

UDC 669.2.018.674

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OXIDATION STUDY OF MINERALS DURING STORAGE AND TRANSPORTATION OF COPPER CONCENTRATE

After a period of storage and transportation, the total weight of copper concentrate increases and its copper content decreases. For this reason, the chemical mechanism of oxidation was studied. The main components, such as copper, iron, and sulfur, were determined and the air T0, humidity, and pH of the sample were measured to determine the potential for oxidation. The experiments were carried out during the hottest from May to September months, and the intensity of the oxidation process and the mechanism of the reactions were determined by changes in the pH of the concentrate.

Key words: *copper, copper concentrate, oxidation, sulfide minerals, pH.*

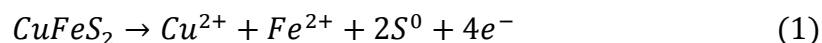
1. Introduction

Copper concentrate contains 20-32 % copper, 25-35 % iron, 30-43 % sulfur, 3-5 % silicon, 8-9 % moisture, including chalcopyrite, pyrite, chalcocite, covellite, arsenopyrite, sphalerite. form of sulfide minerals. In any open system, oxidation occurs under the influence of external factors such as air, moisture, temperature, bacteria, oxidizing agents, which leads to the formation of new products and a

change in mass. In other words, oxidation is the process of losing electrons, and the oxidation products resulting from the transfer of electrons of a certain mass can affect the change in mass [1,2]. Therefore, to study the change in the mass of copper concentrate, it is necessary to study the change in the content of the main components in the concentrate and the chemical mechanism and oxidation process. In nature, sulfide minerals can be oxidized in three ways: Galvanic oxidation, Bacterial oxidation, Chemical oxidation.

Galvanic oxidation: The minerals chalcopyrite and pyrite, which make up the bulk of copper concentrate, have similar surface properties and coexist in nature [1]. Therefore, minerals exhibit galvanic interactions in terms of their redox potential value when they are in place [3; 5]. In this case, pyrite with a high redox potential (0,63) acts as a cathode and is protected from oxidation, and chalcopyrite with a low redox potential (0,52) acts as a catalyst for intense oxidation (equation 1-3).

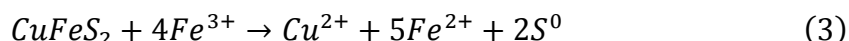
Chalcopyrite oxidation at the anode:



The reduction reaction of iron ions at the cathode:



Combining these reactions:



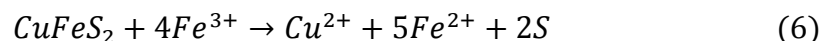
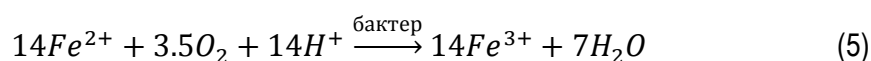
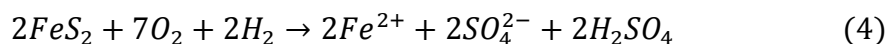
Bacterial oxidation: Bacteria interact with metal sulfide minerals according to the following three mechanisms [5; 6; 7].

A. Fe^{3+} ions are oxidized to Fe^{3+} ions, and the resulting Fe^{3+} ions are an indirect mechanism for the oxidation of minerals.

B. Bacteria adhering to the surface of the mineral oxidizes Fe^{2+} ions to Fe^{3+} ions inside the layer of bacteria and exopolymer materials, and Fe^{3+} ions in this layer are an indirect mechanism for the oxidation of minerals.

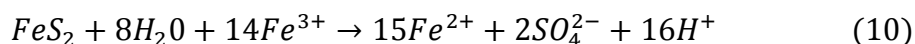
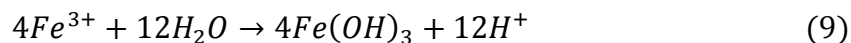
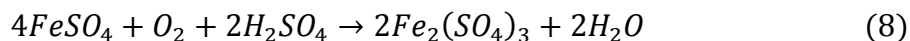
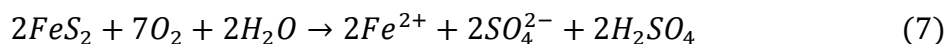
B. Bacteria are biologically oxidized or bind directly to minerals without the need for Fe^{2+} and Fe^{3+} ions.

