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Non-Ferrous Metals and PGM Recovery from Low-Grade Copper–Nickel Concentrate by Bioleaching and Further Cyanidation

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Abstract: The aim of the present work was to perform copper, nickel, and platinum group metals (PGMs) recovery from low-grade copper–nickel concentrate containing pyrrhotite, pentlandite, and chalcopyrite by bioleaching in stirred tank reactors in batch mode and subsequent cyanidation. The concentrate contained (%) Fe 32.7, Cu 0.7, Ni 2.3, S_{total} 20.9, $S_{sulfide}$ 17, 0.1 g/t Pt, and 1.35 g/t Pd. The bioleaching was performed at 30 and 40 °C using two different microbial consortia. At 30 °C, bioleaching was performed using mixed culture including *Acidithiobacillus ferrivorans* strains isolated from the sample of acid mine drainage from copper–nickel deposit. At 40 °C, bioleaching was performed using microbial population formed during long-term bioleaching of copper-zinc concentrate at 40 °C. Bioleaching was performed for 40 days at pulp density of 10% (solid to liquid ratio 1:10). At 30 °C, 70% Ni and 14% Cu were leached, while 72% Ni and 34% Cu were recovered in the solution at 40 °C. PGM were extracted from the concentrate and bioleaching residue obtained at 40 °C by cyanidation. Cyanidation made it possible to extract 5.5% Pt and 17.3% Pd from the concentrate and 37.8% Pt and 87.8% Pd from the bioleaching residue. Thus, it was shown that the concentrate studied might be processed using bioleaching and subsequent cyanidation to extract both non-ferrous metals and PGM.

Keywords: copper–nickel concentrate; bioleaching; platinum group metals (PGM); acidophilic microorganisms

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1. Introduction

The currently applied biohydrometallurgical technologies make it possible to process low-grade and refractory ores, refractory sulfide gold-bearing concentrates, and in some cases non-ferrous metal (Ni, Co) concentrates [1–7]. The most widespread biohydrometallurgical technologies are dump and heap bioleaching of low-grade copper ores [3–5,8] and stirred tank reactor (STR) biooxidation of refractory gold concentrates [1,7]. As dump and heap bioleaching does not require large capital and operating costs, these processes are used to process low-grade metal ores, including copper, zinc, nickel, and uranium [3,8–10], and can also be used to treat refractory gold-bearing ores [11]. STR biooxidation provides high productivity, but requires relative high costs due to complex equipment. Therefore, it is usually used for processing refractory sulfide gold-bearing concentrates [1,7], but it has been successfully used for processing non-ferrous metal (Ni, Co) concentrates [2,6,7].

Biohydrometallurgical processes used for the treatment of sulfide ores and concentrates are performed by mixed populations of acidophilic iron and sulfur-oxidizing microorganisms, which are active at low pH values and in a wide temperature range [1,4,5,7].

An important source of platinum group metals (PGMs) is copper–nickel ores, and significant reserves of PGM are associated with massive and disseminated sulfide nickel-copper ores (Russia, South Africa) [12–14]. Copper–nickel ores are usually treated by means of obtaining sulfide concentrates and subsequent pyrometallurgical processing. In this case, PGMs are concentrated first in nickel (mainly) and copper concentrates, and then in slimes during electrolytic refining of nickel and copper [12,13]. The slime is then used to obtain PGM concentrates, which then are processed at the refining stage.

The depletion of developed deposits of nickel and copper–nickel ores, which can be processed using currently used technologies, and requirement to exploit small and technogenic deposits with low-grade and refractory ores result in the need to develop alternative approaches that can make it possible to extract PGM and non-ferrous metals profitably [13–24].

A number of works have shown that hydrometallurgical technologies can be alternative to the approaches presently used for PGMs extraction [13–16]. Some of these approaches involve the extraction of PGMs into the liquid phase, while others involve the conditioning of PGM concentrates using hydrometallurgical methods or use leaching as a pretreatment to obtain PGM concentrates. For example, it was shown that ammonia leaching can be used for the pretreatment of PGM-containing ores for copper and nickel recovery, which then made it possible to obtain high-grade PGM concentrates [14]. The Panton process involves the use of cyanidation, precipitation of precious metals, and autoclave leaching to obtain high-grade PGM concentrate (up to 4000 ppm) [14,15]. In a number of works, two-stage processes were investigated that involve the use of oxidative leaching processes for the extraction of non-ferrous metals, and subsequent cyanidation for the extraction of PGM and gold, which may also be present in ores [16–19]. For example, it was shown that during autoclave leaching it is possible to extract copper and nickel from sulfide concentrates, and the resulting solid residue can be processed by cyanidation [16].

Since sulfide ores and concentrates containing nickel can be successfully processed using bioleaching [6,9], a series of studies to evaluate the possibility of processing ores and concentrates containing nickel and PGM using biohydrometallurgy has been performed [17–19].

It was shown that bioleaching and subsequent cyanidation of the solid residue, which is successfully used for gold-bearing ores and concentrates [1,11], can be promising approach for the extraction of copper, nickel, and PGM [17–19]. For example, it was shown that bioleaching in columns made it possible to extract 52% copper, 95% nickel, and 85% cobalt from low-grade concentrate, while cyanidation of solid bioleaching residue allowed to extract 20% Pt, 87% Pd, and 46% Rh [17]. Column bioleaching at different temperatures (65–80 °C) made it possible to extract 69.9%–91% copper, 93%–98.5% nickel, and 76.8%–86.1% cobalt from the concentrate containing 2.3% copper, 3.4% nickel, and 0.1% cobalt, while cyanidation of solid bioleaching residue made it possible to extract 32.2%–34.3% Pt, 92.5%–96.5% Pd, and 63.4%–97.5% Au [18]. Column bioleaching of low-grade ore (containing 0.135% copper, 0.35% nickel, and 0.013% cobalt) made it possible to extract 87% copper, 71% nickel, and 47% cobalt, while 54% Pt, 90% Pd, and 86.7% Au were recovered by subsequent cyanidation [19].

At the same time, PGM leaching has certain peculiarities, which suggest the need for further research in this area. Since PGMs in ores can be present in the form of various minerals (sulfides, arsenides, tellurides), they can be partially recovered into the liquid phase during bioleaching, which can prevent their concentration in the solid residue for subsequent cyanidation [17,24]. In addition, in order to achieve high PGM recovery by cyanidation, it is often necessary to use high concentrations of cyanide and to perform cyanidation at high temperatures [17–19]. It was proposed to leach Pt and Pd in cyanide solutions in the presence of thiocyanate and Fe^{3+} ions, which made it possible to increase the extent and rate of PGM extraction [19].

The goal of the present work was to study the bioleaching of low-grade copper–nickel concentrate containing pyrrhotite, pentlandite, and chalcopyrite in stirred tank reactors in batch mode at different temperatures to evaluate possibility of its processing using hydrometallurgical approaches.

