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CHARACTERIZATION OF OXIDIZED COPPER ORES FROM THE KALMAKYR DEPOSIT (UZBEKISTAN)

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Abstract - The most important factor in choosing a processing technology for the ore is its chemical and mineralogical composition. This article presents the results of research conducted on the mineralogical composition of oxidized ores found at the Kalmakyr deposit of JSC "Almalyk Mining and Metallurgical Combine." According to the research, the oxidation degree of the ore is 46% for iron and 61% for copper, which corresponds to a mixed ore category. The average copper content is 0.4%. The minerals identified in the ore include malachite, pseudomalachite, cuprite, biotite, chalcosite, ferritungstenite, covellite, chalcocite, and molybdenite. Their total amount varies from 1–2% to 30–35%, averaging 5–7%. Based on these data, it becomes possible to select effective ore processing technologies.

Keywords: Copper, Oxidized copper ore, Chemical composition, Mineralogical composition, Hydrometallurgy.

1. Introduction

Currently, JSC "Almalyk Mining and Metallurgical Combine" (AMMC) is carrying out large-scale work to increase copper production. The opening of new deposits such as Yoshlik-1 and Yoshlik-2, as well as the launch of the 3rd Copper Concentration Plant, are among the important steps in this direction. Along with sulfide ores, the extracted ores also contain oxidized ores, which are currently being stockpiled separately and not processed. Processing these oxidized ores and extracting valuable components from them would make it possible to increase copper production efficiency, reduce negative environmental impacts, create new jobs, and gain economic benefits.

The development of technology and industry has led to an increase in both copper consumption and production volumes [1-2]. Along with sulfide copper ores, the efficient use of oxidized copper ores is becoming widely established around the world. However, due to their complex mineralogical composition and surface hydrophilic properties, oxidized copper ores are more difficult to process than sulfide ores [3-5].

Unlike sulfide ores, oxidized copper ores are characterized by a more complex composition. Sulfide ores mainly contain chalcopyrite or other copper sulfides such as bornite, chalcocite, and covellite. In oxidized ores, the main copper minerals include malachite, azurite, chrysocolla, brochantite, and cuprite [6-7].

Currently, flotation, hydrometallurgical, and combined methods are widely used in the processing of oxidized copper ores [8-11]. The flotation method presents certain difficulties when processing oxidized copper ores due to their complex mineralogical composition, hydrophilic nature, and high reagent consumption [12-14]. Direct flotation of oxidized copper ores is generally ineffective, and the use of sulfidizing agents significantly increases processing costs [15-16]. The hydrometallurgical method, on the other hand, is considered to be efficient for processing complex oxidized copper ores on an industrial scale [17].

Oxidized copper ores are often coated with gangue minerals, which hinder the interaction of valuable components with leaching solutions under normal conditions. To overcome this, researchers have proposed mechanical activation or ultrafine grinding to create cracks and defects in gangue minerals.

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However, this technology also faces industrial challenges due to high energy consumption [18-21].

2. Materials and Methods

The study of the mineral composition of the presented samples was carried out using a complex of mineralogical and petrographic analyses. Thin and polished sections were examined under transmitted and reflected light microscopy (Nikon Eclipse LV100 Pol). In addition to optical methods, X-ray diffraction analysis (XRD) was used to determine the quantitative mineral composition (DRON-3).

For the main composite sample, mineral mapping was conducted using the automated mineralogical analysis system QEMSCAN based on a Quanta FEG 650F scanning electron microscope. The study was carried out on briquetted polished sections made from composite sample material at different grinding sizes: P80 200 µm, P80 100 µm, and P80 74 µm. The device was operated in PMA mode (Particle Mineral Analysis), and the obtained data were processed using the iDiscover software.

