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Review

Contemporary Research and Developments in the Low-Toxic Chelating Reagents for the Extraction of Non-Ferrous and Noble Metals from Poor Polymetallic Ores and Processing Tailings

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Abstract: An urgent technological, economic and environmental task of mining and metallurgical enterprises is to involve poor, off-balance and hard-to-beneficiate ores in the technological process, as well as accumulated and current waste from mining and metallurgical industries. As the reserves of developed deposits are depleted, technogenic objects may become a priority, and in some cases the only, source of mineral raw materials. Mining wastes represent a large reserve of raw materials for the extraction of non-ferrous and precious metals, and at the same time, they are centers of local or regional environmental pollution. Stale waste re-processing may promote territorial cultivation and reduce the environmental burden. The conventional methods of poor ore and waste treatment do not fully provide for a sufficient separation degree of high metal extraction, and lead to significant valuable ore losses, while the quality of the obtained concentrates often does not meet the requirements for subsequent technological process. In this regard, the development of novel chelating agents with specific functional groups that can selectively adsorb on the mineral surface, change the contrast of chemical surface composition and improve the flotation properties of mineral complexes, is an innovative solution for increasing their flotation selectivity. Furthermore, the synthesis and application of novel flotation reagents may help to replace toxic reagents by ecologically friendly or less-toxic ones.

Keywords: chelating reagents; non-toxic reagents; collectors; non-ferrous metals; precious metals; gold; poor polymetallic ores; enrichment tailings; flotation

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1. Introduction

In current conditions, including permanent decreases in rich ore reserves and increases in hard-to-recover raw mineral materials of fine mutual intergrowth of ore and rock mineral grains, the involvement of poor and off-balance ores of complex composition in processing is the relevant technological, economic and environmental goal of mining and metallurgical plants. Stale accumulated and current processing wastes from mining and metallurgy are one of the important mineral reserves of which beneficiation may give additional metal production and, at the same time, reduce the environment pollution.

The conventional technologies for processing those mineral raw materials are often inefficient and not attractive for investment in the deposits. Mineral form variety and complicated composition, fine impregnation, high dispersion degree and variability of the physical and chemical properties represent regular natural barriers to the development of technologies that meet modern requirements for technical efficiency and economic feasibility for the extraction of non-ferrous and precious metals.

Flotation plays a key role in combined technological schemes, since it allows achievement of high complete extraction of all valuable components into collective concentrates. It also provides for selective recovery of target metals into individual concentrates. However, technical and economic flotation indicators, the complexity of mineral utilization and environmental protection effectiveness largely depend on the range and selectivity of flotation reagents used.

Conventional reagent modes usually do not fully provide a sufficient degree of separation and high metal recovery, which leads to significant losses of up to 35–50% of non-ferrous and precious metals, and the quality of the concentrates obtained often does not meet the requirements for subsequent technological process. At the same time, there is an acute problem of accumulation and further storage of tailings formed during processing, in which the valuable metal content is often higher than in low-grade ores.

The creation of new types of low-toxicity chelating reagents is aimed at increasing the contrast between the valuable minerals and waste rock flotation and, as a result, improving their separation, thus obtaining high-quality concentrates and reducing the loss of valuable metals with waste products [1–6].

Research and development of novel selective collectors is one of the priorities in the creation of innovative technologies for processing low-grade polymetallic ores and waste tailings.

The objectives of the research under review aimed to determine the main research trends in low-toxicity reagent applications during the flotation extraction of non-ferrous and noble metals from poor polymetallic ores and enrichment waste.

2. Poor Polymetallic Ores and Processing Tailings—A New Source of Non-Ferrous and Precious Metals

Mining industry development in Russia and abroad is steadily leading to the depletion of raw material reserves. At the same time, scientific and industrial progress requires increased non-ferrous and precious metals production and a higher quality of metal concentrates. Over the past 30–40 years, the metal content in ores has decreased by 1.3–1.5 times, and the share of the total raw material consumption represented by refractory ores and processing tailings has much increased [7,8].

Russia is one of the world leaders in gold mining, and its output production comes second only to China. At the same time, over the past four years, the domestic reserves have not increased; in fact, output and consumption are equal. The probability of discovering new rich deposits is negligible.

More recently, the exploitation of gold deposits with less than 1 ppm gold content was considered unprofitable. On the other hand, statistics show that in the coming years, the increase in gold production will be associated precisely with the development of hard-to-beneficiate ores. The total losses in gold production from the best proper gold deposits amounted to 612 tons, including 521 tons, or 13%, due to the shortcomings of technologies. Even greater gold losses (60–85%) are associated with complex ore deposits. The reason is the imperfection of mineral processing and extraction technologies [9].

The Gold Producers Union concluded that the results of the precious metal production in the first half of 2021 were 3.46% lower than for the same period in 2020. In absolute terms, gold production assumed 141.4 tons. A steady increase in non-ferrous and precious metals prices has supported industry development even in the situation where the average content of the valuable component is systematically decreasing every year [10].

As the reserves of developed deposits are depleted, technogenic objects can become a priority, and in some cases the only, source of mineral raw materials for mining and metallurgical industry. At the same time, it should be borne in mind that mining waste, representing a large raw materials reserve for metal extraction, is also a source of local or regional environmental pollution [11–13].

More than 40 billion tons of waste have been accumulated in the dumps of mining enterprises in the Russian Federation (RF). In the tailings of non-ferrous metal ore processing, the part of non-extracted components respective to their amount in the original ore is the following, per cent: tin—35; tungsten—30; zinc—26; lead—23; molybdenum—19;

copper—13; nickel—10. In Russia, the extraction index of the main minerals is 65 to 78%, and associated elements (in non-ferrous metallurgy) are 10 to 30%.

The transportation and waste storage costs reach 40% of ore preparation and beneficiation costs. The processing of technogenic and mineral raw materials consumes 10% of all energy generated in the Russian Federation. Estimation of technogenic resources of the Russian Federation in value terms exceeds 43.5 billion US dollars, which is comparable to the value of predicted resources of mineral raw materials in the ground (more than 50 billion US dollars), and is four times higher than the cost of explored resources that are not involved in exploitation [14,15].

About 5 to 7 million tons of flotation tailings of copper-zinc ore processing are formed annually at the Ural Concentrators. The current ore tailings of the Uchalinsky, Aleksandrinsky, Sibaysky and Yubileiny deposits are characterized by the metal content (Cu—0.25–0.58%, Zn—0.53–1.36%), comparable to standard ores (Cu—more than 0.4%, Zn—more than 1.0%). Precious metals (25–45%), copper (10–20%) and zinc (10–15%) are also of the highest value in the tailings of the Ural ores [16].

About 61.3 million tons of the Gaiskaya Concentrator stale tailings contain 170.8 thousand tons Cu (0.278%), 159.5 thousand tons Zn (0.26%), 45.94 tons Au (0.75 ppm) and 485.5 tons Ag (7.92 g/t). More than 100 million tons of copper smelter slag contain 3.7×10^5 tons Cu, 2.2×10^6 tons Zn, 9 tons Au, 175 tons Ag, 38 tons Bi, 10^4 tons Cd.

Mining and processing plants have accumulated a huge amount of pyrite tailings (50 million tons) from non-ferrous sulfide ores processing. Taking into account the current level of engineering and technology development, the main practical interest is to extract gold, copper and zinc. One of the main reasons for the gold losses with pyrite tailings is the presence of different generations of pyrite, which have different physical and flotation properties. Some kinds of pyrite modifications actively float by butyl xanthate together with copper and zinc sulfides, decreasing the quality of Cu and Zn concentrates.