2. Materials and Methods

2.1. Obtaining Flotation Concentrate

The concentrate was obtained from the sample of low-grade ore of Nud II deposit situated on the western slope of Nud (67.900104, 32.936505) (Kola Peninsula, Murmansk Oblast, Russia). The ore minerals found in the Nud II deposit include pyrrhotite, chalcopyrite, pentlandite, and pyrite [20,21]. The sample of copper–nickel ore was used to obtain flotation concentrate. Content of the main elements in the ore is shown in Table 1.

Table 1. Chemical composition of the ore and concentrate.

Product	Content, %						
	Fe	**Cu**	**Ni**	**S_{total}**	**$S_{sulfide}$**	**$S_{sulfate}$**	**S^0**
Ore	19.7	0.37	1.29	13.1	-	-	-
Concentrate	32.7	0.70	2.30	20.9	17.0	1.0	2.9

Flotation of a sample crushed to a particle size of 60% −40 μm was carried out using Mekhanobr FML mechanical flotation machine (Mekhanobr-Tekhnika, Saint Petersburg, Russia). Flotation scheme included rougher and scavenger flotation, with alkalinization of the pulp with sodium hydroxide to pH 8.6. The following reagents was used for rougher flotation: 750 g/t of liquid glass, 500 g/t of carboxymethyl cellulose (Depramin 347, Akzo Nobel, Rotterdam, The Netherlands), 37.5 g/t of Aerophine 3416 (collector, the main components of which were diisobutyl dithiophosphinate, diisobutyl monothiophosphine, and diisobutyl dithiophosphate) (Cytec, Woodland Park, NJ, USA), 12.5 g/t of potassium butyl xanthate, and 20 g/t of methyl isobutyl ketone (MIBK). For the scavenger flotation, the same reagents were used, but their consumption was 40% of that in the rougher flotation.

2.2. Experimental Setup and Bioleaching

Batch bioleaching of the concentrate was performed in glass stirred tank reactors equipped with RW 20 overhead stirrer (IKA, Staufen, Germany) and TW-2.02 heating circulator (Elmi, Riga, Latvia) under the following conditions: temperature—30 or 40 °C, pulp density (S: L)—1:10, residence time—40 days, stirring rate—500 rpm. For the experiments, we used a liquid nutrient medium containing mineral salts (g/L): $(NH_4)_2SO_4$—0.75, KCl—0.05, $MgSO_4 \times 7H_2O$—0.125, K_2HPO_4—0.125, distilled water—1.0 L, which was successfully used in our previous works for sulfide concentrate biooxidation [25].

The mixed culture of two indigenous acidophilic strains of *Acidithiobacillus ferrivorans* strains isolated from the sample of acid mine drainage from copper–nickel deposit with optimum growth temperature of 30 °C, which were identified in our previous work [21] were used for the bioleaching at 30 °C. To obtain the inoculum, the culture was grown in the same reactor, which was used for the bioleaching experiments, using 9K liquid nutrient medium at 30 °C under non-aseptic conditions [26].

Designed consortium of acidophilic microorganisms, which was formed during long-term bioleaching of copper-zinc concentrate, was used as inoculum for bioleaching test at 40 °C [22]. This microbial consortium was adapted for continuous bioleaching in stirred tank reactors at 40 °C and high pulp density.

Cells of the mixed cultures were collected by centrifugation in sterile 500-mL tubes (9500 rpm, 15 min) using Sigma 4–15 centrifuge (Sigma, Osterode am Harz, Germany), resuspended in mineral medium, and inoculated in the reactors in such a way that initial cell number in the pulp was about 1×10^8 cells/mL.

2.3. Sampling and Analysis

Parameters of liquid phase were monitored to evaluate bioleaching activity. The pH and redox potential (Eh) were measured using pH-150MI pH meter (Izmeritelnaya Tehnika, Moscow, Russia). The pH values during the bioleaching were adjusted by adding concen-

trated (98%) sulfuric acid and $CaCO_3$ to the medium. The concentrations of Fe^{2+} and Fe^{3+} ions were determined by trilonometric titration. The concentration of copper and nickel were determined using a Perkin Elmer 3100 flame atomic absorption spectrometer (Perkin Elmer, Waltham, MA, USA). The rates of copper and nickel leaching from concentrate residue were calculated by the concentration of Cu and Ni ions in liquid phase.

Samples of concentrate and bioleaching residue were investigated by optical microscopy. The study was carried out in reflected polarized light on an Axioplan II polarization microscope (Carl Zeiss, Oberkochen, Germany) equipped with ToupCam 3.1 MP V1camera (Micromed, Saint Petersburg, Russia) with a ToupView 3.7.2774 software (Hangzhou, China) in Geological Institute of KSC RAS (Apatity, Russia).

XRD analysis of the concentrates and bioleaching residue was carried out using XRD 7000 X-ray diffractometer (Shimadzu, Kyoto, Japan).

2.4. Microbial Population Analysis

The analysis of the composition of microbial populations that formed under the experimental conditions was carried out by high-throughput sequencing on the MiSeq system (Illumina, San Diego, CA, USA).

Samples of the inoculum biomass used in the experiments at 30 and 40 °C were collected before bioleaching experiments. Samples for the analysis of microbial consortia formed during 40-day bioleaching experiments were collected at the end of the experiment.