3. Results and Discussion

The Kalmakyr deposit is one of the largest open pit mines in Uzbekistan. Construction of the mine began in 1954, and 60 million tons of sulfide copper ore are mined annually, which is enriched at a copper processing plant [20]. In the territory of the Kalmakyr deposit, there are approximately 100 million tons of oxidized and mixed copper ores stored in nine tailings sites [21]. Oxidized copper ores from the Kalmakyr deposit, which accumulate in waste heaps, both compliant and substandard, represent an additional source for the extraction of 250,000 tons of copper, 35.3 tons of gold, 175 tons of silver, and other valuable elements [22-24]. Currently, these ores are not processed due to the lack of profitable technology. The ore consists of 92–95% rock-forming minerals, primarily quartz and feldspars, with smaller amounts of muscovite, chlorite, biotite, and others. Quartz occurs as xenomorphic grains up to 1 mm in size, and its content varies from 20–25% to 60–70%, averaging 40–45%. Potassium feldspar forms angular or sometimes xenomorphic grains, partially replaced by clay minerals, with grain sizes up to 1 mm and an average content of 10–15%. Plagioclase grains reach up to 0.6 mm, with content varying from a few percent to 30–40%. Sericite constitutes 10–15%, while muscovite appears as fine flakes of 0.1–0.2 mm.

A high content of mica-type minerals such as sericite and chlorite can cause difficulties during processing, as these minerals tend to overgrind and produce excessive slimes. Among carbonate minerals, dolomite was identified in amounts of 2.6–3.1%. In addition, amphibole (up to 1.3%) and gypsum (up to 4.1%) were found.

Ore minerals occur in disseminated form, aggregates, or sometimes as veinlets, often associated with quartz veins. They fill voids between non-ore minerals, with grain sizes ranging from 0.1 to 0.3 mm. The following ore minerals were identified: pyrite (up to 1.9%), cubanite (up to 0.6%), turquoise (up to 0.7%), and copper (average 0.4%) represented by malachite, pseudomalachite, cuprite, biotite, chalcosite, ferritungstenite, covellite, chalcocite, and molybdenite. The content of ore minerals varies from 1–2% to 30–35%, averaging 5–7%.

Under the scanning electron microscope, the main copper and molybdenum minerals were identified. Copper occurs as chalcopyrite, covellite, chalcocite, bornite, copper carbonates, and chrysocolla, often forming complex mixtures with iron hydroxides. The average chemical composition of copper and molybdenum minerals is shown in Table 1.

It was established that the main copper minerals in the average sample of oxidized ore are various copper oxides. Among them, copper carbonates (19.96%) and bound copper, including copper associated with chrysocolla (18.7%), predominate. Secondary copper sulfides account for 23.4% of total copper. Chalcopyrite represents 15.9% of the total copper mass (Table 2).

Table 1. Chemical composition of copper and molybdenum minerals in the average sample of oxidized ore (based on electron microscopy data, %)

Mineral	**Cu**	**Fe**	**Mo**	**S**	**O**	**Si**
Chalcopyrite	33.9	33.0	—	33.11	—	—
Molybdenite	—	—	60.4	39.6	—	—
Covellite–Chalcocite	73.3	—	—	26.7	—	—
Bornite	56.2	17.7	—	26.12	—	—
Copper Carbonates	74.8	—	—	—	25.0	—
Copper in Iron Hydroxides	26.2	48.0	—	—	26.0	—
Chrysocolla	43.9	—	—	—	30.0	26.01