Pyrite concentrates of the Urals, besides elevated concentrations of gold (up to $\geq$5–10 ppm) and silver, contain significant impurities of Cd, As, Sc, Te, Tl, In, Ga, Ge and other trace scattered metals. Due to such "metal consumption", pyrite concentrates serve as marketable products abroad. According to studies [17,18], pyrite cinders contain 1.1–2.1 ppm Au, 20–30 ppm Ag, 0.3–0.4% Cu, 0.7–1.0% Zn and 40–50% Fe. Annually, about 0.5 tons of Au are lost in pyrite cinders supply to cement plants.

Many research institutions and companies were engaged in developing an economically viable technology for the pyrite tailings processing for a long time. Previously, Ural Mining and Metallurgical Company (UMMC) worked out a number of options for their possible treatment, but they were economically inefficient due to high costs, and environmentally harmful because of the very toxic reagents utilized and an expensive secondary tailing neutralization after leaching.

The conventional processing of such mineral products is difficult or impossible, since it leads to significant losses of valuable metals—up to 35% Cu, 40% Zn, 50% Pb, 50% noble metals [19]. At the same time, there is an acute problem of accumulation and further tailings storage because the content of non-ferrous and precious metals is often higher than in low-grade ores. Gold is mainly present in finely dispersed and submicroscopic forms in close association with sulfide minerals. The composition of mineral aggregates and their breaking-up during grinding are determined by the textural and structural characteristics of raw material, and can serve as a complex characteristic that directly affects the minerals' disclosure and the efficiency of their flotation extraction in the processing of polymetallic ores and tailings.

It should be noted that Russia has significant reserves of polymetallic ores, but it is not included in the list of the top ten countries in lead and zinc production. This indicates an unrealized potential for opening up prospects for deep and complex processing polymetallic ores. Galena and sphalerite are the main sulfide minerals in the polymetallic ores, as well as pyrite, chalcopyrite, arsenopyrite and cassiterite to a lesser extent. Silver, gold, copper, cadmium, bismuth, tin, gallium and indium are very important associated metals. Half of the world's silver production is obtained from polymetallic ores. The extraction of the main sulfide minerals is 80–90%, while the associated gold extraction is only 30–35%. This is due to the fact that the optimal conditions for non-ferrous metal recovery are not always favorable for gold extraction. For example, fine grinding that is necessary for the full disclosure of Zn and Cu minerals leads to significant losses of free gold with final tailings and by-products because of the overgrinding.

Copper-zinc and polymetallic ores of Russia are complex and difficult-to-process mineral raw materials. The practice of copper-zinc ore beneficiation has shown that obtaining high-quality zinc and pyrite concentrates is impossible without the addition of sphalerite and pyrite flotation modifiers to various flotation operations [20].

Copper-molybdenum ores, along with molybdenum sulfide ores, are the main raw material for molybdenum production. Porphyry copper-molybdenum ores are of the greatest importance. The main ore minerals are chalcopyrite, molybdenite and pyrite. Copper, molybdenum and pyrite concentrates are the final processing products, and gold and silver extract into the main concentrates. Scattered metals, like cadmium, selenium and rhenium, follow chalcopyrite and molybdenite [21].

Based on mineralogical and geochemical studies, the total estimated reserves of useful components in the stale tailings of Solnechny mining and processing plant (GOK) both in terms of the main non-ferrous and rare metals form technogenic deposits that are practically ready for reprocessing and recovery comprise a wide spectrum of elements. Thus, the reserves of copper are 64,000 tons, lead 19,000 tons, tin 25,000 tons, zinc 8000 tons, silver 55 tons [22].

Cassiterite-sulfide and polymetallic deposits of the Far East Region (FER) were mined by open pit and underground methods. This led to the formation of technogenic mineral systems. In stale wastes, the sulfide mineral components are subjected to oxidation and hydrolysis reactions. As a result, highly concentrated technogenic solutions are formed, and then new mineral phases precipitate. Technogenic solution formation and secondary mineral crystallization on the surface and inside the tailings have shown a high intensity of technogenic processes. Since the tailing storage facilities have not been restored in the Far East Region, the process of environmental pollution, including the hydrosphere, will last for many decades [23].

Similar processes are typical to dumps in other mining areas and ore deposits. In particular, dumps and copper-nickel tailings in the Norilsk cluster contain commercial potential in terms of modern processing technologies, with concentrations of platinum group metals, gold and silver that were only partially previously extracted. During the processing of sulfide copper-nickel ores, a large technogenic Pt-Pd-Au deposit [24] has been formed that accumulated a few hundred tons of reserves. The sum of platinum metals and gold content in individual tailing varieties reaches several grams (sometimes tens of ppm) per ton. An imperfect technology for the extraction of platinum group metals from the complex Norilsk ores led to platinum group metals (PGM) transferring into tailings and by-products [25,26].

Summarizing the above, we may obviously conclude that tailing reprocessing is a relevant technological task, since by solving it mining industry will consider a number of economic, social and environmental problems simultaneously. Novel low-toxicity chelating agents are one of the main resolutions in this strategy that will help to create effective techniques for metals recovery from low-grade ores and wastes.

3. Results

3.1. The Use of Low-Toxicity Chelating Agents in the Process of Flotation Extraction of Non-Ferrous and Noble Metals from Poor Polymetallic Ores and Tailings

The synthesis and application of new flotation reagents are aimed at replacing toxic reagents with non-toxic or less-toxic ones, including the selective collectors, frothers and modifiers that are well-destroyed during chemical or thermal treatment [27].

The efficiency of the flotation process primarily depends on the correct reagent selection that ensures the production of high-quality concentrates of non-ferrous and noble metals, with the lowest possible metal losses in heterogenic concentrates and tailings. The list of the most important flotation reagents includes more than 70 items. A wide range of flotation reagents meets the requirement to maximize the extraction of all valuable metals from low-grade "refractory" ores with poor metal content, complicated composition and variable mineral phases in different parts of the deposit [28].

The use of conventional reagents usually leads to their increased consumption, and as a result, high costs of the final product in processing of low-grade polymetallic ores and tailings.

To reduce processing costs, it is necessary to apply new, effective and environmentally friendly domestic reagents that can significantly increase the efficiency of extraction of valuable minerals from hard-to-beneficiate and non-traditional mineral raw materials [6,29]. According to the decree of the President of the Russian Federation "On the strategy of scientific and technological development of the Russian Federation", this is a priority task for sustainable mining industry in Russia.

The mining and hydrometallurgical industries use a wide range of inorganic, organic and synthetic reagents of natural origin, mainly for froth flotation and solid-liquid separation. Some agents appeared in the early years of these processes and have withstood the test of time; others are new or emerging and reflect the ever-changing challenges of the industry. New and improved reagents meet both technological and environmental requirements.

In Russia, several research institutions and universities conduct research and development activities in the design and application of novel and conventional flotation reagents for the recovery of non-ferrous, rare and noble metals from hard-to-beneficiate ores. The Institute of Complex Exploitation of Mineral Resources of the Russian Academy of Sciences (ICEMR RAS), State Research Institute of Non-Ferrous Metals (GINTSVETMET), National Research Technological University Moscow Institute of Steel and Alloys (MISiS), Mining Institute of Siberian Branch RAS, Mining Institute of Kola Science Center RAS and All-Russian Scientific-Research Institute of Mineral Resources named after N. M. Fedorovsky (VIMS) are all engaged in systematic flotation research [30–34]. Joint Stock Company (JSC) "VOLZHSKIY ORGSINTEZ" is the largest producer of buthyl and amyl xanthate, carbamate M in Russia. Russian company "KVADRAT PLUS" produces several kinds of dithiophosphates, and Russian innovation-driven company and designer and manufacturer of "green chemistry" products (ORGKHEM) is specialized in frothers, etc. There are leading international chemical producers—Solvay, Clariant, Flotent, FloMin, etc. Solvay (USA) develops and sells a wide range of flotation reagents—collectors, modifiers and depressants for flotation of copper, zinc, lead, gold and silver minerals. A research group in Kunming University of Science and Technology, Kunming, Yunnan, China is engaged in the creation and improvement of flotation technology for ore and tailing processing [35]. Clariant Mining Solutions produces HOSTAFLOT® collectors of dithiophosphate and dithiocarbamate composition and other classes for the selective flotation of non-ferrous and precious metals. Flotent Chemicals specializes in the rational selection, development and production of high-quality reagents for wastewater treatment, mining and metallurgy (including rare earth and precious metals) and coal enrichment. FloMin, Inc. products are widely used for the flotation of copper, lead, zinc, nickel, gold, platinum group metals and others.

