REVIEW OF THE PROCESSING OF MINERALS AND TECHNOGENIC SULFIDE RAW MATERIAL WITH THE EXTRACTION OF METALS AND RECOVERING ELEMENTAL SULFUR BY ELECTROCHEMICAL METHODS

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ABSTRACT

Due to the economic necessity of complex processing of poor, low-quality and inaccessible raw materials, as well as the production of metals from these ores of products with high added value, there is a problem of a complex study of the electrochemical behavior of metal sulfides in various environments, generalization and systematization of this material, the conclusion of General laws that allow predicting the behavior of these materials in non-stationary conditions. The review presents various methods of processing sulfide raw materials of both mineral and man-made origin. The world experience of using various technologies for extracting metals from sulfide ores and materials with the accompanying extraction of elemental sulfur is considered, which allowed us to choose the best method for electrochemical research of metal sulfides to simultaneously obtain metals with the extraction of elemental sulfur.

Keywords: Electrochemistry, Processing, Extraction, Metal sulfides, Sulfur.

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INTRODUCTION

The mountainous regions of Kazakhstan have the world's richest reserves of sulfide ores. Environmentally friendly sulphide recycling methods are extremely important for the economy of the future. In recent decades, electrochemical and hydrometallurgical methods for processing sulfides have been intensively developed. The latter is associated with the use of highly efficient technologies in new enterprises.¹

Currently, electrochemical processes are becoming increasingly important in the production of metals, as they allow more economical (compared with pyro processes²⁻⁶) to extract the main components from poor ores and concentrates.⁷ According to the calculations of Canadian experts⁸, the processing of sulfide materials into sulfuric acid becomes profitable when consumers are located at a distance of no more than 160 km from the plant. In the conditions of the remoteness of plants, when the main consumers of sulfuric acid and ammonium sulfate are far away, it is also beneficial to receive and transport sulfur in elemental form⁷. Currently, several methods for processing sulfides with the release of elemental sulfur have been developed in the world.

Different Processing Techniques

Treadwell company's process, proceeding by the next overall equation, can be found as one of the oldest processes of chalcopyrite processing:

A process for leaching sulfide concentrates with an iron chloride solution has been developed by the USA company Duval: ^{7,8}

Canadian “Sheritt Gordon Mine” company’s laboratory is carrying out studies to implement the next process:

aimed mainly at the absorption of oxidizing burning gases.

Among the direct electrochemical methods of leaching sulfides, it is important to note a method of Canadian INCO company, implemented at Thompson plant ¹⁰, which leaches anodes b – Ni_3S_2 and bϕ – Ni_3S_2 , electrolyzes these anodes with sulfur on anode deposition and nickel on cathode deposition. In Japan ¹¹ anodes made from 30% ZnS and 70% graphite are pressed and processed as follows:

A process of electrolysis of Cu_2S anodes in 1M H_2SO_4 is also successfully carried out, according to the researchers of the Institute of mining and geological sciences of the USA in three stages ¹²:

In sulfide ores, nickel is most often present as a pentlandite mineral, which is a solid solution of nickel and iron sulfides (Ni, Fe) S, closely related to pyrrhotite Fe_7S_8 , sometimes nickel occurs in nature as a fairly rare mineral – millerite (NiS), which does not (yet) have sufficient industrial use. ¹³ In melting products – nickel mattes – nickel is in the form of Ni_3S_2 . Anode slurries of nickel electrolysis contain 90% of nickel in the form of NiS and 10% in the form of ferrite: $\text{NiO} \cdot \text{Fe}_2\text{O}_3$. ¹⁴

The kinetics of oxidative leaching of fused Ni_3S_2 sulfide was studied by ¹⁵, as a result of which it was found that leaching of Ni_3S_2 proceeds in two stages:

Where, Ni_3S_2 conversion to NiS proceeds quickly and ends within 15 minutes (at 125 °C and p O_2 = 5 atm.).

Ni_3S_2 surface enrichment at NiS sulfuric acid leaching was observed by Kipnis and Muravchik ¹⁶, who noted that NiS has the highest stationary potentials in H_2SO_4 solution among several Ni_3S_2 – Ni_7S_6 – NiS sulfides.