Table 2. Distribution of Copper Among Minerals

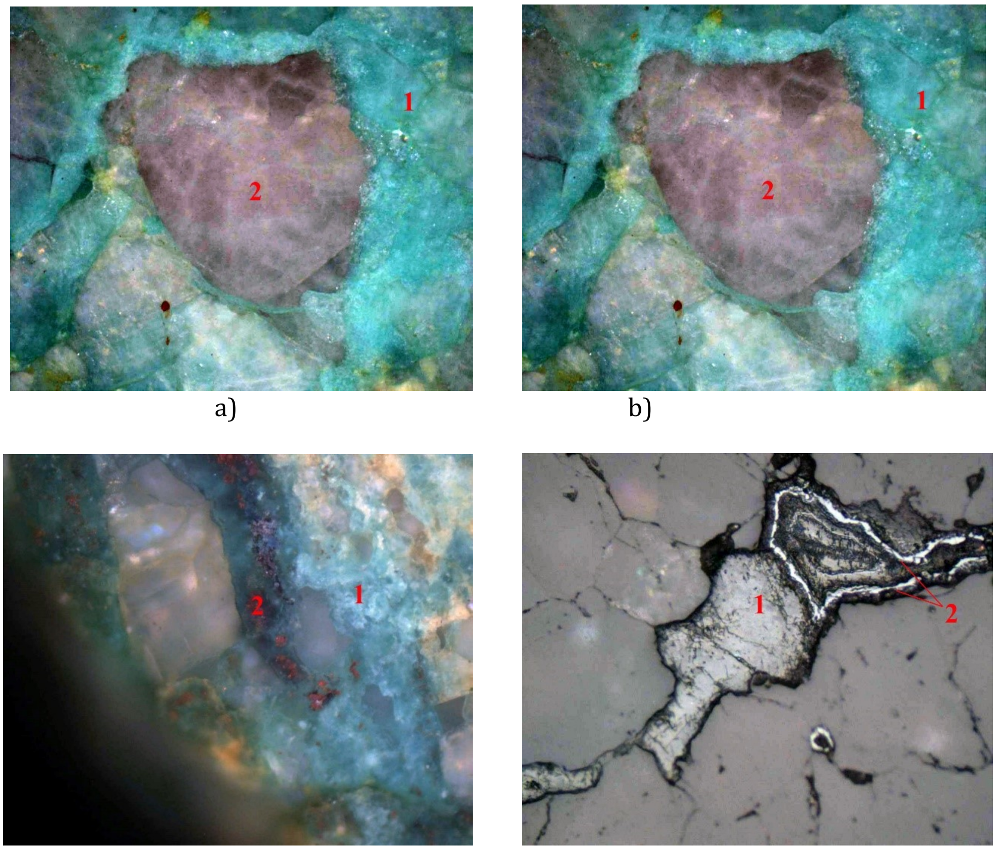
Mineral	**Copper Share, %**
Chalcopyrite	15.90
Bornite	3.85
Covellite–Chalcocite	19.55
Gray Ore (Tennantite–Tetrahedrite)	2.71
Copper Carbonates	19.96
Copper Sulfates	8.99
Chrysocolla and Bound Copper	18.70
Pseudomalachite	3.76
Turquoise	0.60
Cuprite	0.31
Iron Oxides/Hydroxides	5.66
Total	100.00

Description of Minerals. Malachite mainly occurs in disseminated, veinlet, and aggregate forms. It is located along fractures and is often observed mixed with iron hydroxides and sphalerite grains.

The veinlets of malachite fill fine cracks, indicating that it was formed in secondary oxidation zones.

Under the microscope, malachite is easily identified by its bright green reflections (Figure 1). The grain size ranges from 0,02 mm to 0,5 mm, and the grains have irregular shapes. Such morphological features indicate that malachite forms as a relatively stable phase under oxidation conditions. The development of malachite along very fine fractures in the oxidized part of the copper ore and its dense association at the micro-level with iron hydroxides limit the effectiveness of traditional flotation methods. The close growth and association of malachite with iron hydroxides (in particular, goethite - FeO(OH)) is a characteristic paragenesis of the "iron hat" or strongly oxidized part of copper-porphyry or pyrites. Since goethite and iron hydroxides are soft and brittle, they form a large amount of primary sludge during the grinding stage of the ore.

Chalcopyrite mostly occurs as fine disseminations between magnetite and hematite grains. The grains are isometric or xenomorphic in shape, with sizes varying from <0.01 mm to 1.0 mm.