The biomass from the liquid phase of the pulp was collected using an Allegra X-22 centrifuge (Beckman Coulter, Brea, CA, USA). To collect the biomass from the pulp sample, the solid phase was first separated by centrifugation at 1000 rpm, then the biomass was precipitated from the supernatant by centrifugation at 9500 rpm (9299 g). Biomass preparation, DNA isolation, library preparation based on the V3–V4 region of the 16S rRNA gene, amplicon preparation, sequencing using MiSeq system (Illumina, San Diego, CA, USA) were performed as described previously [27,28]. Biomass collected by centrifugation was mixed with 500 µL of the solution containing 0.15 of NaCl and 0.1 M of Na_2EDTA. Then the cells were homogenized for DNA isolation. For this purpose, liquid sample obtained at the previous stage was supplemented with guanidine hydrochloride and Triton X-100 to the final concentrations of 800 mM and 0.5%, respectively, and with a mixture of glass beads, 425–600 µm and less than 106 µm in diameter (~500 µL). The samples were homogenized in FastPrepR-24 Instrument (MP Biomedicals, Irvine, CA, USA) for 40 s at 6 m/s and incubated for 50 min at 50 °C. The standard procedure of phenol-chloroform extraction and isopropanol precipitation of nucleic acids was then used. The libraries of the 16S rRNA gene V3–V4 regions were prepared as described previously [27]. Amplicons were obtained with the following primer system: the forward primer (5′-CAAGCAGAAGACGGCATACGAGATGTGACTGGAGTTCAGACGTGTGCTCTTCCGATCTXXXXXXXXXXXXZZZZCCTAYGGGDBGCWSCAG-3′) consisting of "5′ Illumina Linker Sequence," "Index 1," "Heterogeneity Spacer" and the Pro-mod-341F primer sequence, respectively; the reverse primer (5′-AATGATACGGCGACCACCGAGATCTACACTCTTTCCCTACACGACGCTCTTCCGATCTXXXXXXXXXXXXZZZZGACTACNVGGGTMTCTAATCC-3′) consisting of "3′ Illumina Linker Sequence," "Index 2," "Heterogeneity Spacer" and the Pro-mod-805R primer sequence, respectively. The amplicons obtained were separated by electrophoresis in 2% agarose gel, excised, and purified using a Cleanup Standard PCR Purification Kit (Evrogen, Moscow, Russia). Sequencing was performed with the MiSeq System (Illumina, San Diego, CA, USA) using a kit of reagents that provided the read length of 300 nucleotides at each end of the amplicon. Demultiplexing was carried out with the appropriate scripts of QIIME version 1.9.1 [29]. The subsequent sequence processing and analysis were also performed in QIIME ver. 1.9.1 [29]. The data were passed through a filter with the minimum nucleotide read quality of 30 and the minimum read length of 350 bp. The chimerism testing of the reads was performed using the identify_chimeric_seqs.py script by the algorithm of USEARCH version 6.1544 [30] and the Silva 123 reference base of 16S rRNA reads [31]. The OTU table was formed using the pick_open_reference_otus.py

script. The sequences were grouped in OTUs with a similarity level of 97% using the algorithm of USEARCH version 6.1544 [30] and the Silva 123 version reference base of 16S rRNA reads [31]. In average, 8400 fragments for each sample were analyzed.

Since experiment at each temperature was performed in duplicate (in two reactors in parallel), sample from each reactor was collected and analyzed separately. Results obtained for each reactor as well as average results obtained at 30 and 40 °C are presented in the article.

2.5. Cyanidation Tests

Cyanidation test was performed to extract PGM from the concentrate and bioleaching residue under the following conditions: pulp density of 40% (*w*/*v*), pH 10.2–10.5 (adjusted using 20% CaO), cyanide (NaCN) concentration of 10.0 g/L, 25 °C, 24 h.

2.6. Data Processing

Bioleaching experiments at each temperature were performed in duplicate. Processing of the results was carried out using the MS 15.0.459.1506 Excel 2013 software (Microsoft, Redmond, WA, USA). Average values of the parameters are presented.

3. Results

3.1. Obtaining Flotation Concentrate

To obtain the concentrate for further experiment, concentrates of the main and control flotation were combined. The yield of the combined concentrate was 50.6% with the recovery of 90.2% Ni, 95.1% Cu, 80.7% S. The tailings of the control flotation were discarded and were not used in a further study.

Chemical and mineral compositions of the combined concentrate are shown in Tables 1 and 2. Pt and Pd contents in the concentrate sample were 0.1 and 1.35 g/t, respectively.

Table 2. Mineral composition of the concentrate (based on XRD data).

Content, %								
Pyrite	**Chalcopyrite**	**Pyrrhotite**	**Pentlandite**	**Chlorites**	**Plagioclase**	**Amphibole**	**Talc**	**Goethite**
5	5	35	5	5	30	5	5	5

Thus, Cu and Ni contents in the concentrate increased in 1.9 and 1.8 times compared to the ore, respectively. Despite this, it was shown that ore used in the study was not appropriate to obtain standard copper–nickel concentrate by conventional flotation technique used for similar ores. Concentrate obtained cannot be considered a suitable product for pyrometallurgical processing.

Therefore, hydrometallurgical treatment of such product was studied as alternative approach promising for metal extraction from substandard concentrate.

3.2. Bioleaching Experiments

The pH values of the liquid phase in the beginning of the bioleaching increased to 2.6–2.7, but after 8 days at 40 °C and after 18 days at 30 °C, the pH of the solutions decreased and stabilized at a level of 1.2–1.5 (Figure 1a,a'). This may be explained by dissolution of sulfide minerals of the concentrate (mainly pyrrhotite) accompanied with acid consumption and pH increase. Then, pH level decreased due to biooxidation of reduced inorganic sulfur compounds leading to sulfuric acid formation.

