

Article

Hydrometallurgical Processing of Low-Grade Sulfide Ore and Mine Waste in the Arctic Regions: Perspectives and Challenges

Vladimir A. Masloboev ¹, Sergey G. Seleznev ², Anton V. Svetlov ¹ and Dmitriy V. Makarov ^{1,*}

- ¹ Institute of North Industrial Ecology Problems, Kola Science Centre of the Russian Academy of Sciences, 184209 Apatity, Russia; masloboev@mail.ru (V.A.M.); antonsvetlov@mail.ru (A.V.S.)
- ² Ural State Mining University, 620144 Yekaterinburg, Russia; seleznev.s.ek@mail.ru
- * Correspondence: mdv_2008@mail.ru; Tel.: +7-81555-79-5-94

Received: 1 August 2018; Accepted: 1 October 2018; Published: 7 October 2018



Abstract: The authors describe the opportunities of low-grade sulfide ores and mine waste processing with heap and bacterial leaching methods. By the example of gold and silver ores, we analyzed specific issues and processing technologies for heap leaching intensification in severe climatic conditions. The paper presents perspectives for heap leaching of sulfide and mixed ores from the Udokan (Russia) and Talvivaara (Finland) deposits, as well as technogenic waste dumps, namely, the Allarechensky Deposit Dumps (Russia). The paper also shows the laboratory results of non-ferrous metals leaching from low-grade copper-nickel ores of the Monchepluton area, and from tailings of JSC Kola Mining and Metallurgical Company.

Keywords: heap leaching; bacterial leaching; cryomineralogenesis; low-grade copper-nickel ore; raw materials

1. Introduction

On the one hand, off-balance sulfide ores from abandoned and producing deposits, overburden rocks, mill tailings, and non-ferrous slag are considered to be one of the largest sources for non-ferrous metals production. On the other hand, they are well-known environmental hazards. Therefore, the use of mine dumps and tailings, and the ores left in the ground as raw products accompanied by environmental impact decrease is considered to be a critical objective in terms of the environment and economy [1].

Obviously, methods of heap and bacterial leaching are potentially productive for processing such low-grade ore and mine waste containing non-ferrous metals [2–6]. Introduction of this technology will facilitate step-by-step transition to a circular economy during the implementation of the closed procedures for solution circulation and waste material disposal in construction industry [7–9].

Previously, based on a number of sulfide-containing technogenic deposits that were located in Murmansk region, Russia, it was proved that, not only fine, but also coarse disperse wastes represent environmental hazards. These are the Allarechensky Deposit Dumps, as well as copper-nickel ore processing tailings from the Pechenga deposits. These tailings are characterized by low sulfide content and high chemical activity of nonmetallic minerals [10].

It should also be noted that sulfide oxidation begins even at early stages of waste storage. This has resulted in degradation of ore minerals processing properties. Valuable components also undergo dilution, and start moving to lower levels due to supergene processes [10,11]. It could be seen the redistribution of the ratios of silicate and sulfide nickel forms in tailings. [10,12]. Due to a long-term



storage, technogenic deposits lose their value and they become a constant source of adverse impact on the environment [9,10,13].

A heap leaching process involves the following requirements. Solution containing sulfuric acid, oxidizing agent (oxygen, iron (III) ions, etc.), as well as microorganisms (for example, *Acidithiobacillus ferrooxidans, Acidithiobacillus thiooxidans*), are fed to the surface of a heap (ore stack) or inside. The solution is distributed evenly over the surface and dump heap mass by means of reservoirs, drainage channels, network of perforated tubes, or by spraying. Pregnant solution coming from under the heap is enriched in non-ferrous metals. It is collected in channels or tubes, and directed to further processing [2–6].

In comparison with heap leaching, biological leaching is a very young method of a valuable component recovery in the world processing industry. In the former USSR (Union of Soviet Socialist Republics), pilot tests were carried out in the 60 s of the past century, but they did not become a frequent practice in the industry [2,14,15].

The world's hydrometallurgical experience proves perceptiveness of the heap leaching method mainly for recovery of gold, copper, and uranium, from low-grade ores, mining and processing waste [2–6,16–19]. The twenty percent of the world's copper production is accomplished by heap leaching of ores from mines and processing plants as well as waste ores from dumps and further processing by solvent extraction and electrowinning (SX/EW) [16].

Biological leaching was proved to be efficient for sulfides of Co, Ga, Mo, Ni, Zn, and Pb [16]. Sulfide minerals, including metals of the platinum group (Pt, Rh, Ru, Pd, Os, and Ir) can be also subjected to preprocessing with microorganisms [20]. In recent decade, pilot tests on heap leaching of low-grade copper and nickel sulfide ores were launched (the mines involved are Radio Hill in the Western Australia; Talvivaara, Sotkamo in Finland; Khami, Sintszyan in China) [21–30].

The world industry has accumulated scientific and production experience that is related to assessment of ore amenability to heap leaching, engineering, and design of heap leach pads, solution irrigation systems, and collection of pregnant solutions, heap leaching schemes optimization, and chemicals regeneration [2,3,31]. Mathematical modeling techniques are being developed [32–35].

When using heap leaching, ore grades can be significantly lower than in the conventional metallurgical technologies. For example, for the heap leaching process used by the Finnish Company "Talvivaara Mining Company Plc" at its nickel mine situated in the subarctic zone of the north-east of Finland, average nickel grade amounts to 0.27%, copper 0.14%, cobalt 0.02%, and zinc 0.56% [36]. In cases of technogenic waste processing, the standard ore grade can be even lower. This can be explained by the fact that ore mining costs have been already spent, and transport expenses are allocated to the remediation budget [15].

The Russian Federation has all necessary conditions for a wide use of the heap leaching method for metal recovery. Undoubtedly, certain complications may result from unfavorable climate in the mining and processing regions of Russia. Most of the foreign mines are situated in the regions with warm climate, where the lowest temperature is above zero even in cold seasons. Therefore, it should be considered the specifics of the heap leaching process implementation in the regions with arctic and subarctic climate. The paper addresses these specifics by the example of gold and silver ores, as well as several case studies.

2. Specifics of Metal Heap Leaching in Severe Climatic Conditions

Currently, there are more than 300 heap leaching facilities in the world. About 70 of them (about 25%) are operated in the regions with arctic and subarctic climate with subzero average annual temperatures. These mines are located in North Europe, Asia, North America, as well as in the Andean regions of South America. Leading companies in the Arctic area are gold mines. They include Kinross Fort Knox Gold mine (Fairbanks, Alaska), Eagle and Coffee-Gold (Yukon Territory, Canada), as well as Casino Project (Yukon Territory, Canada) processing sulfide and oxidized copper ores bearing gold [37].