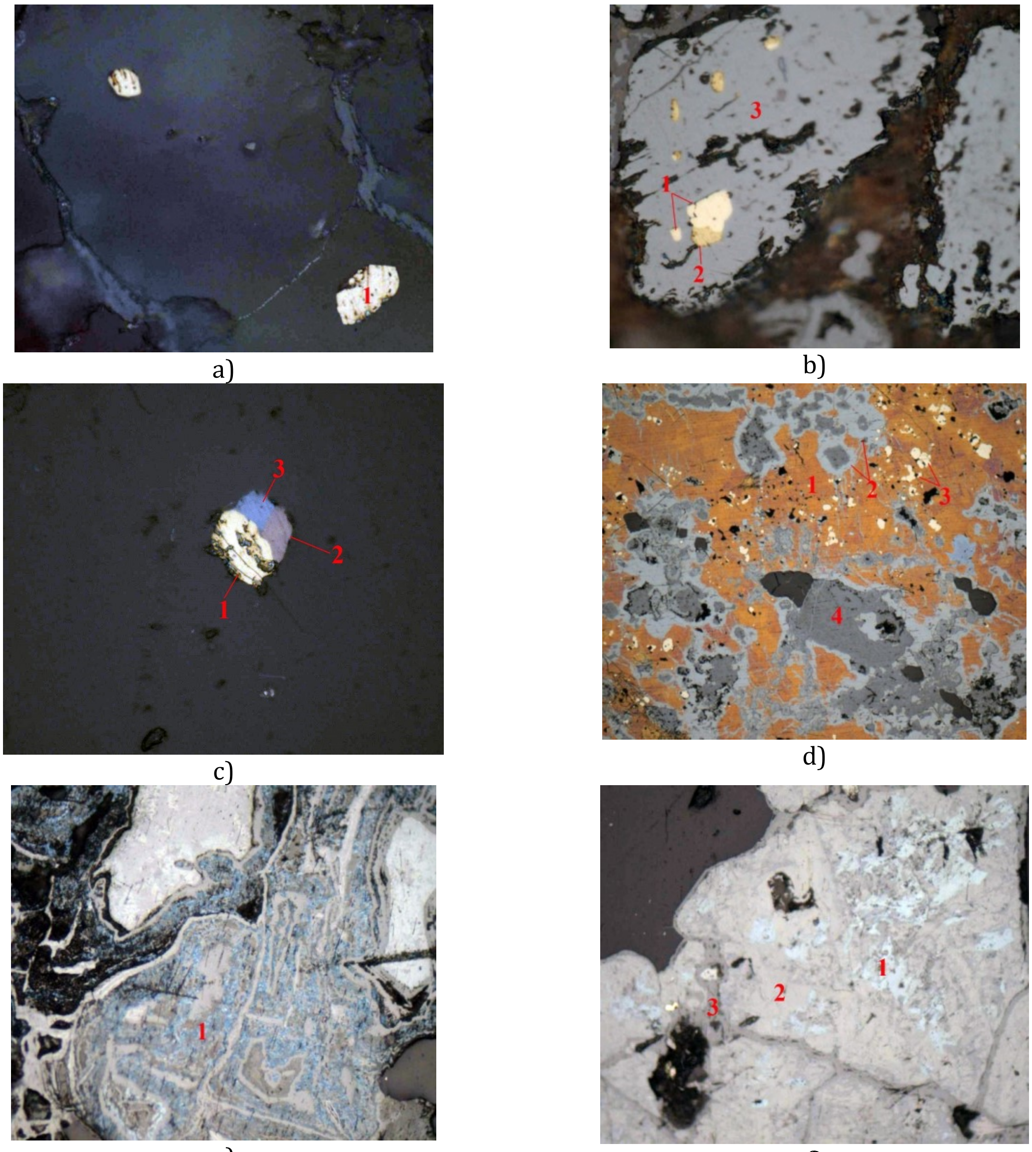
a) b)

c) d)

Figure 1: Malachite in association with iron hydroxides. a) 1 – malachite, 2 – quartz. Magnification 100×; with analyzer. Development of malachite along rock fractures; b) 1 – malachite, 2 – quartz. Magnification 100×; with analyzer. Malachite in association with iron hydroxides; c) 1 – malachite, 2 – iron hydroxides. Magnification 200×; with analyzer. Association of malachite with iron hydroxides; d) 1 – malachite, 2 – goethite. Magnification 200×; without analyzer

Bornite is usually found in association with chalcopyrite, chalcocite, and sphalerite. Its grains are mainly xenomorphic in shape, and it represents a secondary mineral typical of the sulfide mineralization zone. Covellite develops along the margins of chalcopyrite grains and, in some cases, forms complex structures with iron hydroxides (Figure 2).