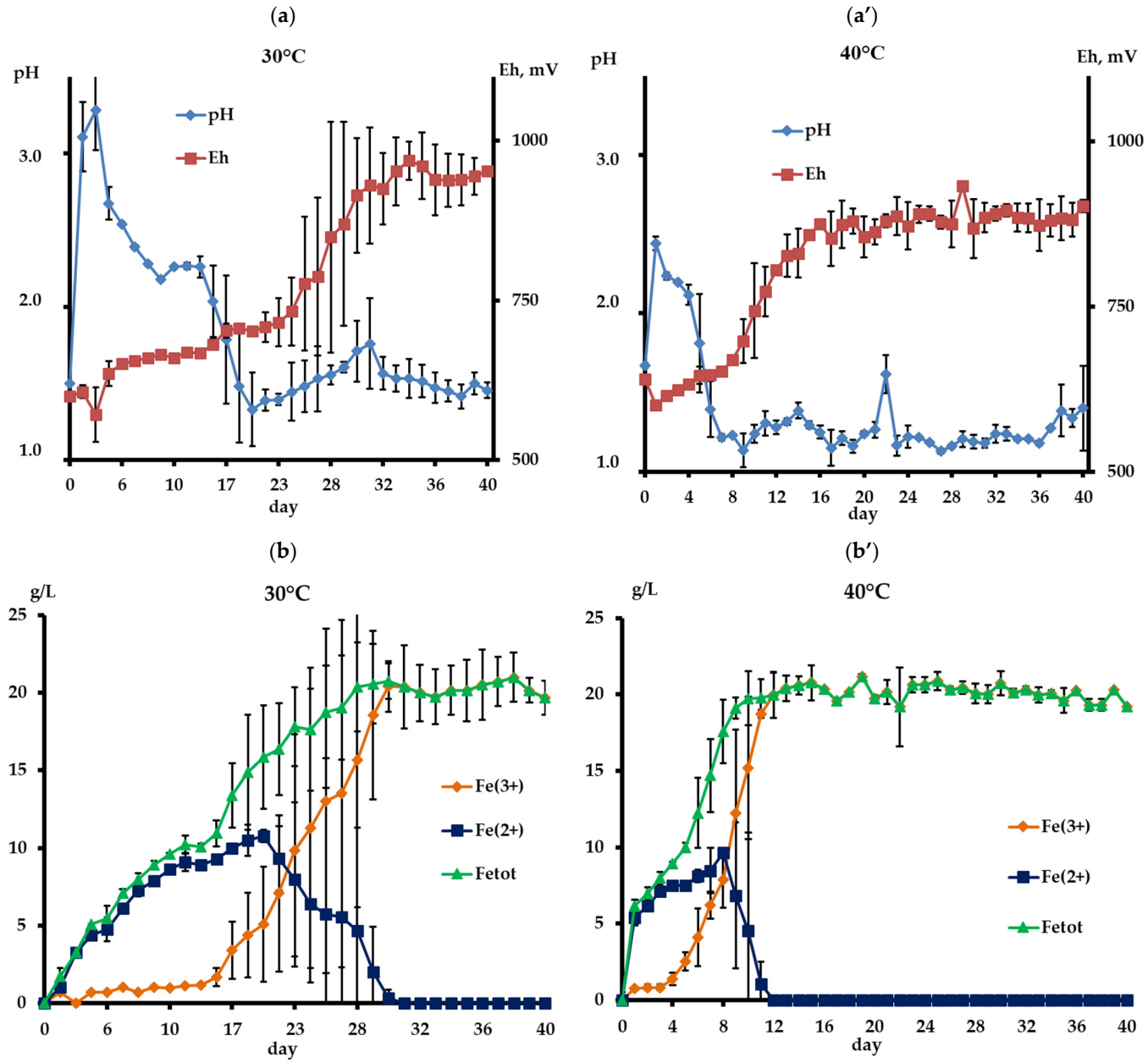

Figure 1. *Cont.*

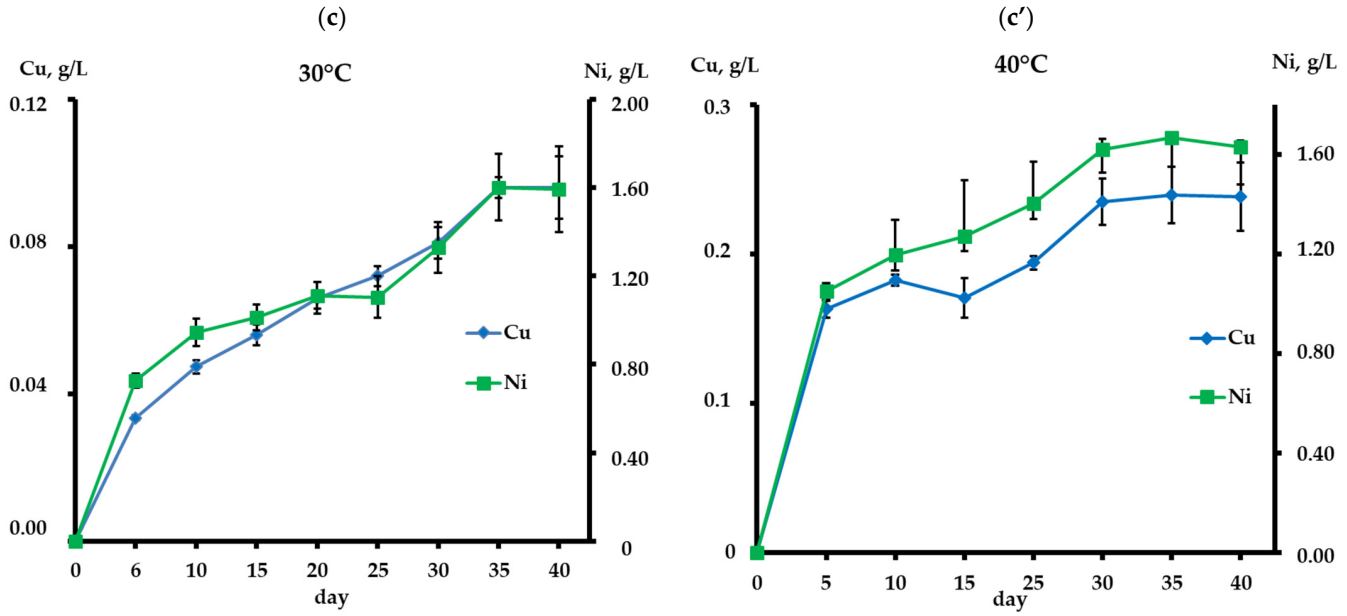

Figure 1. Changes in liquid phase parameters during the bioleaching at 30 and 40 °C: (**a**,**a′**) pH and Eh values, (**b**,**b′**) Fe^{3+} and Fe^{2+} concentrations, (**c**,**c′**) Cu and Ni concentrations.

The Eh values gradually increased during bioleaching and exceeded 800 mV after 15 days of bioleaching at 40 °C and 30 days of bioleaching at 30 °C (Figure 1 a,a′). Changes in Eh of the liquid phase of the pulp corresponded to changes in the concentrations of iron ions Fe^{3+} and Fe^{2+}.

At 40 and 30 °C, ferrous iron was absent in the pregnant solution after 14 and 30 days, respectively (Figure 1b,b′). The observed changes in the parameters of the liquid phase indicated that during the bioleaching, gradual increase in the activity of microorganisms was observed. In the beginning of the experiments, decrease in Eh and accumulation of Fe^{2+} ions in the medium occurred due to the dissolution of minerals in an acidic medium. Then, Fe^{2+} ions were oxidized to Fe^{3+} by iron-oxidizing microorganisms. It should be noted that the increase in the activity of microorganisms of the designed consortium at 40 °C was faster than that of the strains of the mesophilic culture at 30 °C. This is probably due to the fact that the designed consortium was previously adapted to the conditions of reactor bioleaching (intensive mixing, high pulp density, etc.).

The concentrations of copper and nickel gradually increased during bioleaching (Figure 1c,c′). It should be noted that the concentration of nickel ions exceeded the concentration of copper ions by 8–15 times, which is primarily because the chalcopyrite contained in the ore is more resistant to biooxidation than nickel minerals [23,32,33]. In this case, the difference in the concentration of copper and nickel ions at the end of the process was lower at 40 (0.24 and 1.63 g/L) than at 30 °C (0.096 and 1.59 g/L). This can probably be explained by the fact that at 40 °C chalcopyrite was leached at a higher rate, since its leaching is dependent on temperature [23,34–36]. The extraction extents of the metals are shown in Figure 2.