3.2. Sulfhydryl Collectors and Their Modifications

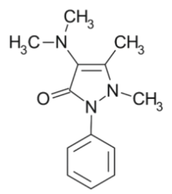
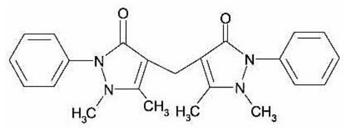
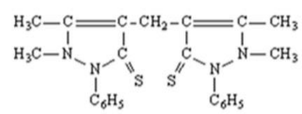
Sulfhydryl collectors are the main flotation reagents used for sulfides and oxidized minerals of non-ferrous and precious metals. Of these, xanthates and dithiophosphates (aeroflots) are the most important and widely used in mining industries all over the world. In practice, mixtures of sulfhydryl collectors, for example, butyl and isopropyl xanthates, are used in the reagent modes.

With the aim to increase the contrast of the similar flotation properties of target sulfide minerals, a combination of the weak and strong collectors of the same class are used, for example, xanthates with different hydrocarbon radical lengths, combinations of xanthates and dithiophosphates, etc. [36,37]. Depending on the mineral composition in the ore, a combination of weak and strong collectors of different classes collectors—ionic and non-ionic, for example, xanthates and thionocarbamates; dithiophosphates and thionocarbamates, xanthate acid esters; xanthates and non-polar oils, etc. are applied [38–40].

In ICEMR RAS (Moscow, Russia), a method for modifying solutions of conventional collectors—xanthate and dithiocarbamate—was developed [41–43]. The procedure helped to incorporate newly formed chemical compounds with functional groups that may form chelate compounds with non-ferrous and noble metal ions on the mineral surface, both independently or together with sulfhydryl collectors. The application of the modified dithiocarbamate in gold ore flotation demonstrated an increase in gold recovery by 5–7%, and the Au concentrate quality rose by 1.3–1.5 times in laboratory tests [41–43].

Analytical non-toxic reagents of the pyrazole group—aminophenazone (AMD, $C_{13}H_{17}N_3O$), diantipyrylmethane (DAM, $C_{23}H_{24}N_4O_2$) and dithiopyrilmethane (DTM $C_{23}H_{24}N_4S_2$) (Table 1), were proposed as selective flotation collectors for Cu-Zn ores (ICEMR RAS, Moscow, Russia). Those chemicals are capable of forming sparingly soluble complex compounds with ions of non-ferrous and noble metals, increasing their hydrophobic properties under flotation conditions in slightly acidic, neutral and slightly alkaline media [44,45]. A new reagent regime was proposed and tested on copper-zinc sulfide ores of the Tarnierskoye and Novo-Shemurskoye deposits. According to the results of enlarged laboratory tests at the Svyatogor processing plant, the use of AMD in combination with butyl xanthates (ButX) helped to increase the extraction of copper into copper concentrate by 7.5% and zinc into zinc concentrate by 4%, with a decrease in copper and zinc losses with flotation tailings [45].

Table 1. Analytical reagents of the pyrazole group.

Aminophenazone $C_{13}H_{17}N_3O$	**Diantipyrylmethane $C_{23}H_{24}N_4O_2$**	**Dithiopyrilmethane $C_{23}H_{24}N_4S_2$**
		

Aminophenazone and diantipyrylmethane are recommended as additions to butyl xanthate selective collectors for sphalerite and chalcopyrite in Cu-Zn ore treatment. Two heterocycles in the DTM molecule and N–C=S functional group promote the formation of a complex compound with gold at flotation conditions [46–49]. Laboratory tests showed that the use of DTM as an additional reagent in flotation of gold-arsenic ore of the Olimpiada deposit helped to increase the quality of the rough Au concentrate from 9.5 up to 28 ppm Au, and Au recovery from 73.55% to 82.85%.

The SIG and SGM collectors synthesized in GINTSVETMET and MISiS (Moscow, Russia) demonstrated weak collecting activity towards pyrite, and as a result, an increase in the extraction of gold and copper minerals into Cu concentrate. Industrial tests of the new reagent mode during the flotation of Cu-pyrite ore containing 1.39% copper, 2.45 g/t gold and 45.7% sulfur showed that the use of SIG together with ButX in a ratio of 1:1 made it possible to obtain an increase in gold, silver, and copper recovery: 4.5%, 1.5–6% and 1.5–2%, respectively [50].

The JSC "Institute of Metallurgy and Enrichment" (Almaty, Kazakhstan) conducted research on the synthesis of new composite reagents of directional action and the development of new reagent modes based on their application for refractory gold-bearing ore treatment. Composite xanthate (CX) and composite aeroflot (CA) were synthesized with the preparation of KS-1, KS-2 and KS-3 mixtures at various ratios for the flotation of refractory sulfide minerals with fine Au dissemination. The initial material for CX and CA reagents was a composite mixture of C_3H_7–C_6H_{13}–OH alcohols isolated from the dried alcohol fraction of fuel oil with an isoamyl alcohol more than 60%. The results showed that KS-1 and KS-2 insignificantly changed in the results of flotation recovery, but reduced the collector consumption by 20–25% compared to the basic mode. KS-3 made it possible to improve the Au content and Au recovery into a foam product.

Compared to the basic mode, KS-3 increased gold recovery by 2.85%, with a decrease in KS-3 consumption by 40 g/t. The reagent KS-3 had a much higher positive effect on gravity tailing flotation: Au extraction increased by 9.02%, Au content rose by 2.58 g/t, while the reagent consumption dropped by 20–33%. Industrial tests on Au ore of the Vasilkovskoye deposit proved the effects achieved. At the Altyntau Kokshetau Limited Liability Partnerships (LLP) plant, the extraction and gold content in the concentrate increased by 10–13.7% and the reagent consumption decreased by 30–33% [51].

FLOTENT has developed a line of collectors, in particular, dithiophosphates with a main substance content of 60–80%, that is much different from the analog products of the other Russian and foreign manufacturers, which provide content of the main substance in the range from 36 to 60%. It is well known that the higher the concentration, the less reagent is required. Furthermore, due to the high content of the main substance, the efficiency in the metal extraction also increases. At JSC POLYMETAL, the use of the FLOTENT DSIB collector (dithiophosphate sodium-isobutyl) simultaneously with the FLOTENT FR-160 frothers resulted in an increase in gold recovery up to 4% [52].

The Florrea ECOXANTHATER series flotation reagents (Shenyang Florrea Chemicals Co., Ltd., Shenyang, China) are new, efficient flotation collectors replacing xanthate in sulfide flotation, which are mainly used for sulfide ore flotation to recover non-ferrous and precious metals such as copper, lead, zinc, molybdenum, gold, nickel, cobalt, platinum group metals, etc. [53]. Florrea C2214 reagents are a mixture of diisobutyl and sodium dithiophosphate, Florrea C2216—diisoamyl and sodium dithiophosphate and Florrea C2000 (analogue of reagent Z-200)—isopropylethyl thionocarbamate. Florrea C2216 is a selective collector for copper, zinc and gold, while Florrea 9200 is for copper-lead-zinc ores. In addition, Florrea 2000, Florrea 2345 and Florrea 9200 are xanthate analogues.