Nonferrous metal sulfides can have a different crystal structure and, accordingly, a phase composition, which is reflected in metal-sulfur state diagrams. ¹⁷ Nickel sulfide crystal form influence on the rate of its solution in sulfuric acid was examined by Belyakov and Kasikov ¹⁸, who concluded that g nickel sulfide obtained from a sulfate solution and identical to natural millerite has the highest rate of the solution; amorphous α-NiS obtained by precipitation of nickel sulfide from NiSO_4 with Na_2S has the intermediate rate, and hexagonal b-NiS obtained by direct synthesis at temperatures above 400°C has the minimum rate 400°C.

From all has been mentioned it follows that hexagonal b-NiS has the minimum rate of the solution in all sulfides in sulfate solutions; furthermore, NiS deposition on lower (sulfur) sulfides surface, of course, slows down the process and, therefore, it is necessary to search ways to solve this particular nickel sulfide.

Artificial hexagonal nickel b-sulfide NiS (50%), and sulfides of other metals, on which it is much better to study the behavior of sulfides under various conditions, can be synthesized from powdered metals and sulfur in an evacuated quartz ampoule by the standard technique. ¹⁹

It should be noted that acid oxidative leaching of natural nickel sulfides and artificial millerite was studied in detail in²⁰⁻³⁴ and summarized in^{35,36}, and electrochemical studies were presented in³⁷⁻³⁹ in the book.¹ During autoclave leaching, nickel sulfide mattes are processed with the release of sulfur-hydrogen²¹, which is generally not very good due to the toxicity of the latter.

Currently, technologies of oxidation solution of sulfides in copper-chloride and copper-sulfate solutions continue to be studied by the next schemes:

Moreover, process (1) proceeds quite efficiently at temperatures of 90°C and overall chloride concentration of 160-200 g/l, process (2) – at temperatures of 90-100°C, and process (3) – at temperatures of about 160°C.

Disadvantages of Both the Processes

Process (1) - large concentrations of chlorides that interfere with further processing of the electrolyte.

Process (2) - the need for high temperatures, as well as the passivation of the NiS surface due to the deposition of Cu₂S.

Understanding that a change in the surface of sulfides upon their dissolution can lead both to a substantial acceleration (for example, due to pitting - cracking of the surface and penetration of the solution deep into the sulfide²²), and to a significant slowdown caused by solid-phase transformations of sulfides or passivation at the formation of films on the sulfide surface²² led to the development of new methods for studying the surface of materials since it is necessary to know which phases, epitaxial or passivation layers are formed on the surface sulphides, as well as in the case of heteropolystructures, the most modern methods for studying the surface of materials are used to study them. In particular, X-ray diffraction analysis can be used to analyze anisotropic samples and epitaxial layers.²³⁻²⁶

Numerical band calculations of MeS sulfides' electronic structure: NiS, CuS, and ZnS, were carried out.²⁷

Following the calculation results, a detailed analysis of the valent states' structure is carried out obtained partial densities of the states are compared with X-ray SL (2, 3) – and SK (b (1, 3)) emission spectra. It is shown that the spectra shape is determined by different hybridization degrees of various Me(3d)-orbitals with 3p-states of sulfur. The hybridization degree and the symmetry of hybridizing Me(3d)-orbitals are determined by the crystal lattice geometry. As a result, binding and anti-binding hybrid states of Me(3d)-S(3p) and weakly hybridizing Me(3d)-states arise.

With the help of electronic spectroscopy and band structure calculations using the model Hamiltonian, the electronic structure of nickel sulfide (NiS) in the millerite phase was studied.²⁸ Compared to the hexagonal NiS phase for a given highly conductive phase, the band structure calculations provide a more accurate description of the experimental valence band spectrum. To describe some features of the experimental spectra in the calculations, it is necessary to consider the electronic correlation effects, even though the system is strictly metallic. The calculations confirm that NiS millerite is a strictly covalent pd-metal. The comparative study of the hexagonal and millerite forms of NiS allows providing information on the dependence of the pd-metal spectral function on covalency.