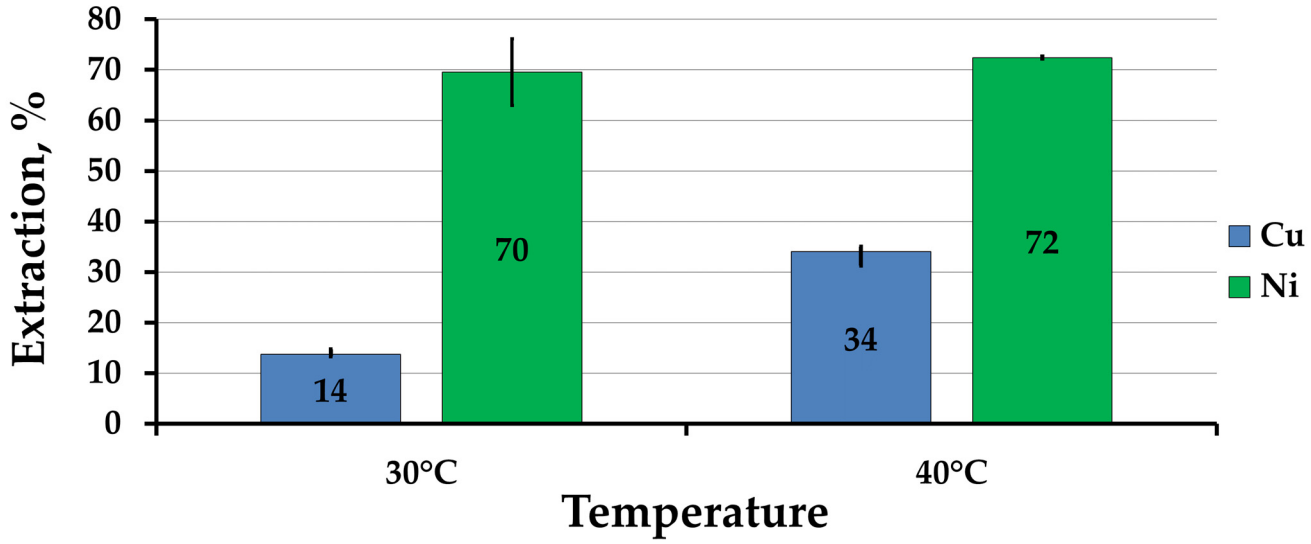

Figure 2. Cu and Ni extraction after 40 days of the bioleaching.

XRD analysis (Figure 3) demonstrated that initial concentrate (Figure 3a) contained a large number of phases with similar concentrations since the absolute intensities were low. The main phases were feldspar and pyrrhotite. Talc, amphibole, serpentine (or chlorite), quartz, pentlandite, chalcopyrite, magnetite, and goethite were also found bioleaching residues (Figure 3b,c), while pyrrhotite disappeared, and pentlandite and chalcopyrite content decreased (Figure 3b,c).