This indicates that covellite forms during oxidation processes. Chalcocite commonly occurs as xenomorphic grains formed at the expense of chalcopyrite and cubanite. It is associated with bornite and chalcopyrite, suggesting that it is a product of secondary alteration. Cubanite is found only in weakly oxidized zones, occurring together with chalcocite and iron hydroxides.



a) b) c) d) e) f)

Figure 2: Form of occurrence of copper minerals and their replacement characteristics. a) Inclusions of chalcopyrite in non-ore minerals.
1 – chalcopyrite. Magnification: 1000×; without analyzer; b) Chalcocite intergrowth with chalcopyrite and bornite.
1 – chalcopyrite, 2 – bornite, 3 – chalcocite. Magnification: 1000×; without analyzer; c) Inclusions of chalcopyrite and pyrite in magnetite.
1 – pyrite, 2 – chalcopyrite, 3 – magnetite. Magnification: 1000×; without analyzer; d) Replacement of cubanite by chalcocite and goethite.
1 – cubanite; 2 – chalcocite; 3 – pyrite; 4 – goethite. Magnification: 100×; without analyzer; e) Complex mixture of covellite–chalcocite–goethite composition.
1 – covellite–chalcocite–goethite mixture. Magnification: 200×; without analyzer; f) Chalcocite among cuprite and goethite.
1 – chalcocite; 2 – cuprite; 3 – goethite. Magnification: 200×; without analyzer

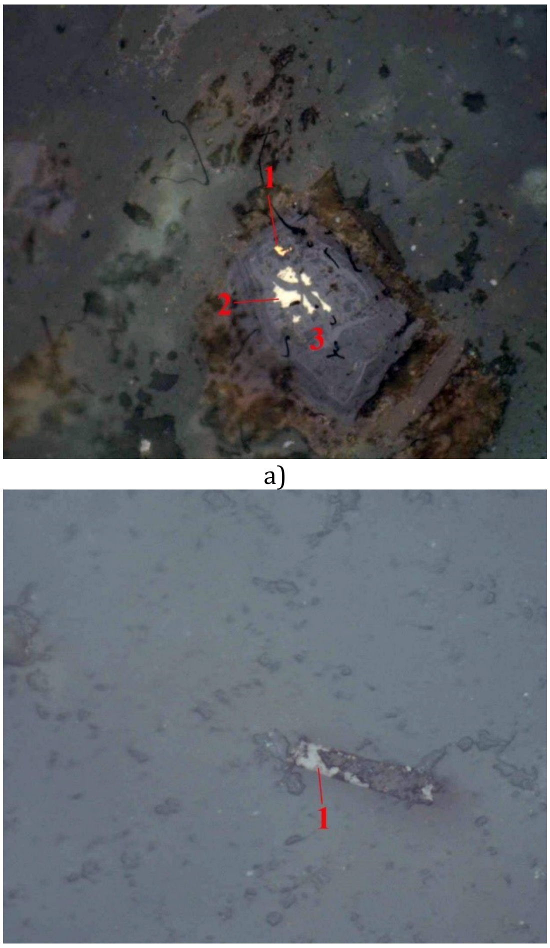
The presence of minor chalcopyrite and pyrite grains indicates its participation in complex paragenetic associations. Cuprite is often associated with chalcocite and iron hydroxides and is characterized as a copper oxide mineral formed in oxidation zones. Native copper occurs as isolated grains of isometric or droplet-like shape. Their size ranges from <0.01 to 0.02 mm, and they are usually detected under microscopic observation.

In the ore, chalcopyrite was observed to be distributed in the form of micron-sized inclusions within minerals and magnetite. The blocking of pyrite and chalcopyrite within magnetite indicates that these minerals participated together in the crystallization process. In addition, the co-occurrence of oxide (cuprite, goethite) and secondary sulfide (chalcocite) minerals confirms that the ore body belongs to a typical "mixed transition zone". The occurrence of chalcopyrite in the form of ultrafine inclusions within magnetite and rock-forming minerals indicates that the ore cannot be separated by crushing at standard sizes. As a result, the micro-level mixture of oxide and sulfide minerals (chalcocite-cuprite-goethite) limits the possibility of using a single universal flotation scheme.