Low temperature and permafrost complicate implementation and operation of heap leaching pads and increase their costs. The following measures are taken to keep the leaching heaps warm [17,38,39]:

- construction of ore stacks in cells;
- use of drip emitters irrigation system consisting of pressure emitter trickles of labyrinth type;
- use of snow cover as a natural thermal insulation layer over a dump;
- freezing of "ice glaze" on a heap surface;
- covering a heap with thermally insulating materials during a cold season (polymer geo-textiles, polyethlene films with heated air supply underneath a covering mining material, with a layer thickness of up to 1 m);
- heating of process solutions.

In addition to these measures, a heap leach pad should be located in a place ensuring the maximum possible use of solar energy and minimum wind impact. A pad should not be built on permafrost soil, and frozen ore should not be placed on a dump as well.

Russian specialists have developed the method for precious metals leaching from mineral raw materials at low temperature (down to -40 °C), without any need for solvent percolation through ore lumps [17]. This method was called a "passive leaching". In brief, the method includes the following steps: the ore is crushed, mixed with alkaline cyanide solution to complete the impregnation of the ore mass and held for some time, until all free gold transfers into a water-soluble state. On completing the process, the ore mass is subjected to water leaching by one of the two methods depending on technical and economic calculations: directly in heaps and dumps in-situ; or, based on a counterflow scheme in any flushing apparatus. The main feature of the passive leaching method is its applicability in severe cold conditions for gold and silver raw material processing. This is important for the Far North regions.

Quite a wide range of specialists used to think that geotechnologies, i.e., leaching in heaps, dumps, sludge storage facilities is unreasonable and unrealistic in cold climates with subzero average annual temperatures, permafrost soils, and short warm period (three months a year). However, yet, in the eighties of the 20th century, processing parameters and indicators of percolation (heap) and passive leaching were studied and determined, based on the ores from 12 deposits and the material of two gold-processing plants in Yakutia and Magadan region, Russia. Those parameters included: water retention capacity of gold- and silver-bearing materials, absorption of chemical agents, optimum solvent concentration, temperature impact, and metal recovery [17]. For the first time, the experiments proved that gold and silver minerals can be transferred into a water-soluble form by addition of cyanides under the temperature range from 0 down to -40 °C.

After many years of cryomineralogenesis studies in mining and technogenic massifs, Ptitsyn developed a geochemical basis for metal geotechnology in the permafrost environment. Analysis of copper ore samples from the Udokan deposit experimentally showed conditions of copper solutions formation and migration under subzero temperatures [40,41]. Corrosive solution originates at the contact between sulfide ores and atmosphere. By reacting with ores during gravity migration, it forms an oxidation zone. The solutions penetrate into ice intergranular space, and between ice and minerals contacts. Cryogenic zones should be considered as a common feature in the areas of permafrost development [41,42].

The most important factors of cryomineralogenesis in mining and technogenic massifs are the following [43]:

- (1) wide development of film water;
- (2) exothermic effect of sulfides oxidation;
- (3) significant impact of psychrophilic bacteria, including understudied silicate bacterium and other simple organisms;
- (4) cryogenic solutions formation and migration conditions;

- (5) low freezing temperature of high-concentrated percolated solutions, mainly sulfate ones;
- (6) multiple geochemical barriers causing and ensuring mineralization;
- (7) long-term existence of tectonic activity zones, which are conductors of both active endogenous fluid streams and exogenous supergenesis agents;
- (8) frequency of changes in thermal conditions with various duration and intensity.

Ptitsyn's monograph describes an essential opportunity for using geotechnology for recovery of non-ferrous, rare, and precious metals in permafrost areas with cold climate [40]. Metals transition into a liquid form is achieved by combined treatment of ores with film-type solutions and solutions produced by cryogenic concentration. An additional factor intensifying a heap leaching process is frost cracking, which increases the contact surface between ore and solution. Due to gravity migration through rock conglomerated by ice, a concentrated freeze-resistant metal-containing solution can be accumulated on a waterproof foundation in the lower part of a massif. It ensures a possibility for the metal extraction and processing. The author pointed out that silting of massif could be reduced considerably during leaching at subzero temperatures.

Ptitsyn recommends using geotechnology methods at subzero temperatures for leaching gold, silver, copper, beryllium, magnesium, mercury, tin, bismuth, molybdenum, tungsten, manganese, nickel, as well as a number of rare metals found in significant quantity in highly-mineralized solutions [40]. The author assumed that lead, zinc, cobalt and platinum group metals can be recovered with the same method. Depending on ore composition, both acid (sulfate, chloride) and alkali (carbonate, ammonium, etc.) solutions can be used for leaching.

Nitrogen oxygen compounds (NO, N₂O₃, NO₂, N₂O₄, HNO₂, NO₂⁻, HNO₃, NO₃⁻, NO⁺, NO₂⁺, etc.) are likely to be oxidizing substances for oxidized leach cap, but they need further studies [42,44–47]. For example, nitrous acid activates various oxidizing processes, including leaching of galena (PbS), pyrites (FeS₂), pyrrhotite (Fe_{1-x}S), sphalerite (ZnS), and chalcocite (Cu₂S) in sulfuric acid solutions [42]. The activating effect of HNO₂ is intensified with its concentration increase and it is limited only by the disproportion of HNO₂ at the positive temperature range and low pH values. The experiments proved that nitrous acid stability under cryogenic conditions increases significantly even in highly acidic medium. Frost weathering modeling on the samples of copper-sulfide ores from the Udokan deposits (Russia) showed that copper-sulfide oxidation accelerated considerably with nitrous acid addition, and it has practically the same intensity throughout the analyzed range of parameters. The experiment involved the leaching of fraction 0.063–0.2 mm with 0.5 M sulfuric acid solution, using 0.1 M of nitrous acid and without it, at the temperatures of -20 and +20 °C, at S:L ratio of 1:5. The activating effect of HNO₂ appears to a greater degree during freezing. Copper recovery from solid phase increases by 2.7 times at a room temperature, and by 4.7 times under cryogenic conditions [45].

Passive leaching of gold and silver raw materials, as well as the justification of metals transition into a liquid phase with new oxidizing agents under subzero temperatures need generalization and experimental proofs for using it for sulfide ores and mine wastes processing.

In the next sections, the authors describe case studies and perspective of non-ferrous metals recovery from sulfide and mixed ores with heap leaching in the northern regions of the Russian Federation and abroad.

