by 5-10 % on average, as the rate of chemical reactions, the diffusion rate and the solubility of corrosion products increases
- cleaning efficiency is inversely proportional to the pH of the purified solution. So at pH = 9, the amount of molybdenum ions extracted from the solution is 3 times lower than at pH = 3, which is due to the high corrosion rate of metal waste in an acidic medium;
- with an increase in the content of dissolved oxygen 2.5 times the efficiency of cleaning the model solution increases by 2 times. This is due to the intensification of the process of steel chips corrosion, as well as to the formation of mainly iron oxide (III), which showed greater efficiency of cleaning compared with iron oxide (II).

The study of the chemisorption process of molybdenum from aqueous solutions showed that steel chips ion exchange capacity is limited only to the passivation process of iron. This process occurring in the formation of iron molybdate on the steel chips surface with a specific surface area less than 15 cm²/g. The obtained results allow concluding about the possibility of purification of JSC "Apatit" mining waters up to the standards values with the chemical adsorbent represented corroded metal steel chips application.

4. Conclusion

The results of the complex scientific and practical research pointed to the prospects of using of the sorbents based on natural materials and industrial waste in the purification process of multi-tonnage sewage from heavy metals, which will make it possible:
to increase the efficiency of sewage purification in relation to manganese and molybdenum up to 99 %;

- to develop environmentally efficient and cost-effective sorption technologies for wastewater treatment using the obtained sorbents;
- to reduce the risk of secondary pollution of purified water by using safe methods to increase the sorption activity of the sorption materials under study and the absence of their chemical treatment;
- significantly reduce the cost of manganese-containing wastewater treatment due to using vermiculite as a sorbent, which is a natural mineral available in the study area with the deposit located in close proximity to the mining facility;
- to implement waste-free technology at the industrial facility as a result of using of metal production waste for the molybdenum-containing waters purification;
- to improve the environmental situation by preventing further formation of hydrochemical anomalies;
- to improve the quality of life of the population in mining areas.

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