Using methods of polarized Raman spectroscopy of crystals, optical phonons in millerite were studied.²⁹

Thin NiS₂ films, which have prospects for use in photoelectrochemical solar cells, were deposited on Ti substrates using triethanolamine as a complexing agent. The optimal deposition conditions were determined. The films' photosensitivity was studied by the voltammetry method in the presence of a sodium thiosulfate solution.³⁰ A mechanism and kinetics of oxidation of synthetic a-NiS, and kinetics of oxidation of a-NiS were studied under isothermal conditions by the DTA-TG-DTG and X-ray diffraction methods. The results on the NiS desulfurization degree were used for calculations using the Sharpe model. The kinetic expressions for the degree of conversion α in the desulfurization reaction were determined: $-\ln(1-\alpha)=k[1] \quad t=27.89 \exp(-9860/T)t$ and $-\ln(1-\alpha)=k[2] \quad t=1.177 \exp(-4810/T)t$, where t – the

reaction time, $k[1]$ and $k[2]$ – the rate constants of the first and second stages of the reaction. The activation energies values were obtained: $E[1]=82+4$ kJ/mol and $E[2]=40+2$ kJ/mol.³¹

It has been experimentally shown that “amorphous nickel sulfide” (a material deposited from aqueous solutions of $\text{Ni}^{(2+)}$ and $\text{S}^{(1-)}$ salts under ambient conditions) is a hydrated nanoparticle material with the approximate formula $\text{NiS} \cdot 1.5\text{H}_2\text{O}$.³² Using solvothermal synthesis, NiS was obtained in the form of 3D nanostructures.³³ It has been shown that NiS nanocrystals are synthesized under hydrothermal conditions from $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{Na}_2\text{S}_2\text{O}_3$, or $\text{S-C}(\text{NH}_2)_2$ at relatively low temperatures.³⁴

Hollow spheres of NiS with a controlled average diameter of 800 nm and a wall thickness of 120 nm were fabricated on a large scale by a simple method with the bifunctional use of cyclohexylamine as a solvent and elemental sulfur-reducing agent, which successfully regulates the slow rate of H_2S release. The latter reacts with spherical micelles of the $\text{Ni}^{(2+)}$ complex - polyvinylpyrrolidone (molar mass 30,000) in solution to form NiS nanoparticles. The low rate of H_2S release favors the self-organization of nanoparticles on spherical micelles. Washing the products with deionized water and ethanol removes the polyvinylpyrrolidone backbone, leaving hollow spheres of NiS. Based on the results, a possible growth mechanism is proposed. This method can be used for the synthesis of hollow spheres of sulfides of other transition metals.³⁵

Hydrothermal methods synthesized NiS millerite nanocrystals with various morphologies. According to X-ray diffraction data, the products are pure NiS millerite with lattice parameters $a=9,624$, $c=3,15$ Å. The use of ethylene diamine and hydrazine hydrate as solvents leads to the formation of rod-shaped NiS nanocrystals, while spherical nanoparticles are formed in a solvent of aqueous ammonia. The resulting products have a relatively high specific area of PV, which favors their use as catalysts.³⁶

“Method for processing sulfide polymetallic iron-containing materials” patent, obtained as a result of many years of work at A.P. Zavenyagin Norilsk Mining-and-Metallurgical Integrated Works³⁷ assumes that processing of polymetallic iron-containing materials involves oxidation leaching of starting materials in a water pulp under oxygen pressure at a temperature above the melting point of sulfur with the conversion of nonferrous metals to the solution, sulfur to elemental, iron to oxides, treatment of oxidized pulp with sulfur redistribution effluent, containing unsaturated sulfur compounds, or at redox potential values of $+390/-+310$ mV by platinum electrode relative to silver chloride comparison electrode and sulfide deposition at a temperature below the melting point of monoclinic sulfur modification, or redox potential values of $+140/-+60$ mV and sulfide deposition at a temperature above the melting point of monoclinic sulfur modification. After the nonferrous metals' sulfide deposition, sulfides and elemental sulfur are separated into a sulfur-sulfide concentrate, and iron oxides into final rejects. Sulfur and sulfide concentrates are obtained from the sulfur-sulfide concentrate using a calcium-containing hydrophilizer reagent, and the obtained calcium effluents of sulfur redistribution containing unsaturated sulfur compounds are sent to treat oxidized pulp. Although this patent has rather positive aspects, such as carrying out processes with controlled redox potentials, the general scheme is rather complicated and does not involve sulfide solution, on the contrary – the nonferrous metals' sulfide deposition and sulfide concentrate obtaining, the further processing of which remains a subsequent problem.