3. Geotechnological Methods of Ore Processing at the Udokan Mine

The Udokan deposit (in the North of Zabaykalsky Krai, Russia) is one of the largest copper deposits in the world, which is located 30 km to the south from the Novaya Chara railway station, on the mountain range Udokan. The territory of the deposit is associated with the Russian Far North. Continuous permafrost area extends with thickness from 65 m under water courses to 950 m under the watershed divide. Permafrost rock temperature is from $-7 \degree$ C to $-8 \degree$ C, the active layer thickness is about 1 m. By 2020, it is planned to build a mining and metallurgical complex with the capacity of

474,000 tons of copper per year. In addition to that, they plan to extract 277 t of silver per year, and to process additionally off-balance ores using the heap leaching method [46,47].

According to Khalezov, high-grade and amenable ores of the Udokan deposit should be processed with a traditional processing method, i.e., melting process [48]. Oxidized, sulfide-oxidized, and low-grade mixed ores should be processed using geotechnologies, i.e., heap leaching. Such ores should be dumped on specially arranged pads during mining. For this purpose, the corresponding ore classification process should be used. This process has already been used for a long time by a number of mining companies in Russia. Pyrometallurgical processing will be a source for sulfuric acid and heat to warm heap leaching solutions. Consequently, pyro- and hydrometallurgical methods are suggested for ore processing. This will ensure a technical and economic effect, and it enables increasing raw material usage. Copper minerals content is as follows: 68.5% of malachite (Cu₂CO₃(OH)₂) and brochantite ($Cu_4SO_4(OH)_6$); 29.6% of chalcocite (Cu_2S), covellite (Cu_5), bornite (Cu_5FeS_4); and, 1.9% of chalcopyrite (CuFeS₂). The ore has a vein, finely disseminated mineralization. Rock-forming minerals include quartz, feldspar, sericite, they amount up to 90%, and resistant to acid. This fact determines the low consumption of sulfuric acid. If leaching at Udokan is carried out only during warm season (140 days per year), leaching of ore with below 400 mm grain size will take 5–7 years. In case of a year-around operation with solution heating, the leaching will take 2–3 years. The SX/EW process is considered to be the most suitable method for copper extraction. The technology with closed water circulation enables recovering accompanying elements from ores, including rare and noble metals [48]. Solid residues of ore processing can be used for land reclamation and in construction industry.

4. Heap Bioleaching of Polymetallic Nickel Ore at the Talvivaara Deposit in Sotkamo, Finland

The Talvivaara deposit of polymetallic ores in Sotkamo, Finland, has become the most striking instance of heap bioleaching implementation for sulfide ores processing under the Far North conditions [49–53]. This deposit is considered to be one of the largest sulfide deposits in Europe situated in the geographical environment that closely resembles the Murmansk region in Russia.

Talvivaara black schist ore contains pyrrhotite ($Fe_{1-x}S$), pyrite (FeS_2), sphalerite (ZnS), pentlandite ((Fe,Ni)₉ S_8), violarite ((Fe,Ni)₃ S_4), chalcopyrite ($CuFeS_2$), and graphite (C). Nickel is distributed in the different sulfide minerals as follows: pentlandite 71%, pyrrhotite 21% and pyrite 8%. Cobalt is distributed in the following mineralogical phases: pentlandite 11%, pyrrhotite 26%, and pyrite 63%. The total copper is concentrated in chalcopyrite and the total zinc in sphalerite. The main silica-containing phases are quartz, mica, anorthite, and microcline [52]. Ore bioleaching in Talvivaara was studied during two decades: beginning from laboratory experiments in leaching columns, and up to construction of a pilot heap [49–53].

The selected mining method is a large-scale open pit mining. During processing, ore is crushed and screened in four stages to 80% passing 8 mm (Figure 1). After primary crushing, ore is conveyed to a secondary crushing plant, where it is crushed and screened in three stages. All of the material below 10 mm reports to agglomeration in a rotating drum, where pregnant leach solution (PLS) is added to the ore in order to consolidate fine particles with coarser particles. This preconditioning step makes ore permeable to air and water for heap leaching. After agglomeration, ore is conveyed and stacked in piles from eight to ten meters hight on the primary heap pad. After 13–14 months of bioleaching on the primary pad, the leached ore is reclaimed, conveyed, and re-stacked onto the secondary heap pad, where it is leached further in order to recover metals from those parts of the primary heaps, which had poor contact with the leaching solution. During the recovery process metals are precipitated from the PLS while using gaseous hydrogen sulfide and pH adjustment [53].

The primary heap is irrigated at a rate of 5 L/($m^2 \cdot h$). The irrigation solution pH is adjusted to 1.7–2.0, and the solution is distributed evenly over the heap surface. PLS is collected with a drainage system and is discharged to PLS collection ponds. About 10–20% of the solution is pumped to a metals recovery plant and the rest is recirculated to the heap (Figure 1).

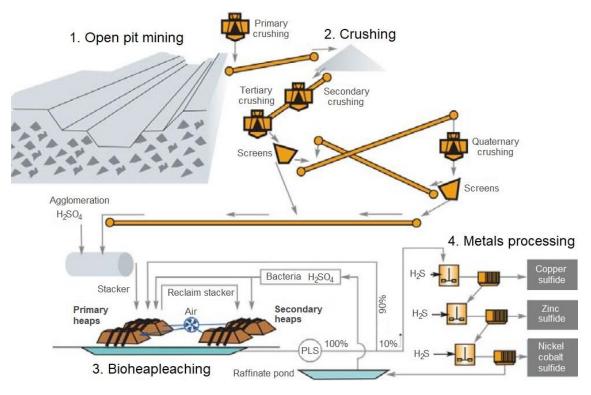


Figure 1. Process flow diagram of the "Talvivaara Mining Company Plc" [52].

The temperatures within the heap varied between 30–90 °C, despite the climate, and the PLS temperatures were 40–50 °C [49]. The microbial community in the heap (monitored by leachate analyses) varied during the first few months, becoming dominated by *At. ferrooxidans* and *Desulfotomaculum geothermicum*; other species identified were *Thiomonas arsenivorans*, *Alicyclobacillus tolerans*, and *Ferromicrobium acidophilum* [51]. Analyses of ore samples from the heap revealed *At. ferrooxidans*, *At. caldus*, and *F. acidophilum*. An uncultured bacterium clone H70 was found in both leachate and ore samples. Cell numbers varied between 10^5-10^8 cells/mL in leachate and between 10^5-10^7 cells/g in ore. In 500 days, recoveries were Ni 92%, Zn 82%, Co 14%, and Cu 2%. The low copper recovery was explained by the minerals' electrochemical properties [21].

Talvivaara became the first commercial nickel sulfide heap leaching operation. Nickel production was launched in October 2008. It was originally planned to reach the design capacity 33,000 t of nickel, 1200 t of cobalt, 60,000 t of zinc, and 10,000 t of copper by 2010 [21]. However, the peak performance was reached only by 2011, and the parameters amounted only to the half of the planned figures (16,087 t of nickel) [54].