The use of the new Aero 7249 collector reagent for lead-zinc tailing flotation confirmed the possibility of maximizing the waste involvement in metal production, with the recovery of valuable metals achieving the following indicators—Cu, 6.78%; Zn, 91.69%; Pb, 80.81%; Au, 95.90%; Ag, 82.50%; Fe, 78.78% [54].

New furan-based compounds obtained from biodegradable green reagent levulinic acid, 5-hydroxymethyl-2 (HMFA) have been studied at the Institute of Serbia [55]. Results gave good performance compared to other known collectors and showed high efficiency in relation to copper.

Summarizing the above, in the conditions the mining industry currently faces of significant challenges in identifying and implementing reagents that can efficiently recover valuable minerals with minimal environmental impact, research and development should be directed towards the synthesis of novel, more environmentally friendly and biodegradable compounds that are suitable to replace toxic flotation collectors without reducing flotation efficiency and selectivity.

3.3. Herbal Extracts

In recent years, a wide range of studies has been carried out in Russia and abroad on the creation and effective use of synthetic directional flotation reagents, while reagents of herbal origin have not been given sufficient attention. Plant reagents, such as starch, dextrin, quebracho, etc. are well-known in flotation practice, and are used as modifiers for some types of sulfide and low-sulfide ores for the depression of oxidized gangue minerals.

In selective flotation of copper-lead-zinc complex polymetallic sulfide ores, the separation of chalcopyrite from galena is rather difficult, because both of them have good flotation ability. Therefore, the development of an environmentally friendly and selective galena depressant is urgently needed. Compared to inorganic depressants, organic depressants such as starch, dextrin, sodium humate and sodium alginate are environmentally friendly and readily available [55,56]. These types of reagents are non-toxic, biodegradable and relatively inexpensive compared to commonly used inorganic depressants. Sodium polyaspartate (PASP), a kind of degradable polyamino acid, is widely used in water treatment technologies and chemical production. In addition, PASP is also used in mineral flotation. PASP has been studied as a galena depressant in its separation from chalcopyrite [57]. The combination of sodium humate (HA) and ammonium persulfate (APS) is an effective non-toxic reagent in the copper-lead flotation cycle [58].

Sodium humate is the sodium salt of humic acid that may form organic compounds with a high relative molecular weight. Research in pyrite and arsenopyrite flotation by xanthate and sodium humate showed that sodium humate suppressed arsenopyrite well [59,60].

New "green" cellulose-based flotation agents have been developed to replace the currently used non-biodegradable and harmful chemicals. An environmentally friendly butylamine cellulose (BAC) was synthesized from hardwood kraft cellulose for the selective isolation of chalcopyrite from sphalerite [61,62].

Tannin is a non-toxic biodegradable reagent approved for use as a flocculant in water treatment plants in several countries, and as a dispersant in drilling fluids due to its surfactant properties in aqueous suspension [63]. Tannin and tannin extracts are used as calcite and dolomite depressants in scheelite and fluorite flotation [64]. Organic polymers, such as guar and carboxymethyl cellulose that also contain phenolic groups with a large amount of OH groups, are used in Pt-containing ore flotation for the depression of talc-containing gangue minerals [65,66].

The wide application of these reagents is hampered by insufficient knowledge about their composition and physicochemical properties. The main disadvantage of tannins' application as depressants is considered to be their non-selectivity. However, it was shown that, depending on the flotation conditions, concentration, and alkalinity of the medium, oxygen-containing organic hydrophilic colloids can have different modifying effects on the floatability of sulfide minerals, which allows us to consider them as promising reagents for the selective sulfide flotation [67].

A method has been developed for obtaining a flotation reagent modifier—an aqueous extract of crushed leaves and stems of Heracleum Sosnowski hogweed (BOe), which has a depressing ability towards iron-containing sulfides, and its post-extraction solid residue may serve as a sorbent for gold ions and finely dispersed gold-containing particles [68]. Hogweed green mass contains surfactants that are soluble and insoluble in water. It was experimentally proved that, depending on the selected extractant, different components pass into the extracts. Pectins and proteins, whose reactive groups can form salts or complex compounds with transition metal ions on the surface of minerals, mainly go into the aqueous extract. Hydrophilic groups in long-chain molecules give them hydrophilic properties. Those compounds' adsorption on the mineral surface leads to their floatability limitation. Extracts of hogweed leaves and young shoots predominantly contain furocoumarins, psoralene, bergaptene and xanthotoxine [69]. Furocoumarin concentration is significantly higher than in other umbrella plants. Selective adsorption of heraclium components in organic extract on gold was determined by scanning electron microscopy and X-ray spectrum (Figure 1) [70]. It was concluded that organic hogweed extract BOe is a promising collector for gold-bearing minerals.

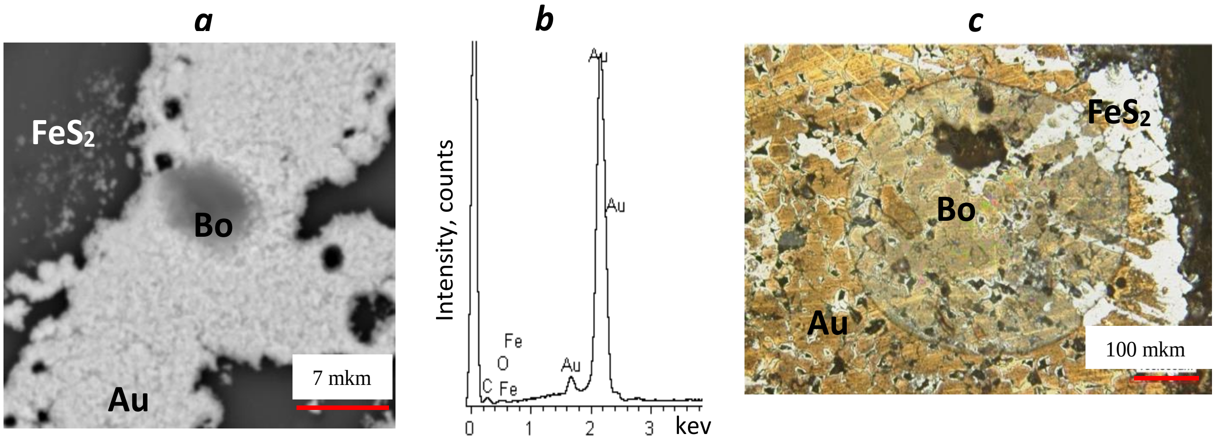


Figure 1. SEM image of a section of a polished section of FeS2 with gold after contact with an organic extract of BOe (LEO 1420VP)—(**a**); and X-ray spectrum of the Au site with the reagent adsorbed on it,—(**b**); Mark—7 microns; color micrograph of a gold section on a polished section of FeS2 with the BOe reagent (KEYNCE VK-9700)—(**c**).

In ICEMR RAS, within the framework of the scientific school Academician V.A. Chanturia, systematic fundamental research is being carried out to search for and experimentally justify the application of new selective collectors for non-ferrous metal sulfides and gold, and to develop effective reagent modes for the flotation of difficult-to-dress complex ores on their basis. Herbal reagents—chemically pure tannin and tannin-containing oak bark extract (OBE)—have been studied in order to float minerals containing noble metals. It has been established that, by changing the pH and concentration of the OBE and the order of introducing the depressant and the collector, it is possible to achieve the separation of some sulfides, in particular pyrite and arsenopyrite, to obtain a gold-bearing pyrite concentrate with an arsenic content of less than 2% [41,71,72].