Canadian patent “Method of hydrometallurgical metal extraction from complex ores” shows that copper and/or zinc sulfides make contact with sulfuric and nitric acid, at that a reaction mixture is formed, which is maintained at a temperature in the range from 110 to 170°C with continuous mixing, then sulfuric and nitric acids are added to the reaction mixture in an amount sufficient to form a light precipitate, containing water-soluble sulfates of copper, zinc and iron, and a dark precipitate that is water-insoluble, and containing elemental sulfur and waste material. An oxygen source is also introduced into the reaction mixture to accelerate the oxidation of sulfides to sulfates and the oxidation of gaseous products of NO_x reaction to regenerate nitric acid. The obtained light and dark precipitates and increased acid solution are removed from the reaction mixture, the light and dark precipitates are separated from the acid solution and processed to extract copper and/or zinc sulfate from the light precipitate, and the acid solution is recycled to the reaction mixture.³⁸ This patent is noteworthy in that it involves the use of nitric acid, and its effect can be characterized by the words “good, but expensive”, although, indeed, the use of additives of nitric acid compounds can be successfully used in some cases of the processing of refractory sulfides.

“Method for leaching products containing metal sulfides” patent involves vat leaching with mixing and a temperature of 20-95°C, a solid phase content of 9-30% in a water solution of sulfuric acid with a concentration of 2.0÷150.0 g/dm³ containing ferric iron ions with a concentration of 3÷20 g/dm³. During the leaching, ultrasonic exposure is carried out from the device at the bottom of the vat and hydrogen peroxide with a concentration of 30-50% and ozone with a concentration in the gas mixture of 100-200 mg/dm³ is continuously supplied, with a ratio of ozone to hydrogen peroxide consumption of 1:1÷2.³⁹ In this method the oxidation-reduction potential (ORP) of the system is increased due to the introduction of ferric iron ions, hydrogen peroxide and ozone; the sulfide surface depassivation is carried out due to the ultrasonic exposure. It is necessary to note that the use of ferric iron is very problematic due to its high corrosivity and the need for subsequent separation of iron and metals from the solution, the use of ultrasound and ozone also leads to premature equipment destruction, and ozone emissions are harmful because ozone, generally speaking, is a rather dangerous substance – its maximum permissible concentration is 0.1 mg/m³, and when it is combined with sulfuric acid, a poisonous fog is formed.²¹

“Method for processing raw materials containing precious metals and sulfides” patent involves mixing raw material with water or solution of sulfuric acid, the additional introduction of halide ions (chlorine, iodine and bromine ions) in the form of soluble salts or natural carnallite minerals containing them (MgCl₂·KCl·6H₂O), or spent electrolytes from the electrolysis of alkali and alkali-earth metals and treatment of the mixture in the autoclave with oxygen. Then, the oxidized pulp is washed with water from sulfuric acid.⁴⁰ A advanced method is that halide ions are used simultaneously as depassivators and complexing agents, although, when the system is watered (during the washing), some compounds may precipitate.

In compliance with the application “Method of silver extraction from sulfide-silicate and sulfide ores”.⁴¹ The method consists of mixing the raw material with a solution of sodium chloride, holding the mixture, drying it, calcining to obtain a cinder containing silver chloride. The cinder is washed, silver is leached from it using sodium thiosulfate, and silver is precipitated from the solution with sodium sulfide. The silver sulfide is treated into metallic silver by the acid-base method or by the reduction melting. According to the prior application, the material is leached in chloride solutions. It might be a wonderful idea, only it would be possible to use not sodium chloride, but other, more concentrated chlorides, and to separate silver from the chloride solution, do not bake the solution to prepare a cinder, but isolate silver using modern effective methods – sorption or cementation.

“Method for processing sulfide raw products including precious metals” patent involves mixing raw material with aqueous solution of reagents and autoclave oxidation treatment with an aqueous solution of reagents when oxygen is supplied with the addition of a component with a halide ion to produce pulp. Then the pulp is isolated to a solution and a solid residue. In this case, the autoclave oxidation treatment is conducted by an aqueous solution including a halide ion component at a temperature of 160-250°C and fractional oxygen pressure of 0.5-5.0 MPa. The precious metals are isolated by leaching from a solid residue with the help of sulfite-thiosulfate solutions. The technical result is the reduction of technological operations and the use of a less valuable and not harmful to the environment solvent.⁴² In this method, the precious metals are converted into insoluble chlorides, although at sufficiently high chloride concentrations, many compounds will be partially solved, so it would be more efficient to leach by more concentrated chloride solutions.