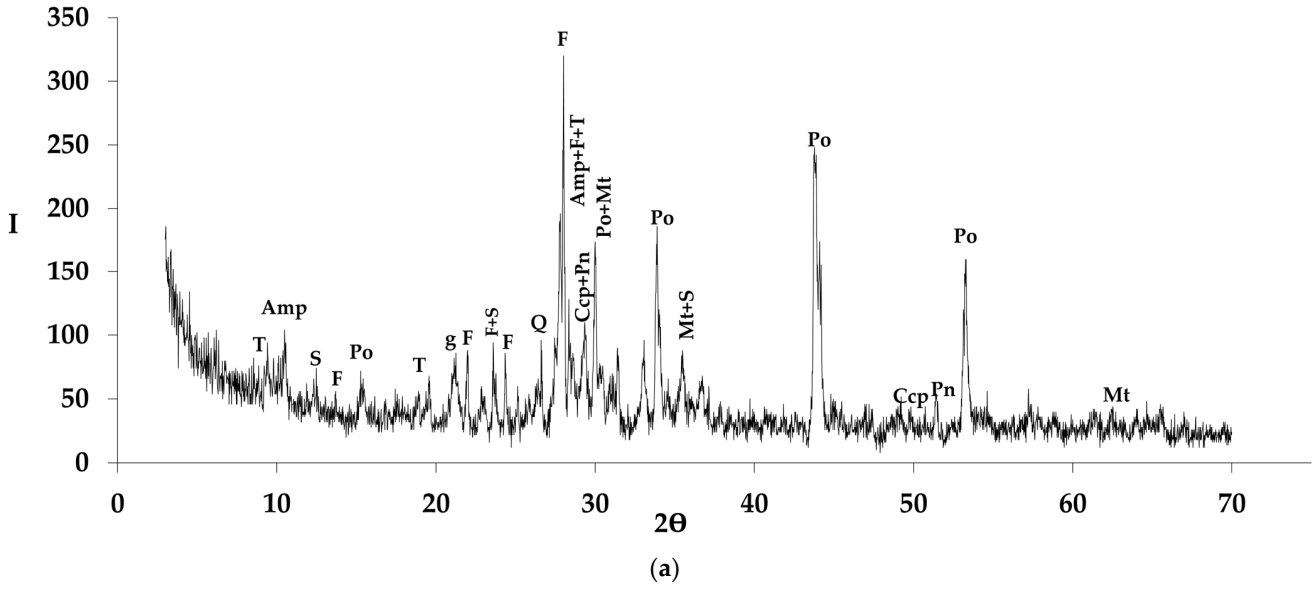

Figure 3. *Cont.*

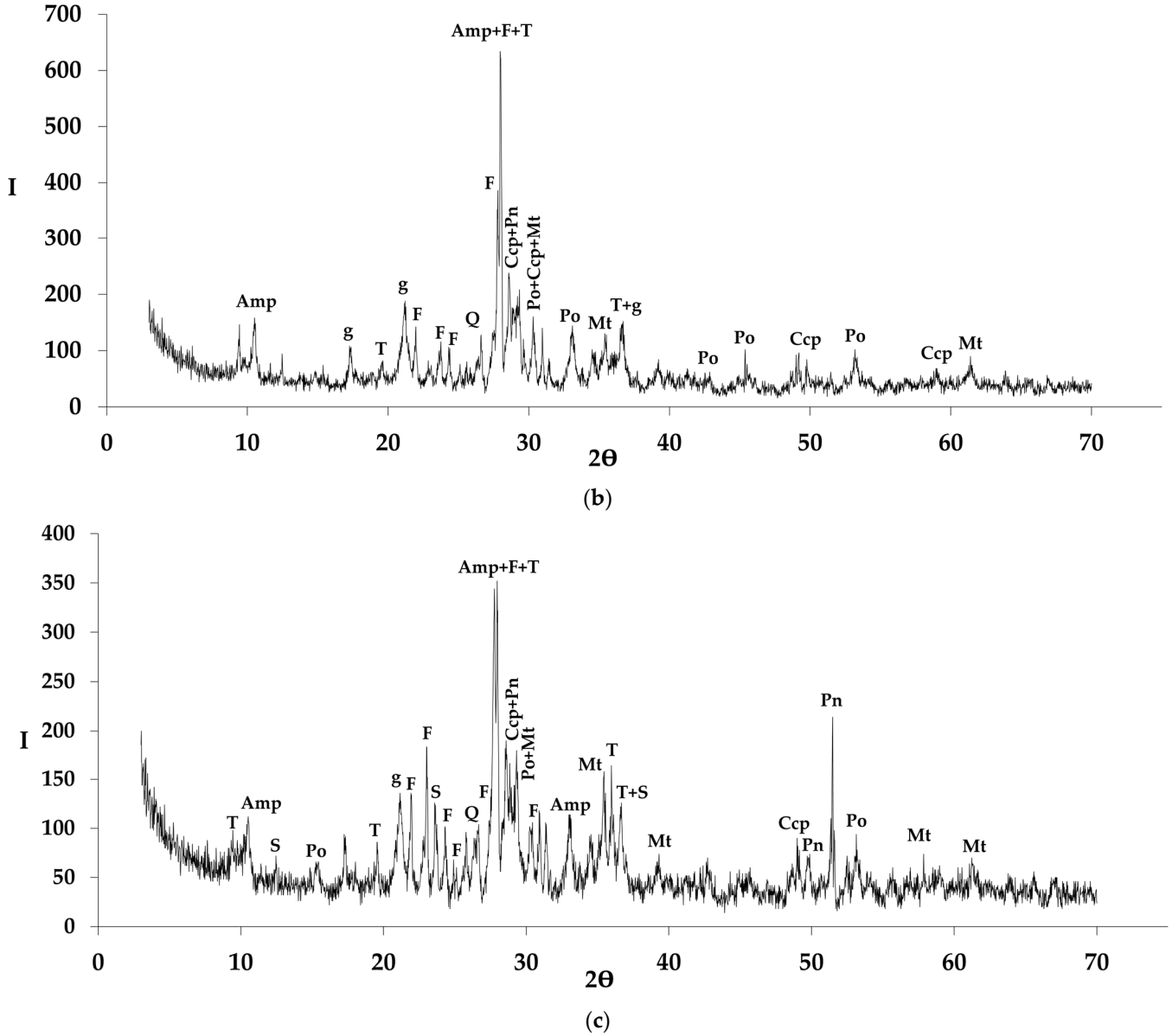

Figure 3. X-ray diffraction pattern of the samples: (**a**) concentrate, (**b**) bioleaching residue after 40 °C, (**c**) bioleaching residue after 30 °C. Amp: amphibole (No. 41-1366); S: serpentine (No. 50-1606); Po: pyrrhotite (No. 24-220); Pn: pentlandite (No. 8-90); Ccp: chalcopyrite (No. 37-471); Mt: magnetite (No. 19-629); F: feldspar (No. 41-1480); T: talc (No. 13-558); g: goethite (No. 29-713); Q: quartz (No. 46-1045). In parentheses, accession numbers in PDF-2 ICDD database (2020 release) are shown.

Optical microscopy revealed that the powder of the concentrate contained 85% sulfides and oxides, and 15% rock-forming minerals. In the initial concentrate (Figure 4a), among the sulfides, pyrrhotite was the main one. Pentlandite, chalcopyrite, and pyrite were observed among the minor minerals. Magnetite and iron hydroxides were detected among the oxides. Sulfides were found in the open state (free grains), but pyrrhotite forms intergrowths with pentlandite and chalcopyrite. Single intergrowths of pyrrhotite and pyrite with rock-forming minerals were also observed (Figure 4a).

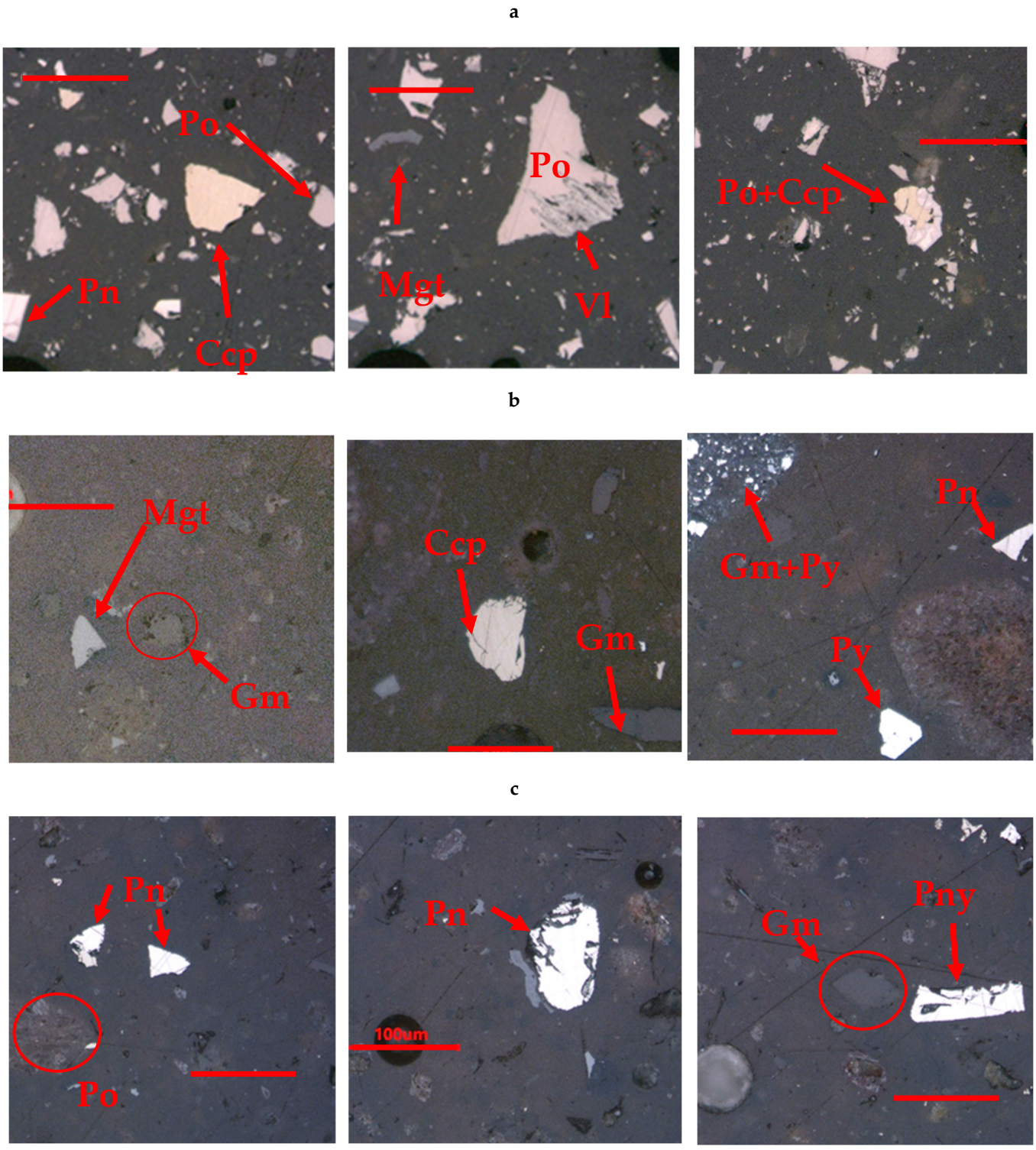

Figure 4. Results of transmitted and reflected polarized light microscopy: (**a**) concentrate, (**b**) bioleaching residue after 40 °C, (**c**) bioleaching residue after 30 °C. Ccp—chalcopyrite; Mgt—magnetite; Pn—pentlandite; Po—pyrrhotite; Py—pyrite; Vl—violaritis; Gm—gangue mineral; scale bar—100 μm.