The project engineering and development at commercial scale occurred during the period, when non-ferrous metal prices were rather high [54]. In 2007, average annual price of refined nickel at London Metal Exchange increased by 52.5% USD/t in comparison with 2006, i.e., from 24,416 to 37,230. The perspectives of successful operation at commercial scale were attractive. However, during the following years, prices for non-ferrous metals (including nickel) dropped dramatically.

The tense situation in the world market led to the bankruptcy of Talvavaara Mining Company Plc [54]. Regardless of the negative economic results, the company left a number of useful experiments, proved by experience, and having strategic value for further research and pilot tests; the microorganisms used in bioleaching process still exist and develop in the feed ore. They are endemic and well-adapted to the environment, what results in processing efficiency; high quality of materials recovered from solutions at commercial scale was demonstrated.

5. Copper-Nickel Ores and Technogenic Waste in Murmansk Region

Early studies of hydrometallurgical methods for processing of copper-nickel ores from the Murmansk region deposits were launched in the 70 s of the previous century [55]. For referencing purposes, the main types of disseminated ores from the deposits Zhdanovsky, Kaula, Sopchinsky Plast, and Lovnoozersky were selected. The metal content varied: 0.46-1.49% Ni and 0.01-0.62% Cu. In the first experiments, the solution containing 150 g/L of H₂SO₄ and 135 g/L of NaCl was used as a leaching reagent. The laboratory and further large-scale tests proved the possibility of underground metal leaching from the Lovnoozersky deposit ores.

The first data on a number of thionic bacteria in mine water of copper-nickel deposits in the Murmansk region are presented in the works of Lyalikova and Karavaiko et al. [56,57]. The possibility of their use for non-ferrous leaching was studied by Golovko et al. [55].

Currently, the research on justification of non-ferrous metal leaching from sulfide-containing natural and technogenic deposits of the Murmansk region continues [58–63].

5.1. Perspectives for Biological Leaching of Sulfide Copper-Nickel Ores from the Allarechensky Deposit Dumps

The technogenic deposit, the Allarechensky Deposit Dumps, is situated in the north-western part of the Murmansk region, 45 km to the south from the village Nickel, the Pechenga district. The deposit is a dump of mine waste that formed after open-pit mining of the Allarechensky sulfide copper-nickel ore deposit, which was completed in 1971 [13].

The ores of the deposit are represented by two morphological types: massive ore containing the following valuable components: 5–18% Ni, 0.15–8% Cu, up to 0.3% Co; and, disseminated ore containing 0.2–7.9% Ni, 0.12–4.9% Cu, up to 0.12% Co; with grades ranging: from 7.9%, 4.9%, and 0.12% (for high-grade ores) and up to 0.2%, 0.12%, and 0.008% (for low-grade ores), respectively. Ore studies enabled to define two key properties, which could be useful for ore processing: gravity and magnetic contrast [13,58,59].

Industrial tests showed that magnetic separation enables to efficiently process both raw and high-grade ones within the size range of 5–60 mm, and to produce a high-grade concentrate with cumulative content of Ni 2.0–3.7%, Cu 1.5–2.2%, and Co 0.03–0.08% [13,58,59].

For the processing of a fine fraction constituting 10–15% of all the deposit volume, it was studied whether non-ferrous metal recovery is possible by using biotechnology. The deposit ores are amenable to bioleaching due to their structural and textural properties. The chain of sulfide leaching was determined: pyrrhotite (Fe_{1-x}S) \rightarrow pentlandite (Fe,Ni)₉S₈ \rightarrow chalcopyrite (CuFeS₂), and pyrite (FeS₂). The crystal structure, fracturing, substitution by violarite ((Fe,Ni)₃S₄) and bravoite ((Fe,Ni,Co)S₂), contributing to faster mineral destructurization, encourage pentlandite (Fe,Ni)₉S₈ leaching. A large portion of minerals has excessive sorption capacity and it is characterized by ore mineral binding. These factors are referred to adversity [13,58,59].

JSC Irgiredmet has performed large-scale laboratory tests and calculation of technical and economic parameters on applicability of non-ferrous bacteria heap leaching technology for magnetic separation products in the dumps. One of the analyzed process flow diagrams is presented in Figure 2 [13,59].

Regardless of the fact that the resources of the deposit are not large, and, according to various estimates, amount to about one million tons of ore containing on the average 0.54% Ni and 0.47% Cu, the development of only explored reserves is considered to be a commercially viable investment project with low risks [59].



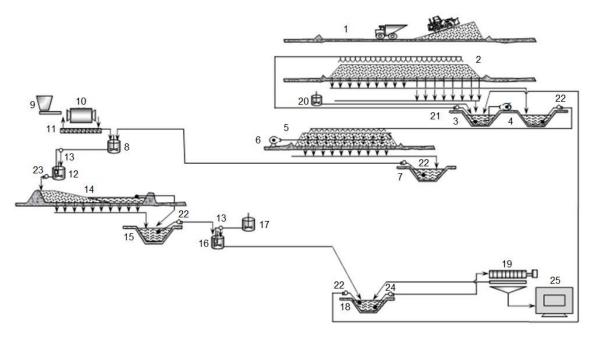


Figure 2. Process flow diagram of the ore heap leaching process at the Allarechensky Deposit Dumps [59]. 1—heap at the forming stage; 2—heap at the irrigation stage; 3—raffinate pond; 4—pregnant leach solution (PLS) pond; 5—heap for iron oxidation; 6—aeration system; 7—oxidized PLS pond; 8—neutralizing tank; 9—crushed lime bunker; 10—ball mill; 11—spiral classifier; 12—setting tank; 13—automatic titration system; 14—sludge storage; 15—storage pond for neutralized PLS; 16—precipitating tank; 17—reagent tank; 18—settling pond; 19—filter-press; 20—bacteria cultivation tank; 21–24—pumps; 25—furnace.

5.2. Copper-Nickel Ore Tailings

Copper-nickel ore processing tailings from the Processing Plant no.1 of the Pechenganickel Complex of JSC Kola Mining and Metallurgical Company in the town of Zapolyarny, the Murmansk region, are thought to be one of the largest technogenic deposits in Russia. These ores are characterized by the predominance of grain size below 0.1 mm. In many cases, up to 50% of grains are below 0.044 mm. Serpentines (about 60%) prevail in the mineral composition of tailings [10]. Piroxenes, amphiboles, talcum, chlorites, quartz, and feldspar are abundant, as well. The main ore minerals are magnetite (Fe₃O₄), pyrrhotite (Fe_{1-x}S), pentlandite ((Fe,Ni)₉S₈), and chalcopyrite (CuFeS₂). Total content of sulfide minerals is 1–3%. The losses of nickel with tailings during the enrichment of disseminated copper-nickel ores is up to 30%. Processing of finely-dispersed technogenic products or natural raw materials with high content of laminal hydrosilicates (clay minerals) involve colmatation problems, which decrease dump permeability for leaching solutions, and they lead to the process shutdown. Such effects were observed during the storage of copper-nickel ores processing tailings. Presence of chlorites, and mixed layer buildups in mature tailings results in formation of artificial clay-like ground, and decrease of filtration coefficient by more than 100 times [12].