“Isolation of base metals from sulfide ores and concentrates” patent was obtained by authors from Great Britain.⁴³ The invention refers to the method for isolation of base metals from sulfide ores and concentrates. The method includes the steps of mixing base metals involving ore with ferric iron salts. The base metals include copper, nickel and zinc. Later the mixture is warmed, water is supplemented for the formation of a suspension that is mixed and filtered. The technical result is to improve the effectiveness of these metals’ isolation in the treatment of ores and concentrates with a low sulfide content. The method could be significantly improved if leaching was conducted in concentrated chloride solutions with the addition of ferric iron or other mediator ions.

The patent “Metal isolation from sulfide minerals”⁴⁴ was developed for nickel solution in leaching acid using two stages. A suspension of minerals and acid is oxidized. This is conducted during T₁ using electrolysis or chemically, with the addition, for example, the oxidized acid to the mineral. After the

oxidation, the suspension is held upon anoxic conditions over T_2 time. During T_2 , sulfide begins to be solved much faster, the quick decomposition of sulfide allows nickel to be solved and, thus, leached from the mineral. Such a nickel is isolated from the leaching acid, for instance, by electrochemical isolation. This is a very genial idea using electrochemical activation – as it is affordable to electrochemically move the process from the passive region to the active solution region. It is expedient to conduct this activation in a more effective, pulse-periodic mode.

“Method for leaching metal sulfides using reagents having thiocarbonyl functional groups” patent⁴⁵ assumes to isolate metals from sulfides in acidic sulfate solutions including iron sulfate and reagents with thiocarbonyl functional groups. In all probability, these thiocarbonyl functional groups can exclude the passivation of sulfides, quite possibly owing to adsorption on the sulfide surface and thereby excluding the growth of passivation films – this mechanism still needs to be studied.

“Precious metals’ leaching process” patent⁴⁶ describes non-ammonia leaching of precious metals (silver or gold) in copper thiosulfates’ solutions stabilized by organic ligands. There is nothing new here, as far back as 70 years ago, strong complexing agents such as EDTA were used to stabilize copper ions

“Hydrometallurgical method of metal sulfides” patent states that successful metal sulfides’ leaching is gained with the addition of a suitable complexing agent and catalyst to the leaching solution, with subsequent metal isolation by electrolysis. Catalysts can be of three types – mediator ions in solution, surfactants, and solid (or – liquid) additives, which, upon contact with the surface of sulfides, will have a positive influence on the solution of sulfides.⁴⁷

It should be noted that in nature metal sulfides make rather complicated, complex ores, the processing of which involves not only leaching but also the isolation of components. Some processing methods describe just such complicated systems.

The well-known Norilsk Nickel patent “Method to treat sulfide concentrates using a high pyrrhotite content”⁴⁸ involves mixing a starting concentrate with the addition of mineral stabilizing additive, the autoclave oxidation leaching of the gained mixture in aqueous pulp under oxygen pressure at a temperature above the melting point of sulfur in the presence of a surfactant with the transfer of nonferrous metals to a solution, sulfur to elemental, iron to oxides, the precipitation of nonferrous metal sulfides from the solution of oxidized pulp, accompanied by the isolation of nonferrous metal sulfides and elemental sulfur by flotation into a collective sulfur-sulfide concentrate, and iron oxides into final rejects. A rather complicated and complex method-nonferrous metals are solved, then again deposited in sulfides, iron oxides in final rejects, presumably, capture platinum group metals.

American patent “Process for deriving platinum group metals from ores also including nickel, copper and iron”⁴⁹ describes a method for isolation of platinum group metals from ores including iron, nickel and copper in the form of sulfides. To isolate the latter nonferrous metals and iron, it is proposed to leach using sulfuric acid and oxygen, while the platinum group metals are concentrated in the residue.

Another American patent, the Hydrometallurgical process for recovering copper and other metal values from metal sulphides⁵⁰, involves leaching non-ferrous and noble metal sulfides in solutions of iron chloride and copper chloride, with gold and sulfur remaining in the insoluble residue, and copper stand out from hydrolysis solution in the form of hydroxychloride.

And the «Recovery of metal values from complex sulfides» patent⁵¹ proposes to extract copper, lead, and zinc from complex sulfides, such as ores or flue gases, by leaching in solutions of calcium chloride or barium chloride under the influence of oxygen.