The possibility of flotation separation of gold-bearing pyrite and arsenopyrite with similar technological properties using new complexing reagents of 2-hydroxypropyl ether of diethyldithiocarbamic acid (OPDETC) and a plant extract of the class of phenoloxy acids (EKD reagent) has been theoretically and experimentally substantiated. As a result of studying the conditions of complex formation and sorption activity of these reagents with respect to gold-containing sulfides, the ability of OPDETC to form a stable compound with gold under flotation conditions was established. The developed reagent regime made it possible to obtain a gold-bearing concentrate with an arsenic content of less than 2%, and to reduce gold losses in flotation tailings by 5–7% in laboratory tests [42,73–75].

3.4. Thermomorphic Polymers

The development of new, effective, environmentally safe organic flocculants for the flotation separation of fine and ultrafine mineral components remains an urgent task.

In recent years, the attention of researchers has been attracted by the so-called "smart" or "stimulus-sensitive" polymers, which can significantly change their properties and structure with relatively small variations in thermodynamic variables, as well as with changes in environmental parameters. Under external action (pH, temperature, light, chemical signal, pressure, electric or magnetic field, etc.), the microstructure of such polymers can quickly and reversibly change from a hydrophilic to a hydrophobic state [29,40,43,76,77].

Many surface-active substances (surfactants) have been proposed as collecting agents, but only a few have proven their suitability and industrial use. The selectivity of organic reagents is associated with functional groups that provide the interaction with metal ions on mineral surfaces and subsequent change in mineral hydrophobicity. In this regard, water-soluble polymers with complex-forming groups capable of obtaining stable chelate complex compounds with metal ions have the greatest practical value.

The most important water-soluble complexing polymers are polyacrylic acid, polyvinyl alcohol, poly-N-vinylpyrrolidone (PVP) and their copolymers, polyethyleneimine and a complex of polyethyleneimine with copper (II) ions [78,79].

Water-soluble polymer complexes with heavy and transition metal ions are chelates. The flotation surfactant has both a chelating and a hydrophobic side. The selectivity of flotation surfactants always depends on the chelating side. The stability of the complexes and the stable bond between the metal ion and the macromolecule depends on the structure of polymer chain, side functional groups, macromolecule length, pH solution, oxidation degree and metal ion size, temperature and the concentration of a low molecular weight electrolyte. As a rule, the most durable are polymer complexes with Cu (II) ions. For many polymers, for example, PVP, the complex stability is the following: Cu (II) > Ni (II) > Zn (II) > Co (II) > Pb (II) > Mn (II). Heavy and transition metal complexes with polymeric reagents are most stable in weakly acidic and slightly alkaline media (pH 5–8). Poly-N-vinylpyrrolidone and polyacrylic acid are selective reagents and help to divide Cu (II), Pb (II) and Zn (II), Co (II) ions from other transition metals, while polyvinyl alcohol selectively releases only Cu (II). As a perspective reagent for flotation micro- and nanoparticles of noble metals, PVP has nitrogen and oxygen atoms that may form a coordination donor-acceptor bond with gold and silver [80].

In ICEMR RAS, a technique for the flotation separation of finely ground products containing valuable components in the presence of thermomorphic (thermo-sensitive) polymers—TMP—has been developed. The studied polymer samples were obtained on the basis of N-isopropylacrylamide and N-acryloxysuccinimide. When a pulp containing a thermomorphic polymer is heated, the polymer structure changes, which leads to a change in its state of aggregation and the formation of a new phase, as well as a change in the hydrophilicity / hydrophobicity parameters of the molecule, resulting in the formation of solid hydrophobic particles. A complexing group attached to the TMP molecule interacts with particles containing noble metals in the aqueous phase of the pulp. Heating the pulp to 30–40 °C leads to a phase transition of the unfolded amphiphilic polymer molecules to a compact globule (Figure 2).

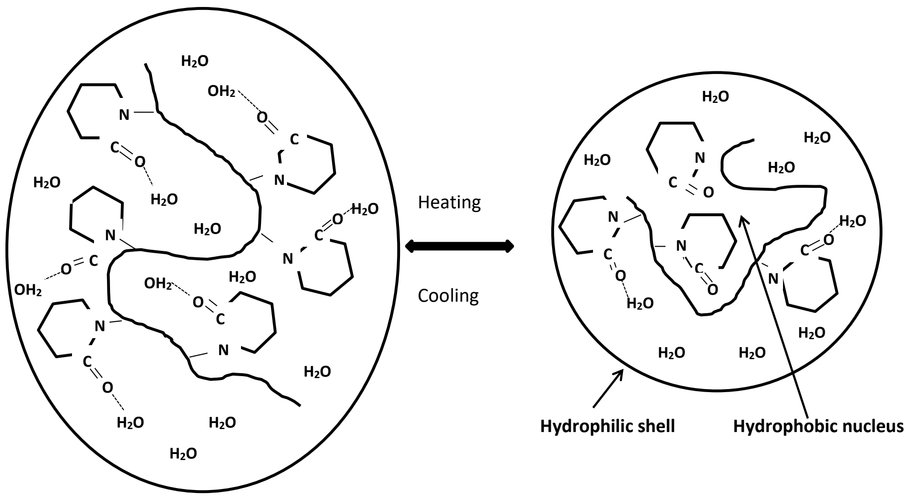


Figure 2. Interaction between thermomorphic polymer and water in solution.

The surface of the formed solid polymer particles is hydrophobic, so they are able to pass in the froth flotation product. The selectivity of the polymer is ensured by attaching to its molecule a functional group capable of forming a strong complex compound with valuable components. The chemical interaction of noble-metal-bearing particles or minerals with functional groups attached to a molecule of a water-soluble (at room temperature) thermomorphic polymer, and further transfer of the polymer to a solid state when the pulp is heated, reduces the loss of valuable components with flotation tailings. They are directional reagents intended for the flotation separation of finely divided products containing valuable components; therefore, they must, in addition, be stable and retain their thermosensitive properties under the conditions of a multicomponent flotation pulp (mineral suspension). Polymers are modified using reagents that interact with noble metals in neutral and alkaline media.

Flotation tests carried out on refractory gold ore showed the possibility of effective application of cloud point polymers to improve the quality of gold concentrate and recovery of gold. Usage of TMP in combination with ButX (1:1) helped to increase gold content in the concentrate by 1.25 times, and gold recovery by 4.34%. Application of TMP in the flotation of copper-nickel-platinum ores can improve recovery of nickel and platinum group metals by 5–17% without reducing the quality of the concentrate [81].

4. Conclusions

The mining industry currently faces significant challenges in increasing the efficient recovery of valuable minerals and obtaining high-quality concentrates from low-grade ores and tailings with minimal environmental impact. In the developed "Strategy for the development of the precious metals industry of the Russian Federation for the period up to 2030", the production of gold should increase from 338 (2021) to 427 tons (2030), silver from 1126 to 1392 tons and PGM from 126 to 165 tons. It is possible to achieve such production indicators only by creating economically profitable and environmentally acceptable technology with modern, environmentally friendly reagents for the extraction of low-dimensional non-ferrous and precious metal minerals from low-grade polymetallic ores and tailings. Flotation is one of the main technological processes in low-grade polymetallic ore and waste tailing treatment. Flotation efficiency greatly depends on a set of flotation reagents. The conventional processing modes lead to high (up to 35–50%) losses of valuable metals and have a negative impact on the environment. At the same time, many ore-dressing plants in Russia and abroad rarely use eco-friendly collectors and modifiers, preferring traditional xanthates, dithiophosphates and their modifications of a similar hazard class.

The modern trends in research and development should be directed towards the synthesis of novel, more environmentally friendly and biodegradable compounds that could replace toxic flotation collectors without reducing flotation recovery. Organic depressants such as starch, dextrin, sodium humate, sodium alginate and polyaspartate, guar and carboxymethyl cellulose and herbal extracts are increasingly used. Smart or "stimulus-sensitive" polymers with chelating and hydrophobic groups are perspective reagents for metal extraction of finely dispersed valuable minerals from low-grade polymetallic ores and tailings.