Native gold occurs in the ore in a free state. It is mainly found as fine filaments within iron hydroxides and sometimes appears together with pyrite (Figure 3). This indicates that the gold was formed through a secondary separation process. Molybdenite is also identified in a dispersed form within the ore, occurring as prismatic grains (Figure 3). Although it is relatively rare, molybdenite is considered an economically important ore mineral.

In addition to copper minerals, microscopic studies revealed micron-sized phases of precious and rare metals in the ore: Native gold and pyrite residues are observed to be trapped in the form of micro-inclusions within the goethite massif. This structure indicates that the gold in the primary pyrite was separated from its sulfide matrix as the ore was oxidized, but was not fully released and remained physically encapsulated within the secondary iron hydroxides (goethite) that were formed. The prismatic grains of molybdenite are shown to crystallize as a separate phase within non-ore (gangue) minerals (most likely quartz or silicates). This condition at 1000× magnification confirms that molybdenite is distributed in a very fine-grained state.

Iron hydroxides occur along fractures as veins, aggregates, and isolated disseminated grains. Their content ranges from 2–4%, with grain shapes that are cubic, xenomorphic, and angular, and sizes varying from 0.02 to 0.5 mm. They often contain inclusions of pyrite and occasionally native gold. Iron hydroxides form complex mixtures with secondary copper minerals such as covellite, chalcocite, and cuprite. Under the microscope, their color varies depending on the degree of oxidation.



a)

b)

Figure 3: Form of occurrence of gold, molybdenum, bismuth, and tellurium minerals in the oxidized ores of the Kalmakyr deposit. a) Inclusions of native gold and pyrite relics in goethite. 1 – native gold; 2 – pyrite; 3 – goethite. Magnification: 1000×; without analyzer; b) Prismatic grain of molybdenite in a non-ore matrix.1 – molybdenite. Magnification: 1000×; without analyzer

Forms of Occurrence of Ore Minerals (Chalcopyrite and Molybdenite) in the Composite Sample of Oxidized Ore were studied at different grinding sizes: P80 200 µm, P80 100 µm, and P80 74 µm. The purpose of this study was to obtain comparative characteristics of the main ore minerals at various degrees of ore grinding.

The oxidized copper ore studied exhibits high "resilience" to conventional flotation processes due to the extremely fine aggregation of mineral phases and strong secondary transformations. The greatest metallurgical risk is the loss of gold in the flotation tailings due to micro-encapsulation with goethite.

Table 3 presents the granulometric characteristics of the composite sample at different grinding sizes, obtained from Qemscan mapping results.

Table 3. Granulometric Characteristics of the Composite Sample at Different Grinding Sizes

Particle size class, µm	**Sample fineness**					
	R80 200 µm		**R80 100 µm**		**R80 74 µm**	
	Class Yield, %	**Cumulative Yield, %**	**Class Yield, %**	**Cumulative Yield, %**	**Class Yield, %**	**Cumulative Yield, %**
250–500	7.03	100.00	0.52	100.00	–	–
150–250	15.61	92.97	6.23	99.48	2.46	100.00
100–150	13.27	77.36	14.18	93.25	8.07	97.54
71–100	8.64	64.09	11.40	89.47	9.71	89.47
45–71	10.90	55.45	14.68	67.68	17.63	79.75
38–45	3.62	44.55	4.49	53.00	5.57	62.12
20–38	9.98	40.93	11.42	48.51	14.74	56.56
10–20	14.91	30.95	17.58	37.08	21.57	41.82
5–10	11.03	16.04	13.36	19.50	14.29	20.25
0–5	5.01	5.01	6.14	6.14	5.96	5.96
Total	100.00	—	100.00	—	100.00	—

Figure 4 illustrates the average size of the main ore minerals at different grinding levels. From the figure, it can be seen that with increasing grinding fineness, the average grain size decreases most significantly for pyrite — from 26.38 to 19.18 µm. The average grain size of chalcopyrite changes from 10.95 to 9.87 µm, while molybdenite, regardless of ore size, maintains an average grain size in the range of 8.01–9.57 µm.