The content of sulfides in biooxidation residues was 2%–3%, the amount of rock-forming minerals was close to that in the concentrate (Figure 4b,c). Pyrrhotite was practically not observed, the main sulfides were pentlandite and chalcopyrite presented as open grains, and no intergrowths were observed. Magnetite was also present. Almost all material was a fine powder of iron hydroxides.

Thus, mineralogical analysis demonstrated mineral transformation during biooxidation leading to the decrease in sulfide mineral content and appearance of iron hydroxides.

3.3. Microbial Population Analysis

Molecular biological analysis of microbial population in the reactors revealed that the species composition of microorganisms varied at different temperatures in the reactors (Tables 3 and 4).

Table 3. Analysis of microbial populations performing bioleaching at 30 °C (proportion of the 16S rRNA gene fragment, %).

Genus	Inoculum	Reactor 1	Reactor 2	Average of Reactor 1 and 2 ± SD
Acidithiobacillus	68.0	42.4	49.0	45.7 ± 4.7
Leptospirillum	11.0	55.4	6.0	30.7 ± 34.9
Sulfobacillus	0.0	0.5	4.0	2.3 ± 2.5
Staphylococcus	0.02	0.02	0.0	0.01 ± 0.014
Ferrimicrobium	0.01	1.0	0.02	0.5 ± 0.7
Acidiferrobacter	0.00	0.00	41.0	20.5 ± 29.0
Acidiphillium	14.0	0.0	0.0	0.0 ± 0.0
Ferroplasma	7.0	0.704	0.0	0.4 ± 0.5

Table 4. Analysis of microbial populations performing bioleaching at 40 °C (proportion of the 16S rRNA gene fragment, %).

Genus	Inoculum	Reactor 1	Reactor 2	Average of Reactor 1 and 2 ± SD
Acidithiobacillus	67.3	25.2	0.4	12.8 ± 17.5
Leptospirillum	0.0	0.5	3.0	1.8 ± 1.7
Sulfobacillus	0.1	1.9	0.2	1.0 ± 1.2
Ferrimicrobium	0.0	0.03	0.0	0.015 ± 0.02
Leifsonia	0.0	0.01	0.0	0.05 ± 0.005
Syntrophus	0.0	0.01	0.0	0.005 ± 0.005
Bacteroidia uncultured	0.0	0.01	0.0	0.05 ± 0.005
Cuniculiplasma	0.0	31.9	3.0	17.4 ± 20.4
A-plasma	0.0	10.1	1.4	5.7 ± 6.1
Ferroplasma	32.6	30.4	92.0	61.2 ± 0.014
Acidiplasma	0.0	0.02	0.0	0.01 ± 0.003

At 30 °C, the inoculum grown in the reactor included representatives of several genera despite pure cultures of *A. ferrivorans* were used (Table 3). This was due to the fact that the growth of microbial culture was carried out in a reactor with 9K mineral medium containing ferrous sulfate under non-aseptic conditions. In the inoculum obtained at 30 °C, representatives of the genera *Acidithiobacillus*, *Leptospirillum*, *Acidiphilium*, and *Ferroplasma* were predominant. *A. ferrivorans*, *Leptospirillum*, and *Ferroplasma* are iron-oxidizing microorganisms capable of growing under mesophilic conditions [4]. At the same time, *Acidiphilium* representatives are heterotrophic acidophilic microorganisms consuming organic compounds excreted by iron-oxidizing autotrophic microorganisms [37]. At the end of the experiment, *Acidithiobacillus*, *Leptospirillum*, *Acidiferrobacter*, and *Sulfobacillus* were predominant (Table 3). It should be noted that composition of microbial populations formed in the reactors during the bioleaching at 30 °C differed from the composition of the inoculum.

Acidiphilium and *Ferroplasma* were eliminated, while relative abundance of *Sulfobacillus* and *Acidiferrobacter*, which were not revealed in the inoculum, was comparatively high. It may be explained by difference in the conditions in the reactors during inoculum growth and concentrate bioleaching (pH, metal ions presence, high pulp density).

At 40 °C, archaea of the family *Ferroplasmaceae* were predominant both in the inoculum and in bioleach reactor populations (Table 4). This may be due to the resistance of these archaea to elevated temperature as well as by the low pH values of reactor pulp. At 40 °C, average pH level was about 1.2 after 10 days of the bioleaching (Figure 1a'), while 30 °C, it was about in the range of 1.5 to 1.8 (Figure 1). In addition, at 40 °C more rapid oxidation of iron was observed, which may occurred due to the activity of acidophilic archaea (Figure 1b,b'). Iron-oxidizing archaea of the genus *Ferroplasma* were predominant in the inoculum and in both reactors. At the same time, archaea of the genus *Cuniculiplasma* and uncultivated group A-plasma, which were not revealed in the inoculum, were of the most abundant in the bioleach reactors at 40 °C. Archaea of the genus *Cuniculiplasma* are heterotrophic acidophiles [38], while representatives of the group A-plasma have not been described, but are considered as potential iron-oxidizers based on metagenomic data [39].

It should be noted that presence of *Cuniculiplasma* and A-plasma archaea in the bioleach reactors was shown in our previous work [25,40], while potential role of these microorganisms in bioleaching of sulfide concentrates has not been understood.

Bacteria of the genus *Acidithiobacillus* (closely related to sulfur-oxidizer *A. caldus*) were also among predominant groups at 40 °C, which may be explained by capability of this microorganism to grow at elevated temperatures in bioleach reactors [4,7,40].

Thus, microbial population analysis demonstrated that temperature affected population composition and different microbial groups were the most abundant under different conditions.

3.4. Cyanidation Tests

Concentrate and bioleaching residue obtained at 40 °C were subjected to cyanidation. It was shown that the extraction of PGM from the bioleaching residue was significantly higher than those from the concentrate sample (Figure 5).