One of the ways to solve this problem is material agglomeration with binders. Taking into account the excess amount of sulfuric acid produced by operations of the Kola Mining and Metallurgical Company (Zapolyarny City, Russia) and problems with it is sales; it is believed that a sulfatisation process involving pelletizing in agglomerators would be a promising technology. H_2SO_4 is used as a binding material in this process [60]. Pellets were experimentally produced at the ratio S:L = 5–3:1. H_2SO_4 solution with concentration of 10% was used as a binder. The pellet diameter for the tests was 0.8–1 cm. The highest pellet hardness under compression amounted to 2.8–3 MPa.

The tailings contained: Ni 0.17%, Cu 0.07%, Co 0.01%. Percolation leaching was fulfilled using 1% sulfuric acid in the columns with 45 mm diameter during 110 days.

About 60% of nikel contained in tailings transfers into solution during 110 days. Copper demonstrates a lower leaching rate (about 44%) as the metal occurs in the form of chalcopyrite (CuFeS₂) [2,21]. Relatively low leaching rate for cobalt (about 41%) are likely to be explained by the metal existence in the form of isomorphic contaminant in magnetite (Fe₃O₄). The leaching rate of metals per day amounted to: 0.55% of nickel, 0.37% of cobalt, and 0.4% of copper.

5.3. Low-Grade Copper-Nickel Ores of the Monchepluton Deposits

Previous mineralogical and processing tests that were performed on the off-balance copper-nickel ores from the Monchepluton deposits demonstrated their general amenability to hydrometallurgical processing [60,61]. It was necessary then to find process design solutions, which could ensure the intensification of sulfide mineral dissolution.

The samples of low-grade copper-nickel ores from three deposits were used for studies: Lake Moroshkovoye, Nyud Terrasa, and Nittis-Kumuzhya-Travyanaya (NKT). Nickel and copper content in the samples is presented in the Table 1 below.

To intensify heap leaching, we carried out ore grinding with further sulfuric agglomeration. The ore was ground to 0.05–1 mm.

Content, %								
Nickel			Copper					
Lake Moroshkovoye 0.547	NKT 0.567	Nyud Terrasa 0.465	Lake Moroshkovoye 0.036	NKT 0.363	Nyud Terrasa 0.044			

Table 1. Nickel and copper content in the ore samples.

The ore from the Lake Moroshkovoye deposit demonstrated the most intensive nickel leaching. After 32 days, the recovery was more than 60%. Herewith, about 20% of nickel that was transferred to solution at the stage of water leaching during one day (Figure 3a).

Nickel from the Nyud Terrasa deposit showed much worse leaching performance. The Ni recovery was about 10% during the same period. Obviously, it can be explained by fine sulfide impregnations prevailing in this type of ore. Therefore, after dissolving coarser minerals at the water leaching stage, the next growth of nickel recovery amounted to less than 2% up to the end of the test (Figure 3a).

As anticipated, copper leached much slower in comparison with nickel, and that was due to its presence in the form of chalcopyrite [2,21]. The best copper recoveries were achieved during the tests with the NKT deposit ore, they amounted to 8% (Figure 3b). The lowest Cu recovery, as in the case with Ni, was observed for the Nyud Terrasa deposit ore, it amounted to 1.95%. Leaching intensities of the non-ferrous metals per day are presented in Table 2.

Table 2. Leaching	; intensities of non-ferrous metals	per	day.
-------------------	-------------------------------------	-----	------

Nickel			Copper		
Lake Moroshkovoye	NKT	Nyud Terrasa	Lake Moroshkovoye	NKT	Nyud Terrasa
1.87%	0.97%	0.32%	0.13%	0.24%	0.06%

Consequently, sulfuric acid agglomeration of finely ground ores leads to considerable improvement of leaching performance. For example, during leaching of the Lake Moroshkovoye deposit ore crushed to 2–3 mm, the rate of recovery into solution per day amounted to 0.48% for nickel, 0.08% for copper, which is lower than the values that were demonstrated by ore in pellets by 3.9 and 1.6 times, respectively.

An optimization of the agglomeration mode and parameters is necessary to allow for the usage of increased grain sizes for pellets production. An increase of acid concentration for pelletizing enables further water leaching with solution circulation [62].



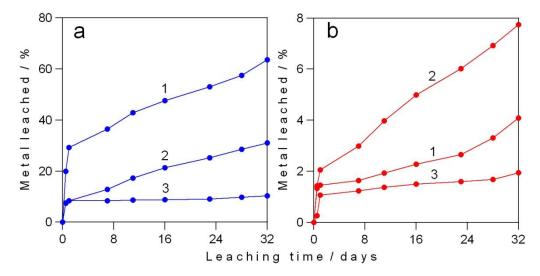


Figure 3. Kinetics of nickel (**a**) and copper (**b**) leaching from the ore samples. Deposits: Lake Moroshkovoye (1), Nittis-Kumuzhya-Travyanaya (NKT) (2), and Nyud Terrasa (3).

5.4. Percolation Bioleaching of Non-Ferrous Metals from Low-Grade Copper-Nickel Ore

Thionic bacteria facilitating bioleaching of sulfide ores were produced from sulfides and runoffs from the Allarechensky Deposit Dumps copper-nickel ores. For further work in a bioreactor at 27 °C and steady aeration bacterial biomass with a cell number of 10⁹ cells/mL was produced. A scale-up process was carried out during 10–12 days on the mineral medium containing ferrous iron.

Test leaching of ores from the Nyud Terrasa deposit was conducted. The content of Ni and Cu in the ore amounted to 0.42% and 0.15%, respectively. The ore was crushed to 1–3 mm, and loaded to percolators. Bacterial leaching was carried out with circulation of a certain solution portion. The ore was preliminary saturated with water. Solution was added once in two days in the amount of 25 mL.

Figure 4 demonstrates changes of solutions pH and Eh after filtration in a percolator during 76 days of the test. The first data points indicate ore water saturation.