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References

1. Komogortsev, B.V.; Varenichev, A.A. Improvement of flotation technologies for finely dispersed gold-bearing sulfide ore. *MIAB Min. Inf. Anal. Bull.* **2018**, *10*, 180–190. (In Russian) [CrossRef]
2. Chernousenko, E.V.; Mitrofanova, G.V.; Kameneva, Y.S.; Vishnyakova, I.N. Evaluation of complexing agents in the flotation of copper-nickel ores. *Tsvetnye Met.* **2019**, *1*, 7–12. (In Russian) [CrossRef]
3. Mitrofanova, G.V.; Chernousenko, E.V.; Bazarova, E.A.; Tyukin, A.P. The search for new complexing reagents for copper-nickel ore flotation. *Tsvetnye Met.* **2019**, *11*, 27–33. (In Russian) [CrossRef]
4. Miki, H.; Hirajima, T.; Muta, Y.; Suyantara, G.P.W.; Sasaki, K. Investigation of reagents for selective flotation on chalcopyrite and molybdenite. In Proceedings of the 29th International Mineral Processing Congress (IMPC 2018), Moscow, Russia, 17–21 September 2018; pp. 1854–1861.
5. Yudaev, P.; Chistyakov, E. Chelating Extractants for Metals. *Metals* **2022**, *12*, 1275. [CrossRef]
6. Marabini, A.M.; Ciriachi, M.; Plescia, P.; Barbaro, M. Chelating reagents for flotation. *Miner. Eng.* **2007**, *20*, 1014–1025. [CrossRef]
7. Domracheva, V.A.; Trusova, V.V.; Leonov, V.Y.; Ostapchuk, D.E. Justification of the possibility of extraction of heavy metals with carbon sorbents from wastes of mining and concentrating factories. In Proceedings of the 19th International Scientific and Practical Conference "Prospects for the Development of the Mining and Metallurgical Industry" (Igoshinsky readings—2019), Irkutsk, Russia, 28–29 November 2019; Publishing House INRTU: Irkutsk, Russia, 2020; pp. 6–11. (In Russian)
8. Omarova, G.; Baibatsha, A.; Abdykirova, G.Z. Flotation enrichment of enrichment factory tailings for use as technogenic ore. In Proceedings of the 19th International Multidisciplinary Scientific GeoConference SGEM 2019, Albena, Bulgaria, 30 June–6 July 2019; Volume 19, pp. 195–202. [CrossRef]
9. Mikhailov, B.K.; Sedelnikova, G.V.; Benevolsky, B.I.; Romanchuk, A.I. Innovation technologies of gold refractory and low grade ores processing as basis of rational mineral resources using. *Ores Met.* **2014**, *1*, 5–8. (In Russian)
10. Mining Industry 2022, 4, 162–169. (In Russian). Available online: https://dprom.online/wp-content/uploads/Issue/DP_4_2022.pdf?ysclid=lb9d1kk27i468798122 (accessed on 25 August 2022).
11. Lindsay, M.B.J.; Moncur, M.C.; Bain, J.G.; Jambor, J.L.; Ptacek, C.J.; Blowes, D.W. Geochemical and mineralogical aspects of sulfide mine tailings. *Appl. Geochem.* **2015**, *57*, 157–177. [CrossRef]
12. Shengo, L.M. Review of Practices in the Managements of Mineral Wastes: The Case of Waste Rocks and Mine Tailings. *Water Air Soil Pollut.* **2021**, *232*, 273. [CrossRef]
13. Bevandić, S.; Blannin, R.; Gomez Escobar, A.; Bachmann, K.; Frenzel, M.; Pinto, A.; Relvas, J.M.R.S.; Muchez, P. Metal deportment in Pb-Zn mine wastes from a historic tailings pond, Plombières, East Belgium. *Miner. Eng.* **2022**, *184*, 107628. [CrossRef]
14. Mustafin, S.K. Man-made gold-bearing mineral raw materials of the southern urals: Nature, composition and prospects for use. In Proceedings of the Problems of Mineralogy, Petrography and Metallogeny, Scientific Readings in Memory of P.N. Chirvinsky, Permian, Russia, 5 February 2019; Volume 22, pp. 236–242. (In Russian)
15. Mustafin, S.K.; Anisimova, G.S.; Trifonov, A.N.; Struchkov, K.K. Technogenic Mineral Raw Materials of the Subsoil Use Regions: Nature, Composition and Prospects of Rational Development. *Sci. Educ. Arct. Subarct. Nat. Resour.* **2017**, *4*, 7–16. (In Russian)
16. Mikhailov, B.K.; Kiperman, Y.A.; Komarov, M.A. *Technogenic Mineral Resources*; Mikhailov, B.K., Ed.; Scientific World: Moscow, Russia, 2012; p. 236. (In Russian)
17. Melentiev, G.B.; Ovcharova, E.S.; Malinina, E.N.; Zabolotsky, A.I. Resource and technological problems of the integrated use of natural and technogenic copper-sulfide raw materials with the production of associated copper-sulfide products. In *Technogenic Resources and Innovations in Technoecology*; Shelkov, E.M., Melentiev, G.B., Eds.; JIHT RAS: Moscow, Russia, 2008. (In Russian)
18. Gorbatova, E.A.; Melentiev, G.B.; Ovcharova, E.S.; Vdovina, O.K.; Emelianenko, E.A. Particularly valuable and environmentally friendly limited components in the tailings of enriched Ural licensed raw materials. In *Comprehensive Development and Processing of Technogenic Formations Using Innovative Technologies*; Mikhailov, G.G., Chernobrivets, T.F., Eds.; JIHT RAS: Moscow, Russia, 2013. (In Russian)
19. Panshin, A.M.; Mamyachenkov, S.V.; Tropnikov, D.L.; Anisimova, O.S.; Rogozhnikov, D.A. Research of regularities of leaching the sulfated cinders obtained during roasting of copper-zinc middlings. *Izv. Vuzov Tsvetnaya Metall.* **2017**, *3*, 23–30. [CrossRef]
20. Kyaw, Z.Y.; Tiagalieva, Z.A.; Htet, Z.; Phyo, K.K. Improvement of reagent flotation modes of sphalerite and pyrite from deposits of copper-zinc pyrite, polymetallic copper-zinc pyrite and polymetallic ores. *IOP Conf. Ser. Earth Environ. Sci.* **2021**, *942*, 012004. [CrossRef]
21. Bobrakova, A.A. Increasing the Complexity of Processing Molybdenum-Containing Ores by Obtaining Concomitant Concentrates of Aluminosilicate Composition. Ph.D. Thesis, National Mineral Resources University "Gorny", Saint Petersburg, Russia, 2015. (In Russian).
22. Khanchuk, A.I.; Kemkina, R.A.; Kemkin, I.V.; Zvereva, V.P. Mineralogical and geochemical substantiation for processing aged sands from tailing dumps of the Solnechny mining and processing plant (Komsomolsky district, the Khabarovsk territory). *Vestn. Kraunts Nauk. O Zemle* **2012**, *1*, 22–40. (In Russian)
23. Zvereva, V.P.; Frolov, K.R.; Lysenko, A.I. Chemical reactions and conditions of mineral formation at tailings storage facilities of the Russian Far East. *Min. Sci. Technol.* **2021**, *6*, 181–191. (In Russian) [CrossRef]
24. Spiridonov, É.M.; Kulagov, É.A.; Kulikova, I.M. Palladium, platinum and goldmineral assamblages in ores of the Norilsk deposit. *Geol. Ore Depos.* **2004**, *46*, 150–166.