The mechanism of bacterial oxidation of sulfide ore is expressed by the reaction equation 4-6:

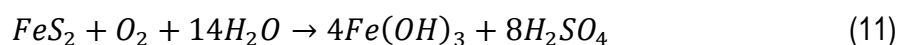


Chemical oxidation:

A. Oxidation of Pyrite: Oxidation of pyrite occurs naturally in four stages [8].

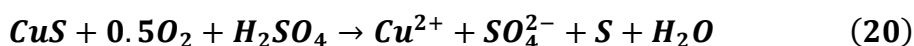
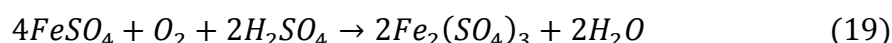
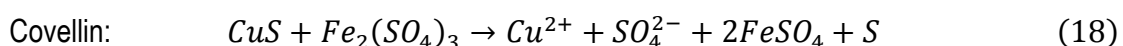
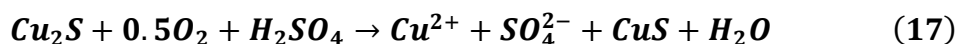
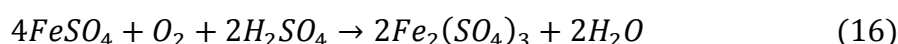
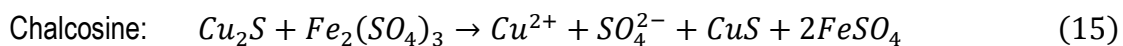
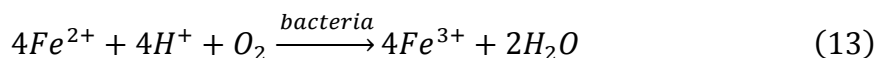
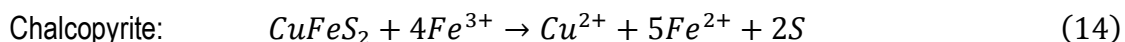


Combine these 4 reactions:



B. Oxidation of copper sulfide minerals: Fe^{3+} and O_2 are used as oxidizing agents to dissolve all copper sulfides. The oxidation of Fe^{2+} / Fe^{3+} acts as a catalyst for the oxidation of copper sulfide

minerals, since the Fe^{2+} ions formed during the oxidation of copper sulfide Fe^{3+} are again converted to Fe^{3+} by the action of O_2 [5; 9; 10; 11; 12; 13; 14].



There are many works on the oxidation of minerals in copper and ore concentrates at high temperatures, but rarely works on the oxidation of copper concentrates under normal atmospheric conditions. Therefore, we have studied the process of copper concentrate oxidation during storage and transportation under atmospheric conditions.

2. Materials and methods

2.1. Sampling

Samples of two different copper concentrate minerals were collected over 126 days from May 14 to September 18, 2021 in a three-day cycle.

The composition of the concentrate tested is shown in Table 1.

Table 1

The composition of the concentrate

Sample No	Cu, %	Fe, %	S, %	SiO ₂ , %	Zn, %	CaO, %	H ₂ O, %
1.	24.58	27.59	33.68	8.49	0.11	0.60	8.464
2.	21.09	29.68	36.58	7.85	0.22	0.43	8.295