Japanese patent "Chlorine leaching method for metal sulfide"⁵² proposes to leach sulfides in chloride solutions with chloride ions in the range of 270-350 g / l.

As can be seen from the latest patents, chloride leaching schemes are gaining industrial importance, however, the question of the separation of metals from chloride solutions remains open.

To solve the problem of copper extraction from a solution of nickel chloride, the Japanese concern Sumitomo Metal proposed introducing nickel sulfide into a copper-containing solution of nickel chloride, taking on this idea two patents “Nickel refining method”⁵³ and “Method of removing nickel chloride solution and method of producing” elektro-nickel”.⁵⁴ Both methods were proposed to save money since copper from these solutions is quite successfully removed by cementation on nickel powder, only nickel sulfide is much cheaper than nickel powder. However, Sumitomo Metal could save even more by using

not pure nickel sulfide, but nickel concentrate and reduce its amount by introducing activating additives, such as elemental sulfur.

In the Patent "A method for producing highly pure sulphides of p-elements of group III of the periodic system"⁵⁵ it is noted that sulfides of p-elements of group III of the Periodic system are obtained by the interaction of sulfur and the corresponding p-element in a vacuum quartz ampoule, while the p-element is used in the form of the corresponding iodide, the synthesis is carried out in a 2-section ampoule, the starting components are placed in the lower section, which is heated to a temperature of 250-400 ° C, after which the sulfide obtained is calcined at a temperature of no higher than 700 ° C. That is, metal sulfides can be synthesized not from elements, but by the exchange reaction of sulfur and iodide, which significantly reduces the synthesis temperature. His method can be used for the synthesis of refractory sulfides of metals of the platinum group, rhenium, zirconium, etc.

Application "A method of producing metal sulfides"⁵⁶ describes the possibility of producing metal sulfides by reacting metal compounds with sulfur in an organic solvent medium, characterized in that liquid organic hydrocarbons of the C_nH_{2n+2} series are taken as organic solvents, and sulfides are precipitated in the presence of elemental sulfur for 4-8 hours at 170-250 ° C, while the organic solvent and sulfur are taken in a ratio of 1: (0,01 – 0,05), and the metal and sulfur are taken in stoichiometry. The production of sulfides in an environment of organic solvents is advisable to use when applying thin sulfide films. In our studies, this method can also be used when applying a thin sulfide film on the surface of smooth platinum for subsequent studies of its electrochemical behavior in various environments.

The patent "Nickel sulfide-cadmium sulfide nanowire heterostructure and preparation method thereof"⁵⁷ relates to the preparation of a heterostructure based on nickel-cadmium sulfides and relates to the field of preparation of new energy materials. According to the composite material of the invention, the main body is cadmium sulfide nanowire, and beta-NiS sheets are deposited on the surface. The production method includes the following stages: obtaining a cadmium sulfide nanowire by a thermal method; using the obtained cadmium sulfide nanowire as a matrix, nickel acetate is taken as a source of nickel, thiourea as a source of sulfur, sodium hypophosphite is added as a reducing agent, beta-NiS nanoselects are uniformly grown on the surface of cadmium sulfide in a hydrothermal medium, thus obtaining a heterostructure sulfide sulfide-cadmium-nickel sulfide with a dense combination and dispersing uniformity. The product obtained by the method has a high yield, with a high degree of purity and is controlled by morphology and does not need further processing; and, also, this method has the advantages of simplicity in equipment and technological process, strict and controlled synthesis conditions, high product yield, inexpensive, clean and environmentally friendly production process. This material has excellent catalytic decomposition ability for water to produce hydrogen.

CONCLUSION

As can be seen from this review, a considerable number of publications devoted to both the processing of sulfides and the production of new nanohetero compounds of highly functional sulfides are devoted to the study of sulfides of non-ferrous and noble metals, and both of these directions are currently being intensively developed - depletion of rich sulfide ores the need to search for new technologies for processing poor and inaccessible sources of sulfides, and the transition of mankind to a new technological order does not dictate the need for new highly functional substances.

It follows that just now the need has arisen for generalizing, fundamental work carried out with the use of modern methods of analysis of surface structures, the result of which will be generalizing patterns that allow us to predict the behavior of metal sulfides in a wide variety of environments and conditions, which is in the best possible agreement with the need for new technological breakthroughs.

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