25. Komarov, M.A.; Aliskerov, V.A.; Kusevich, V.I.; Zavyortkin, V.L. Mine waste—An additional source of mineral resources. *Miner. Resour. Russ. Econ. Manag.* **2007**, *4*, 3–9. (In Russian)
26. Masloboev, V.A.; Seleznev, S.G.; Makarov, D.V.; Svetlov, A.V. Assessment of eco-hazard of copper-nickel ore mining and processing waste. *J. Min. Sci.* **2014**, *50*, 559–579. [CrossRef]
27. Abramov, A.A. *Collected Works. Vol. 7. Flotation. Reagents-Collectors*; Publishing House "Mining Book": Moscow, Russia, 2012. (In Russian)
28. Ryaboy, V.I. Production and usage of flotation reagents in Russia. *Gorn. Zhurnal* **2011**, *2*, 49–53. (In Russian)
29. Roy, D.; Brooks, W.L.A.; Sumerlin, B.S. New directions in thermoresponsive polymers. *Chem. Soc. Rev.* **2013**, *42*, 7214–7243. [CrossRef]
30. Ignatkina, V.A.; Bocharov, V.A.; Kayumov, A.A. Basic principles of selecting separation methods for sulfide minerals having similar properties in complex ore concentrates. *J. Min. Sci.* **2016**, *52*, 360–372. [CrossRef]
31. Bocharov, V.A.; Ignatkina, V.A.; Kayumov, A.A. Methods of gold recovery during the concentration of refractory gold-bearing pyritic copper-zinc ores. Part 1. Analysis of practice and choice of ways of selective recovery of mineral phases of gold from pyritic copper-zinc ores. *Tsvetnye Met.* **2017**, *4*, 11–16. (In Russian) [CrossRef]
32. Kondrat'ev, S.A.; Sem'yanova, D.V. Relation between Hydrocarbon Radical Structure and Collecting Abilities of Flotation Agent. *J. Min. Sci.* **2018**, *54*, 1024–1034. [CrossRef]
33. Yusupov, T.S.; Kondratyev, S.A.; Baksheeva, I.I. Production-induced cassiterite-sulfide mineral formation structural-chemical and technological properties. *Obogashchenie Rud* **2016**, *5*, 26–31. (In Russian) [CrossRef]
34. Kurkov, A.V.; Pastukhova, I.V. Method for Flotation of Rare Metal and Tin Ores. RU Patent 2 381 073 C1, 10 February 2010.
35. Zhou, Y.; Tong, X.; Song, S.; Wang, X.; Deng, Z.; Xie, X. Beneficiation of cassiterite fines from a tin tailing slime by Froth Flotation. *Sep. Sci. Technol.* **2014**, *49*, 458–463. [CrossRef]
36. Bocharov, V.A.; Ignatkina, V.A.; Chanturia, E.L.; Lapshina, G.A.; Melnikova, S.I. Technology of complex concentration of sulfide gold-containing ores difficult for concentration. *Izv. Vyss. Uchebnykh Zaved. Tsvetnaya Metall.* **2004**, *5*, 4–9. (In Russian)
37. Kakovsky, I.A. Sulfhydryl reagents. In *Physical and Chemical Foundations of the Theory of Flotation*; Nauka: Moscow, Russia, 1983; pp. 102–135. (In Russian)
38. Abramov, A.A. *Technology of Enrichment of Oxidized and Mixed Ores of Non-Ferrous Metals*; Nedra: Moscow, Russia, 1986. (In Russian)
39. Konev, V.A. *Sulfide Flotation*; Nedra: Moscow, Russia, 1985. (In Russian)
40. Ng, W.S.; Connal, L.A.; Forbes, E.; Franks, G.V. A review of temperature-responsive polymers as novel reagents for solid-liquid separation and froth flotation of minerals. *Miner. Eng.* **2018**, *123*, 144–159. [CrossRef]
41. Matveeva, T.N.; Gromova, N.K.; Koporulina, E.V. Analysis of adsorption of phytogenous collecting agents at the gold-containing sulfides during flotation. *J. Min. Sci.* **2015**, *51*, 601–608. [CrossRef]
42. Matveeva, T.N. Scientific substantiation of highly effective methods of flotation extraction of gold and platinum-containing ores. Doctoral Thesis, ICEMR RAS, Moscow, Russia, 2012.
43. Kirsh, Y.E. *Poly-N-vinylpyrrolidone and Other Poly-N-vinylamides: Synthesis and Physicochemical Properties*; Nauka: Moscow, Russia, 1998; ISBN 5-02-004498-9.
44. Chanturiya, V.A.; Ivanova, T.A.; Chanturiya, E.L.; Zimbovskiy, I.G. Mechanism of the selective operation of 1-phenyl-2,3-dimethyl-4-aminopyrazolone-5, during the process of flotation separation of sphaterite and pyrite. *Tsvetnye Met.* **2013**, *1*, 25–29. (In Russian)
45. Matveeva, T.N.; Chanturiya, V.A.; Getman, V.V.; Gromova, N.K.; Ryazantseva, M.V.; Karkeshkina, A.Y.; Lantsova, L.B.; Minaev, V.A. The Effect of Complexing Reagents on Flotation of Sulfide Minerals and Cassiterite from Tin-Sulfide Tailings. *Miner. Process. Extr. Metall. Rev.* **2022**, *43*, 346–359. [CrossRef]
46. Dolgorev, A.V.; Lysak, I.G.; Zibarova, Y.F.; Lukoyanov, A.P. Dithiopyrilmethane and its analogues as analytical reagents. Synthesis and properties. *J. Anal. Chem.* **1980**, *35*, 854–861. (In Russian)
47. Shcherbakova, L.V. Physicochemical Parameters of Complexes of Metal Ions with Pyrazole Thio Derivatives and a Method for Determining the Equilibrium Constants. Ph.D. Thesis, ASU, Barnaul, Russia, 2005. (In Russian)
48. Scherbakova, L.V.; Petrov, B.I.; Chebotarev, V.K. Potentiometricdetermination of noble metals by dithiopyrilmethane. *Izv. Altai State Univ.* **2000**, *3*, 28–30. (In Russian)
49. Matveeva, T.N.; Getman, V.V.; Karkeshkina, A.Y. Flotation and Adsorption Capacities of Dithiopyrilmethane in Gold Recovery from Rebellious Arsenical Gold Ore. *J. Min. Sci.* **2020**, *56*, 648–653. [CrossRef]
50. Bocharov, V.A.; Ignatkina, V.A.; Lapshina, G.A.; Hachatryan, L.S. Features of extracting gold from gold-bearing sulfide ores. *MIAB Min. Inf. Anal. Bull.* **2004**, *12*, 297–302. (In Russian)
51. Tusupbaev, N.K.; Turysbekov, D.K.; Semushkina, L.V.; Narbekova, S.M. Processing gold tailings of gravity using composite reagents. In *Proceedings International Scientific Conference "Modern Problems of Complex Processing of Refractory Ores and Technogenic Raw Materials" (Plaksinsky Readings—2017), Krasnoyarsk, Russia, 12–15 September 2017*; Siberian Federal University: Krasnoyarsk, Russia, 2017; pp. 154–156. (In Russian)
52. Marfitsin, A.V. Economic effect of using Flotent reagents for the mining industry. *Gold Technol.* **2020**, *4*, 102. (In Russian)
53. Bagheri, B.; Vazifeh Mehrabani, J.; Farrokhpay, S. Recovery of sphalerite from a high zinc grade tailing. *J. Hazard. Mater.* **2020**, *381*, 120946. [CrossRef] [PubMed]