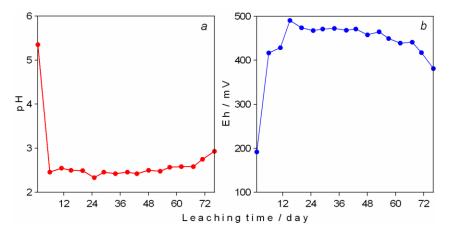


Figure 4. Changes of pH (a) and redox potential (b) in the solutions after filtration.

Correlation of ferrous and ferric iron concentrations in the solutions after filtration in a percolator indicates the oxidation of Fe^{2+} (Figure 5a).

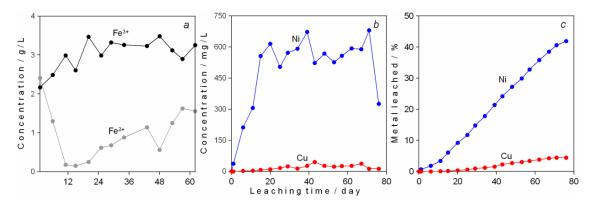


Figure 5. Ferrous and ferric ion concentrations (**a**), non-ferrous metal concentrations in the leach solutions (**b**), and their extraction (**c**).

Figure 5b,c present non-ferrous metal concentrations in pregnant solutions. As can be seen, nickel concentrations are sufficiently high. Copper concentrations are expectedly much lower. In general, the solutions are acceptable for further processing. Figure 5c shows the curves of nickel and copper recovery vs. process duration. Obviously, bioleaching enabled achieving acceptable values of non-ferrous metal recovery [63].

6. Conclusions

Experience of precious metals heap leaching in the regions with arctic and subarctic climate, and subzero average annual temperatures proves the applicability of these methods for geotechnological processing of sulfide ores containing non-ferrous metals.

Cryomineralogenesis studies in natural and technogenic sulfide-containing massifs, development of passive leaching methods for gold- and silver-bearing raw materials, as well as metals transfer into liquid phase under subzero temperature with new oxidizing agents deserve consideration and comprehensive experiments that are based on sulfide copper-nickel ores.

When processing the Udokan deposit copper ores, it is economically reasonable to combine pyro- and hydrometallurgical methods to increase the use of raw materials. Oxidized, oxide-sulfide, and low-grade complex ores should be processed with heap leaching.

The authors analyzed the experience of Talvivaara Mining Company Plc (a Finnish company), related to the nickel mine operation at the Talvivaara polymetallic deposit situated in the subarctic area, in the north-east of Finland.

Using the technogenic deposit, Allarechensky Deposit Dumps, as an example, we determined optimal combination of magnetic separation and biological leaching for sulfide copper-nickel ores processing ensuring the operation profitability and investment attractiveness of such technogenic deposits.

At the level of laboratory tests, we showed solutions and directions for more intensive methods of non-ferrous metals leaching from low-grade ores and waste of the mining and processing complex in the Murmansk region. The results will form a scientific basis for development of optimal conditions and parameters for ore and mine waste hydrometallurgical processing. This will enable justifying the involvement of low-grade copper-nickel ores and processing tailings containing strategic non-ferrous metals into commercial processing.

Author Contributions: Conceptualization, V.A.M., S.G.S., A.V.S. and D.V.M.; Methodology, V.A.M., S.G.S., A.V.S. and D.V.M.; Investigation, V.A.M., S.G.S., A.V.S. and D.V.M.; Writing-Original Draft Preparation, V.A.M., S.G.S., A.V.S. and D.V.M.; Writing-Review & Editing, V.A.M., S.G.S., A.V.S. and D.V.M.; Visualization, V.A.M.; Visualization, V.A.M., S.G.S., A.V.S. and D.V.M.; Visualization, V.A.M.; Visualization, V.A.M.; Visualization, V.S., Visualization, V.A.M.; Visualization, V.S., VIS, Visualization, V.S., VIS, VISUALI, VISU

Funding: The work has been performed with support of RFBR (project No. 18-05-60142 Arctic).

Conflicts of Interest: The authors declare no conflict of interest.