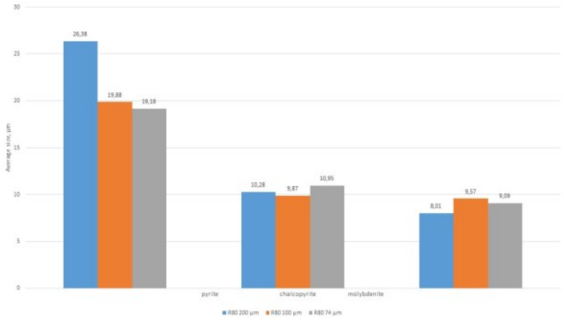


Figure 4: Average size of the main ore minerals at different grinding sizes of the composite oxidized ore sample

The extremely complex microstructure of oxidized copper ore, in particular, micro-associations of copper oxides (malachite, cuprite), secondary sulfides and goethite, limit the capabilities of the traditional direct flotation scheme. To overcome these problems and maximize the recovery of the Cu-Au-Mo complex, the results of the study suggest the use of an acidic selective dissolution and subsequent flotation scheme. During the initial stage of selective dissolution using dilute sulfuric acid (H_2SO_4), phases that are easily soluble in acid, such as malachite and cuprite, pass into the solution and are subsequently extracted using SX-EW technology. The advantage of this stage is that the acidic environment chemically removes the secondary sulfides (chalcosine, covellite) and the iron hydroxide (goethite/limonite) coating on the surface of primary chalcopyrite.

When the surface-cleaned and activated sulfide residue (cake) is directed to the next stage of flotation, the flotation kinetics of sulfide copper and molybdenite are dramatically improved. In addition, the partial erosion and porosity of the goethite matrix under the influence of sulfuric acid increases the mechanical release of native gold particles inside the metal particle. This reduces the risk of gold loss in the flotation residue.

4. Conclusions

Based on the results of high-resolution optical microscopy of oxidized copper ores, the causes of metallurgical losses were revealed and the following conclusions were drawn:

1. The oxidized copper ores of the Kalmakyr deposit are mainly represented by variously silicified, sericitized, and chloritized magmatic rocks, intersected by fine fractures, veinlets, and dispersed ore mineral spots. Rock-forming minerals constitute 92–95% of the ore composition. Among them, quartz and feldspars are predominant, while muscovite, chlorite, and biotite occur in smaller amounts.
2. X-ray diffraction analysis revealed that the main mineral components of the ores are quartz (40.0–46.7%), orthoclase (15.7–20.3%), and sericite (8.3–11.4%). The clay–mica mineral group (including kaolinite up to 7.8% and chlorite 13.1–14.8%) accounts for a total of 23.5–32.3%. The high proportion of minerals such as sericite and chlorite may cause technological difficulties during processing, as these minerals easily form slurries in water.

3. Among carbonate minerals, dolomite (2.6–3.1%) was identified. The ore minerals include pyrite (up to 1.9%), cubanite (up to 0.6%), turquoise (up to 0.7%), native copper (up to 0.4%), and other sulfide and oxide forms such as malachite, pseudomalachite, cuprite, covellite, chalcocite, and molybdenite. Ore minerals occur along fractures and sometimes in rock voids, binding the rock mass together.
4. Mineralogical and technological studies of oxidized ore samples from the "Almalyk MMC" JSC Kalmakyr deposit revealed the presence of valuable elements such as copper, molybdenum, gold, and silver. Gold occurs mainly in native form, but is also found as electrum, kustelite (silver compounds), and petzite (tellurium compounds). The average fineness of gold is 890, with particle sizes not exceeding 20 µm.
5. Although the mineral composition and distribution of ore phases may complicate the technological processing of oxidized ores, the presence of valuable components indicates that these ores are economically viable for processing.
6. The mixed composition of the oxidized copper ore from the Kalmakyr deposit limits the efficiency of using only hydrometallurgical methods. Therefore, to achieve complete extraction of valuable and rare metals, the application of combined methods—flotation beneficiation and hydrometallurgical processing—is the most appropriate and effective approach.
7. For the complex separation of metals according to the determined mineralogical composition, the most optimal technology is the scheme of acid selective dissolution and flotation. The initial acid treatment stage not only increases economic efficiency by transferring oxidized copper (malachite, cuprite) into solution, but also cleans the surface of sulfide minerals from iron coatings and partially dissolves goethite, improving the mechanical release of gold particles blocked in it.

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