54. Seksenova, N.; Bykov, R.; Mamyachenkov, S.; Daumova, G.; Kozhakanova, M. Optimization of Conditions for Processing of Lead–Zinc Ores Enrichment Tailings of East Kazakhstan. *Metals* **2021**, *11*, 1802. [CrossRef]
55. Liu, D.; Zhang, G.; Chen, Y. Investigations on the selective depression of fenugreek gum towards galena and its role in chalcopyrite-galena flotation separation. *Miner. Eng.* **2021**, *166*, 106886. [CrossRef]
56. Milosavljević, M.M.; Marinković, A.D.; Rančić, M.; Milentijević, G.; Bogdanović, A.; Cvijetić, I.N.; Gurešić, D. New Eco-Friendly Xanthate-Based Flotation Agents. *Minerals* **2020**, *10*, 350. [CrossRef]
57. Zhang, J.; Zhang, X.-G.; Wei, X.X.; Cheng, S.-Y.; Hu, X.Q.; Luo, Y.-C.; Xu, P.-F. Selective depression of galena by sodium polyaspartate in chalcopyrite flotation. *Miner. Eng.* **2022**, *180*, 107464. [CrossRef]
58. Liu, R.-Z.; Qin, W.; Jiao, F.; Wang, X.-J.; Pei, B.; Yang, Y.-J.; Lai, C.-H. Flotation separation of chalcopyrite from galena by sodium humate and ammonium persulfate. *Trans. Nonferrous Met. Soc. China* **2016**, *26*, 265–271. [CrossRef]
59. Qiu, T.-S.; Zhang, B.-H.; Zhang, W.-X.; Zhao, G.-F. Current status and progress of technology of separating arsenopyrite and pyrite. *Min. Process. Equip.* **2013**, *41*, 1–5.
60. Lin, S.; Liu, R.; Bu, Y.; Wang, C.; Wang, L.; Sun, W.; Hu, Y. Oxidative Depression of Arsenopyrite by Using Calcium Hypochlorite and Sodium Humate. *Minerals* **2018**, *8*, 463. [CrossRef]
61. Spooren, J.; Binnemans, K.; Björkmalm, J.; Breemersch, K.; Dams, Y.; Folens, K.; González-Moya, M.; Horckmans, L.; Komnitsas, K.; Kurylak, W.; et al. Near-zero-waste processing of low-grade, complex primary ores and secondary raw materials in Europe: Technology development trends. *Resour. Conserv. Recycl.* **2020**, *160*, 104919. [CrossRef]
62. Lopéz, R.; Jordão, H.; Hartmann, R.; Ämmälä, A.; Carvalho, M.T. Study of butyl-amine nanocrystal cellulose in the flotation of complex sulphide ores. *Colloids Surf. A Physicochem. Eng. Asp.* **2019**, *579*, 123655. [CrossRef]
63. Sarquísa, P.E.; Menéndez-Aguadob, J.M.; Mahamudb, M.M.; Dziobac, R. Tannins: The organic depressants alternative in selective flotation of sulfides. Author links open overlay pane. *J. Clean. Prod.* **2014**, *84*, 723–726. [CrossRef]
64. Shubov, L.Y.; Ivankov, S.I.; Shcheglova, N.K. *Flotation Reagents in Mineral Processing, Book 1*; Kondratieva, L.V., Ed.; Nedra: Moscow, Russia, 1990; ISBN 5-247-02668-3. (In Russian)
65. Robertson, C.; Bradshaw, D.; Harris, P. Decoupling the effects of depression and dispersion in the batch flotation of a platinum bearing ore. In Proceedings of the 22th International Mineral Processing Congress (IMPC 2003), Cape Town, South Africa, 29 September–3 October 2003.
66. Somasundaran, P.; Wang, J.; Pan, Z.; Nagaraj, D.R.; Chen, H.-L.; Anastassakis, G. Interactions of gum depressants with talk: Study of adsorption by spectroscopic and allied techniques. In Proceedings of the 22th International Mineral Processing Congress (IMPC 2003), Cape Town, South Africa, 29 September–3 October 2003.
67. Ivanova, T.A.; Chanturia, E.L. Application of complexing reagents to flotation separation of the varieties of pyrite. *J. Min. Sci.* **2007**, *43*, 441–449. [CrossRef]
68. Ivanova, T.A.; Zimbovsky, I.G.; Koporulina, E.V. Enhancing multipurpose use of cow-parsnip in processing of gold-bearing sulfides. *J. Min. Sci.* **2017**, *53*, 327–333. [CrossRef]
69. Orlin, N.A. About the extraction of coumarins from hogweed. *Successes Mod. Nat. Science. Biol. Sci.* **2010**, *3*, 13–14. (In Russian)
70. Ivanova, T.A.; Chanturia, V.A.; Zimbovsky, I.G. New experimental evaluation techniques for selectivity of collecting agents for gold and platinum flotation from fine-impregnated noble metal ores. *J. Min. Sci.* **2013**, *49*, 785–794. [CrossRef]
71. Chanturia, V.A.; Matveeva, T.N.; Ivanova, T.A.; Gromova, N.K.; Lantsova, L.B. New complexing agents to select auriferous pyrite and arsenopyrite. *J. Min. Sci.* **2011**, *47*, 102–108. [CrossRef]
72. Matveeva, T.N. Scientific grounds for high-performance agent modes in platiniferous sulfide mineral flotation from rebellious ores. *J. Min. Sci.* **2011**, *47*, 824–828. [CrossRef]
73. Matveeva, T.N.; Ivanova, T.A.; Getman, V.V.; Gromova, N.K. New flotation agents for recovery of micro- and nanoparticles of precious metals from rebellious ore. *Gorn. Zhurnal* **2017**, *11*, 89–93. [CrossRef]
74. Chanturija, V.A.; Ivanova, T.A.; Matveeva, T.N.; Gromova, N.K.; Lantsova, L.B. Method for Separation of Pyrite and Arsenic Pyrite. RU Patent 2 397 025 C1, 20 August 2010.
75. Matveeva, T.N.; Chanturia, V.A.; Gromova, N.K.; Lantsova, L.B. Effect of chemical and phase compositions on adsorption and flotation properties of tin-sulfide ore tailings with dibutyl dithiocarbamate. *J. Min. Sci.* **2018**, *54*, 1014–1023. [CrossRef]
76. Ng, W.S.; Connal, L.A.; Forbes, E.; Mohanarangam, K.; Franks, G.V. In situ study of aggregate sizes formed in chalcopyrite-quartz mixture using temperature-responsive polymers. *Adv. Powder Technol.* **2018**, *29*, 1940–1949. [CrossRef]
77. Aguilar, M.R.; Román, J.S. 1—Introduction to smart polymers and their applications. In *Smart Polymers and Their Applications*; María, R.A., Julio, S.R., Eds.; Woodhead Publishing: Sawston, UK, 2014; pp. 1–11. [CrossRef]
78. Yanul, N.A.; Zemlyanova, O.Y.; Kirsh, Y.E.; Kalnin'sh, K.K. Interaction of aqueous associates with poly-n-vinylcaprolactam in concentrated polymer solutions. *Russ. J. Phys. Chem. A* **1998**, *72*, 1687–1692.
79. Gembitskii, P.A.; Zhuk, D.S.; Kargin, V.A. *Polyethyleneimine*; Nauka: Moscow, Russia, 1971.
80. Olenin, A.Y.; Krutyakov, Y.A.; Lisichkin, G.V. Formation echanisms of anisotropic silver nanostructures in polyol synthesis. *Nanotechnol. Russ.* **2010**, *5*, 421–426. (In Russian) [CrossRef]
81. Chanturia, V.A.; Matveeva, T.N.; Ivanova, T.A.; Getman, V.V. Mechanism of interaction of cloud point polymers with platinum and gold in flotation of finely disseminated precious metal ores. *Miner. Process. Extr. Metall. Rev.* **2016**, *37*, 187–195. [CrossRef]