References

- 1. Chanturiya, V.A.; Kozlov, A.P. Development of physical-chemical basis and working out of innovation technologies of deep processing of anthropogenic mineral raw materials. *Gorn. Zhurnal (Min. J.)* **2014**, *7*, 79–84. (In Russian)
- 2. Halezov, B.D. *Copper and Copper–Zinc Ore Heap Leaching*; Ural Branch of Russian Academy of Sciences: Ekaterinburg, Russia, 2013; p. 360. (In Russian)
- 3. Petersen, J. Heap leaching as a key technology for recovery of values from low-grade ores—A brief overview. *Hydrometallurgy* **2016**, *165*, 206–212. [CrossRef]
- 4. Karavaiko, G.I.; Rossi, D.; Agate, A.; Grudev, S.; Avakyan, Z.A. *Biogeotechnology of Metals: Practical Guide*; Tsentr Mezhdunarodnykh Proektov GKNT: Moscow, Russia, 1989; p. 375. (In Russian)
- 5. Kondrat'eva, T.F.; Bulaev, A.G.; Muravyov, M.I. *Microorganisms in Biotechnologies of Sulfide Ores Processing*; Nauka: Moscow, Russia, 2015; p. 212. (In Russian)
- 6. Watling, H.R. Review of biohydrometallurgical metals extraction from polymetallic mineral resources. *Minerals* **2015**, *5*, 1–60. [CrossRef]
- 7. McDonough, W.; Braungart, M.; Anastas, P.T.; Zimmerman, J.B. Applying the principles of GREEN engineering to cradle-to-cradle design. *Environ. Sci. Technol.* **2003**, *37*, 434A–441A. [CrossRef] [PubMed]
- 8. Pakhomova, N.V.; Richter, K.K.; Vetrova, M.A. Transition to circular economy and closed-loop supply chains as driver of sustainable development. *St Petersbg. Univ. J. Econ. Stud.* **2017**, *33*, 244–268. [CrossRef]
- 9. Lèbre, É.; Corder, G.D.; Golev, A. Sustainable practices in the management of mining waste: A focus on the mineral resource. *Miner. Eng.* 2017, 107, 34–42. [CrossRef]
- 10. 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*, 559–572. [CrossRef]
- Chanturiya, V.A.; Makarov, V.N.; Makarov, D.V.; Vasil'eva, T.N.; Pavlov, V.V.; Trofimenko, T.A. Influence exerted by storage conditions on the change in properties of copper-nickel technologies products. *J. Min. Sci.* 2002, 38, 612–617. [CrossRef]
- 12. Chanturiya, V.A.; Makarov, V.N.; Makarov, D.V.; Vasil'eva, T.N. Forms of nickel in storage tailings of copper–nickel ores. *Dokl. Earth Sci.* 2004, *399*, 1150–1152.
- 13. Seleznev, S.G.; Boltyrov, V.B. Ecology of Mining-Generated Object "Allarechensky Deposit Dumps" (Pechenga District, Murmansk Region). *News High. Inst. Min. J.* **2013**, *7*, 73–79. (In Russian)
- 14. Adamov, E.V.; Panin, V.V. *Biotechnology of Metals: Course of Lectures*; MISiS: Moscow, Russia, 2008; p. 153. (In Russian)
- 15. Kashuba, S.G.; Leskov, M.I. Heap leaching in the Russian practice—An overview of the experience and analysis of prospects. *Zoloto I Tehnologii* **2014**, *1*, 10–14. (In Russian)
- 16. Watling, H.R. The bioleaching of sulphide minerals with emphasis on copper sulphides—A review. *Hydrometallurgy* **2006**, *84*, 81–100. [CrossRef]
- 17. Dement'ev, V.E.; Druzhinina, G.E.; Gudkov, S.S. *Heap Leaching of Gold and Silver*; Irgiredmet: Irkutsk, Russia, 2004; p. 252. (In Russian)
- 18. Sovmen, V.K.; Gus'kov, V.N.; Belyi, A.V.; Kuzina, Z.P.; Drozdov, S.V.; Savushkina, S.I.; Maiorov, A.M.; Zakraevskii, M.P. *Processing of Gold-Bearing Ores with the Use of Bacterial Oxidation in the Conditions of Far North*; Nauka: Novosibirsk, Russia, 2007; p. 144. (In Russian)
- 19. Golik, V.I.; Zaalishvili, V.B.; Razorenov, Yu.I. Uranium leaching experience. *Min. Inf. Anal. Bull.* **2014**, *7*, 97–103.
- 20. Anjum, F.; Shahid, M.; Akcil, A. Biohydrometallurgy techniques of low grade ores: A review on black shale. *Hydrometallurgy* **2012**, *117–118*, 1–12. [CrossRef]
- 21. Watling, H.R. The bioleaching of nickel sulphides. *Hydrometallurgy* 2008, 91, 70–88. [CrossRef]
- Watling, H.R.; Elliot, A.D.; Maley, M.; van Bronswijk, W.; Hunter, C. Leaching of a low-grade, copper-nickel sulfide ore. 1. Key parameters impacting on Cu recovery during column bioleaching. *Hydrometallurgy* 2009, 97, 204–212. [CrossRef]
- 23. Maley, M.; van Bronswijk, W.; Watling, H.R. Leaching of a low-grade, copper-nickel sulfide ore 2. Impact of aeration and pH on Cu recovery during abiotic leaching. *Hydrometallurgy* **2009**, *98*, 66–72. [CrossRef]
- 24. Maley, M.; van Bronswijk, W.; Watling, H.R. Leaching of a low-grade, copper-nickel sulfide ore 3. Interactions of Cu with selected sulfide minerals. *Hydrometallurgy* **2009**, *98*, 73–80. [CrossRef]

- Halinen, A.-K.; Rahunen, N.; Kaksonen, A.H.; Puhakka, J.A. Heap bioleaching of a complex sulfide ore: Part I. Effect of temperature on base metal extraction and bacterial compositions. *Hydrometallurgy* 2009, *98*, 92–100. [CrossRef]
- Halinen, A.-K.; Rahunen, N.; Kaksonen, A.H.; Puhakka, J.A. Heap bioleaching of a complex sulfide ore: Part II. Effect of temperature on base metal extraction and bacterial compositions. *Hydrometallurgy* 2009, *98*, 101–107. [CrossRef]
- 27. Qin, W.; Zhen, S.; Yan, Z.; Campbell, M.; Wang, J.; Liu, K.; Zhang, Y. Heap bioleaching of a low-grade nickel-bearing sulfide ore containing high levels of magnesium as olivine, chlorite and antigorite. *Hydrometallurgy* **2009**, *98*, 58–65. [CrossRef]
- Zhen, S.; Yan, Z.; Zhang, Y.; Wang, J.; Campbell, M.; Qin, W. Column bioleaching of a low grade nickel-bearing sulfide ore containing high magnesium as olivine, chlorite and antigorite. *Hydrometallurgy* 2009, *96*, 337–341. [CrossRef]
- 29. Yang, C.; Qin, W.; Lai, S.; Wang, J.; Zhang, Y.; Jiao, F.; Ren, L.; Zhuang, T.; Chang, Z. Bioleaching of a low grade nickel-copper-cobalt sulfide ore. *Hydrometallurgy* **2011**, *106*, 32–37. [CrossRef]
- 30. Bhatti, T.M.; Bigham, J.M.; Vuorinen, A.; Tuovinen, O.H. Chemical and bacterial leaching of metals from black schist sulfide minerals in shake flasks. *Int. J. Miner. Process.* **2012**, *110–111*, 25–29. [CrossRef]
- 31. Mandziak, T.; Pattinson, D. Experience-based approach to successful heap leach pad design. *Min. World* **2015**, *12*, 28–35.
- 32. Petersen, J.; Dixon, D.G. Modelling zinc heap bioleaching. Hydrometallurgy 2007, 85, 127–143. [CrossRef]
- 33. Mellado, M.E.; Galvez, E.D.; Cisternas, L.A.; Ordonez, J. A posteriori analysis of analytical models for heap leaching. *Miner. Metall. Process.* **2012**, *29*, 103–112.
- 34. Ding, D.; Song, J.; Ye, Y.; Li, G.; Fu, H.; Hu, N.; Wang, Y. A kinetic model for heap leaching of uranium ore considering variation of model parameters with depth of heap. *J. Radioanal. Nucl. Chem.* **2013**, *298*, 1477–1482. [CrossRef]
- 35. McBride, D.; Gebhardt, J.E.; Croft, T.N.; Cross, M. Modeling the hydrodynamics of heap leaching in sub-zero temperatures. *Miner. Eng.* **2016**, *90*, 77–88. [CrossRef]
- 36. Lodeyschikov, V.V. Processing of nickel ores by heap leaching bacteria. The experience of the Finnish company Talvivaara. *Zolotodobyicha*. **2009**, *132*, 12–14. (In Russian)
- 37. Sinha, K.P.; Smith, M.E. Cold climate heap leaching. In Proceedings of the 3rd International Conference on Heap Leach Solutions, Reno, NV, USA, 12–16 September 2015.
- 38. Smith, K.E. Cold weather gold heap leaching operational methods. JOM 1997, 49, 20–23. [CrossRef]
- 39. Shesternev, D.M.; Myazin, V.P.; Bayanov, A.E. Heap gold leaching in permafrost zone in Russia. *Gornyi Zhurnal (Min. J.)* **2015**, *1*, 49–54. (In Russian)
- 40. Ptitsyn, A.B. Geochemical Fundamentals of Metal Geotechnology in Permafrost Conditions; Nauka: Novosibirsk, Russia, 1992; p. 120. (In Russian)
- Ptitsyn, A.B.; Sysoeva, E.I. Cryogenic mechanism of the Udokan oxidizing area formation. *Russ. Geol. Geophy.* 1995, *36*, 90–97.
- 42. Abramova, V.A.; Ptitsyn, A.B.; Markovich, T.I.; Pavlyukova, V.A.; Epova, E.S. *Geochemistry of Oxidation in Permafrost Zones*; Nauka: Novosibirsk, Russia, 2009; p. 88. (In Russian)
- 43. Yurgenson, G.A. The cryomineralogenesis of minerals in the technological massifs. In *Proceedings of Mineralogy of technogenesis*—2009; Institute of Mineralogy, Ural Branch of RAS: Miass, Russia, 2009; pp. 61–75. (In Russian)
- 44. Markovich, T.I. Processes of Heavy Metal Sulphides Oxidation with Nitrous Acid. Ph.D. Thesis, Trofimuk Institute of Petroleum Geology and Geophysics, Siberian Branch of the Russian Academy of Sciences (IPGG SB RAS), Novosibirsk, Russia, February 2000. (In Russian)
- 45. Ptitsyn, A.B.; Markovich, T.I.; Pavlyukova, V.A.; Epova, E.S. Modeling cryogeochemical processes in the oxidation zone of sulfide deposits with the participation of oxygen-bearing nitrogen compounds. *Geochem. Int.* **2007**, *45*, 726–731. [CrossRef]
- 46. Abramova, V.A.; Parshin, A.V.; Budyak, A.E. Physical and chemical modeling of the influence of nitrogen compounds on the course of geochemical processes in the cryolithozone. *Kriosfera Zemli.* **2015**, *9*, 32–37. (In Russian)
- 47. Abramova, V.A.; Parshin, A.V.; Budyak, A.E.; Ptitsyn, A.B. Geoinformation modeling of sulfide frost weathering in the area of Udokan deposit. *J. Min. Sci.* **2017**, *53*, 501–597. [CrossRef]