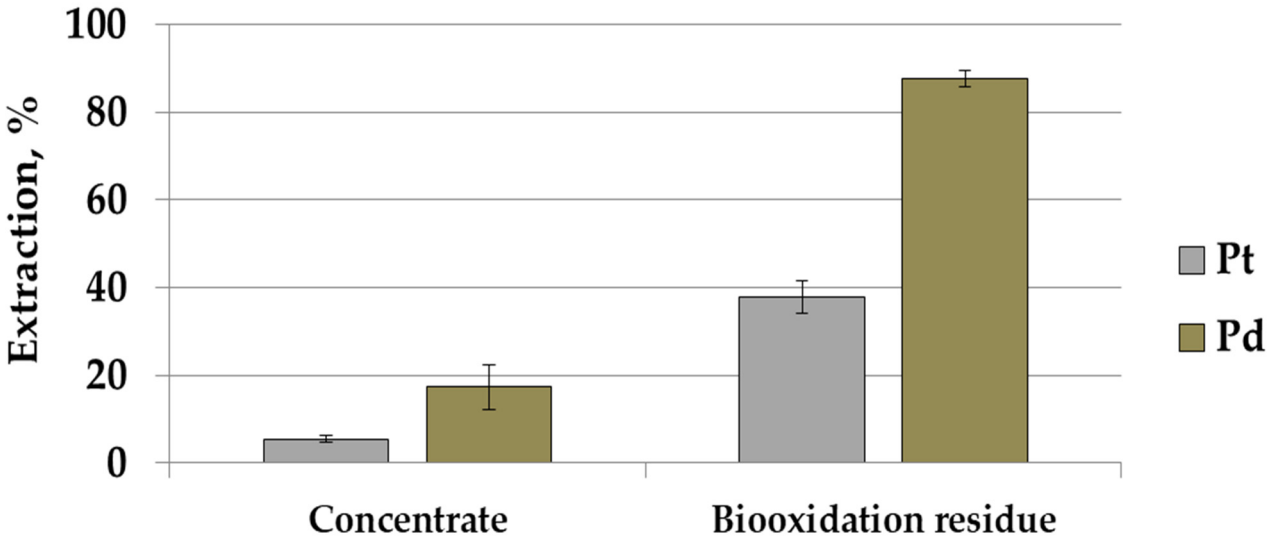

Figure 5. PGM extraction by cyanidation from the concentrate and biooxidation residue.

This can be explained by the fact that during bioleaching oxidation rate of sulfide sulfur was about 97%. The dependence of gold extraction from refractory sulfide concentrates on oxidation of sulfide minerals is well-known [1]. PGM recovery from sulfide ores and concentrates may also correlates with the oxidation state of sulfide sulfur, which may explain the great effect on PGM recovery in the case of reactor bioleaching. From the

other point of view, the increase of PGM cyanidation efficiency might be explained by elimination of nickel and copper from the concentrate as well as by pyrrhotite destruction. It was shown that copper and nickel form complexes with cyanide ions that suppress both gold leaching and gold sorption on the activated carbon [41,42]. Pyrrhotite may react with cyanide and oxygen that leads to consumption of cyanide and suppress gold extraction [43–45]. These phenomena might probably affect PGM recovery by caudation. Therefore, bioleaching of the concentrate in the present study led to the increase in PGM extraction by cyanide leaching.

4. Discussion

The results obtained in the present work demonstrated that studied low-grade concentrate might be processed using hydrometallurgical methods (e.g., bioleaching and cyanidation). Therefore, these methods may be promising for numerous small and exhausted deposits of low-grade copper–nickel ores situated in the Kola Peninsula (mainly in Murmansk Oblast, Russia), which presently cannot be economically exploited [20,21]. At the same time, development of methods suitable for processing of low-grade mineral raw materials corresponds to global trends, which impede to exploit novel sources of valuable metals (e.g., small deposits of low-grade ores, mining, and metallurgical wastes) [46].

It was shown that conventional concentration methods did not make it possible to obtain high-grade concentrate, which can be economically treated using pyrometallurgical methods, from the studied sulfide ore. At the same time, hydrometallurgical techniques are often considered as alternative approach for treatment of low-grade sulfide ores and substandard concentrates containing copper, nickel, and PGM [12–19,22]. Concentration in turn may provide obtaining low-grade concentration for further hydrometallurgical processing. Despite valuable metal content in the concentrate was low, it was almost two times higher than in the ore that can decrease the amount of the material, which should be treated to produce required amount of metal.

In the present study, bioleaching made it possible to extract significant part on nickel (70%–72%) and up to 34% of copper from the concentrate. Nickel extraction extent was similar in both experiments (at 30 and 40 °C), while copper extraction levels were lower in comparison to nickel and significantly differed at different temperatures (14 and 34% at 30 and 40 °C, respectively). This may be explained by the dependence of chalcopyrite leaching rate on temperature [23,34–36,47,48] and because the chalcopyrite is more resistant to biooxidation than nickel minerals [23,32,33].

Differences on bioleaching rates at 30 and 40 °C might be caused both by chemical reactions acceleration according to Arrhenius model and increase in microbial activity at higher temperature. The results shown in Figure 1 demonstrated that microbial activity at 40 °C was higher than at lower temperature, as ferrous oxidation as well as pH decrease rates were significantly higher at higher temperature. This suggests that temperature effect on the bioleaching was at least in some extent caused by differences in microbial activity and microbial population composition, but not only by acceleration of chemical reactions at higher temperature.

PGM extraction extent by cyanidation from biooxidation residue was significantly higher than that from the concentrate. This may be explained by several reasons. In first, it may be due to sulfide mineral disruption during the bioleaching that deliberate noble metals for cyanide leaching, which is well-known for gold-bearing concentrates [1]. In second, bioleaching led to the elimination of copper and nickel. These metals form complexes with cyanide ions, which in turn impede PGM cyanide leaching and further sorption on the activated carbon [41–45].

Thus, hydrometallurgical methods used in this work provided comparatively high recovery of nickel and PGM from the studied concentrate. At the same time, further studies are required for the development economically promising approach for the studied concentrate and similar product. Stirred tank reactor biooxidation is usually used for treatment of gold-bearing concentrates containing several tens of grams of gold per ton [1].

Therefore, other methods may be optimal for the products containing up to several percent of copper and nickel as well as several grams of PGM per ton. These methods may include heap bioleaching and methods similar to GEOCOAT® technology, which may provide high rates of bioleaching and require comparatively low CAPEX [49]. In addition, in order to achieve high PGM recovery by cyanidation, it is necessary to modify cyanidation process, as PGM are more resistant to cyanide leaching in comparison to gold [17–19].

5. Conclusions

The results of the present work demonstrated that non-ferrous metals (mainly nickel) may be extracted from the studied concentrate by bioleaching. In addition, bioleaching provided high PGM extraction by cyanidation. Thus, for the complex processing of Cu-Ni concentrates, bioleaching may be a promising method allowing both extracting non-ferrous metals and disrupting iron-containing sulfide minerals for subsequent PGM extraction by cyanidation. At the same time, further studies are required for evaluation of the approach recommended from the practical point of view. Optimization of both bioleaching and cyanidation stages are required.

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