- 48. Khalezov, B.D. Problems of Udokansky field ores processing. *Min. Inf. Anal. Bull.* **2014**, *8*, 103–108. (In Russian)
- 49. Riekkola-Vanhanen, M. Talvivaara black schist bioheapleaching demonstration plant. *Adv. Mater. Res.* 2007, 20–21, 30–33. [CrossRef]
- 50. Puhakka, J.A.; Kaksonen, A.H.; Riekkola-Vanhanen, M. Heap leaching of black schist. In *Biomining*; Rawlings, D.E., Johnson, D.B., Eds.; Springer-Verlag: Berlin, Germany, 2007; pp. 139–151.
- 51. Halinen, A.K.; Rahunen, N.; Määttä, K.; Kaksonen, A.H.; Riekkola-Vanhanen, M.; Puhakka, J. Microbial community of Talvivaara demonstration bioheap. *Adv. Mater. Res.* **2007**, 20–21, 579. [CrossRef]
- 52. Riekkola-Vanhanen, M. Talvivaara Sotkamo mine—Bioleaching of a polymetallic nickel ore in subarctic climate. *Nova Biotechnol.* **2010**, *1011*, 7–14.
- Riekkola-Vanhanen, M.; Palmu, L. Talvivaara Nickel Mine—From a project to a mine and beyond. In Proceedings of Symposium Ni-Co 2013; Battle, T., Moats, M., Cocalia, V., Oosterhof, H., Alam, S., Allanore, A., Jones, R., Stubina, N., Anderson, C., Wang, S., Eds.; Springer International Publishers: Cham, Switzerland, 2016; pp. 269–278.
- 54. Annual Report Talvivaara 2013; Talvivaara Sotkamo Ltd.: Tuhkakylä, Finland, 2013.
- 55. Golovko, E.A.; Rozental, A.K.; Sedel'nikov, V.A.; Suhodrev, V.M. *Chemical and Bacterial Leaching of Copper-Nickel ores*; Nauka: Leningrad, Russia, 1978; p. 199. (In Russian)
- 56. Lyalikova, N.N. Bacteria role in the sulfide ores oxidizing of the copper-nickel deposits on the Kola Peninsula. *Microbiology* **1961**, *30*, 135–139. (In Russian)
- 57. Karavaiko, G.I.; Kuznetsov, S.I.; Golomzik, A.I. *Role of Microorganisms in Leaching Metals from Ores;* Nauka: Moscow, Russia, 1972; p. 248. (In Russian)
- 58. Seleznev, S.G. Unconventional effective ways to enrich the sulfide copper-nickel ores on the example of Allarechenskiy technogenic deposit. *News High. Inst. Min. J.* **2011**, *8*, 118–125. (In Russian)
- 59. Seleznev, S.G. The Specificity and Development Problems for the Dumps of Sulfide Copper-Nickel Ores Allarechensky Deposit. Ph.D. Thesis, Ural State Mining University, Yekaterinburg, Russia, December 2013. (In Russian)
- 60. Svetlov, A.; Kravchenko, E.; Selivanova, E.; Seleznev, S.; Nesterov, D.; Makarov, D.; Masloboev, V. Perspectives for heap leaching of non-ferrous metals (Murmansk Region, Russia). *J. Pol. Min. Eng. Soc.* (*Inzynieria Mineralna*) **2015**, *36*, 231–236.
- 61. Svetlov, A.; Seleznev, S.; Makarov, D.; Selivanova, E.; Masloboev, V.; Nesterov, D. Heap leaching and perspectives of bioleaching technology for the processing of low-grade copper-nickel sulfide ores in the Murmansk region, Russia. *J. Pol. Min. Eng. Soc. (Inzynieria Mineralna)* **2017**, *39*, 51–59.
- 62. Svetlov, A.V.; Makarov, D.V.; Goryachev, A.A. Directions for intensification of leaching of non-ferrous metals on the example of low-grade copper-nickel ore deposits in the Murmansk region. In *Proceedings of Mineralogy of Technogenesis*—2017; Institute of Mineralogy, Ural Branch of RAS: Miass, Russia, 2017; pp. 154–162. (In Russian)
- 63. Fokina, N.V.; Yanishevskaya, E.S.; Svetlov, A.V.; Goryachev, A.A. Functional activity of microorganisms in mining and processing of copper-nickel ores in the Murmansk Region. *Vestnik of MSTU (Murmansk State Technical University)* **2018**, *21*, 109–116. (In Russian)



© 2018 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).