2.2. Methods

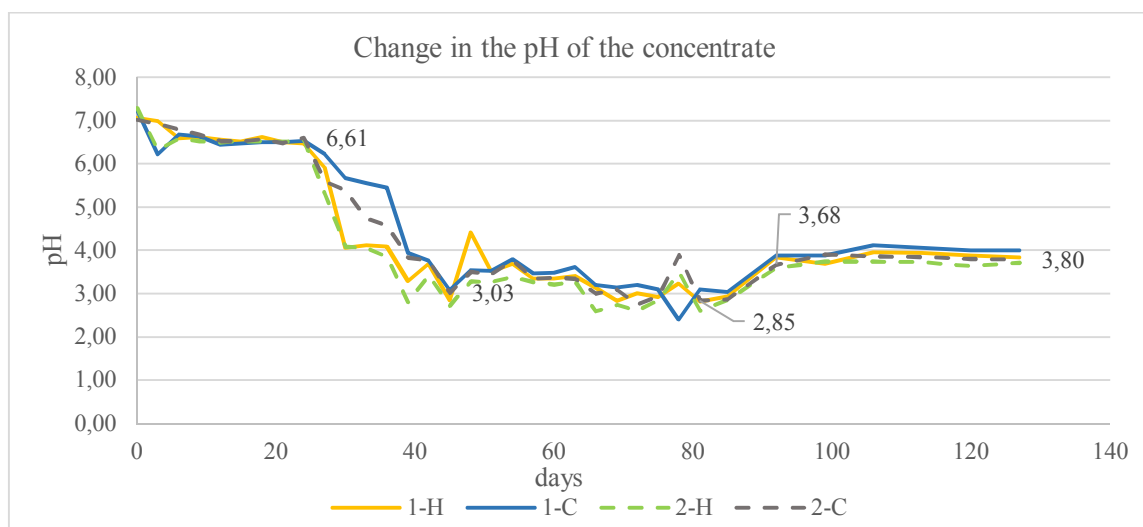
H₂O-, Cu, Fe, S, Zn, SiO₂, CaO were determined in the copper concentrate, the mineral and phase analysis of the concentrate was carried out, and the pH of each sample was measured. The studies were carried out by the following methods: Moisture content according to ISO 10251:2006, Copper content according to ISO 10258:2018, Iron content according to MNS 2078:1984, Sulfur content according to MNS ISO 351:2001, Copper phase analysis according to MNS4594:1998, SiO₂, Zn, CaO according to XRD. The sample was mixed with distilled water, shaken, and the pH of the homogeneous mixture was measured on a pH meter.

3. Result and Discussion

Environmental measurements: Temperature and humidity of the concentrate were measured in each samples during the study, the temperature was below 20°C, and then on July 19 the temperature warmed up to a maximum of 33°C. Since August 28, it has dropped below 17°C. In the same period (June 4-16), relative humidity gradually decreased from 50% to 22%, and increased from July 19 to 25, reaching a maximum of 90% on August 21. it rose again to about 60%.

pH medium concentrate: over time, the pH changes in the following way (Figure 3.1). These include:

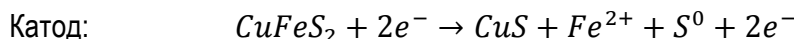
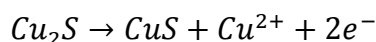
In the first 24 days with V / 14 in VI / 07, the pH value was neutral or slightly decreased. After 21 days at pH VI / 07-VI / 28, it dropped sharply from 6.61 to 3.03 (acidic environment). VI / 28-VIII / 03 Almost constant for 36 days or pH 3.03-2.8.



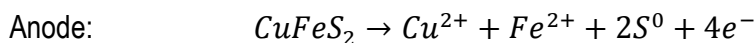
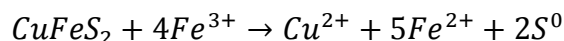
At the first stage, when the concentrate oxidation rate was low, the temperature was low, at this stage, the pyrite of which had a galvanic effect on the oxidation of chalcopyrite. From the second period from June 7, the increase in pH is that the resulting acid due to the interaction of bacteria and the formation of aggressive chemical reagents such as ferric iron increases the rate of oxidation, at the third stage the pH becomes stable with the formation of end products, sulfates and hydroxides. It is assumed that the oxidation reaction of the concentrate proceeds as follows:

1. The stage at which the reaction begins: At this stage, the process of galvanic oxidation takes place.

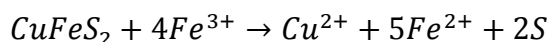
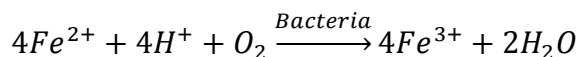
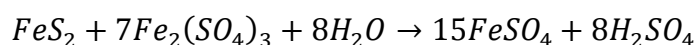
The low-potential covelline is oxidized first in accordance with its redox potential. Chalcopyrite is isolated as a cathode. Then the chalcopyrite will be oxidized and the pyrite will be the cathode in this case. Anode:

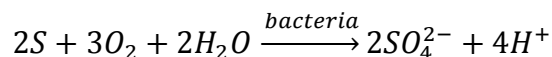
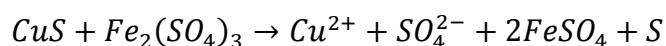
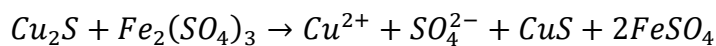


$\text{CuFeS}_2 - \text{FeS}_2$ galvanic interactions of minerals:

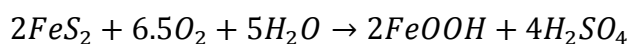
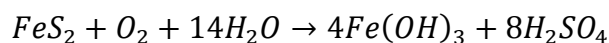
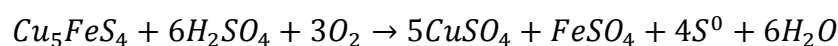
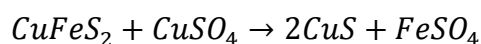
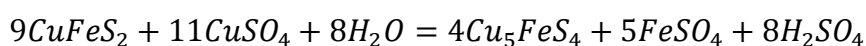
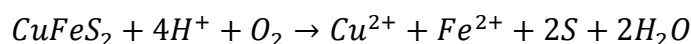
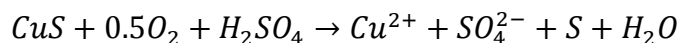
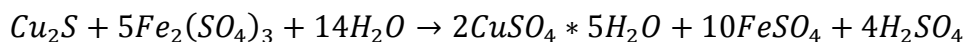
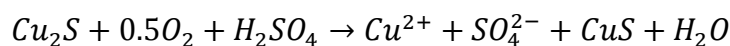


2. The stage of active reaction: In the presence of atmospheric oxygen and bacteria, Fe^{2+} ions are converted into Fe^{3+} , and the resulting Fe^{3+} ions oxidize sulfide minerals. Near pH = 5, the $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$ reaction proceeds intensively in the presence of bacteria, and an increase in temperature and a decrease in pH create a favorable environment for bacterial oxidation.



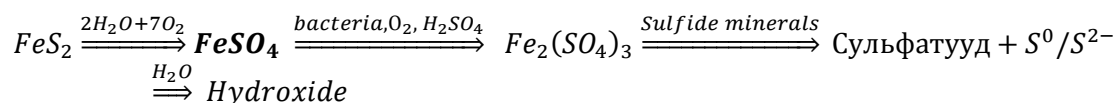


3. Stage of slow reaction:



4. Conclusions

The concentrate oxidation process is divided into three stages depending on the change in pH. The first process is characterized by a galvanic oxidation reaction. Since the temperature and moisture content are unstable at this stage, the content of elements and mineral phases fluctuates between increase and decrease. At the second stage, the outside air temperature rises above 20°C, and in the presence of air oxygen and bacteria, Fe²⁺ ions are converted into Fe³⁺, and the resulting Fe³⁺ ions oxidize sulfide minerals. In addition to the oxidation of sulfide minerals, Fe³⁺ ions are an important source of sulfuric acid. At the third stage, the air temperature and humidity were high, and pyrite, chalcopyrite and chalcocite are oxidized under the action of Fe³⁺ with the release of sulfuric acid, which continues to acidify the environment. Chemical oxidation predominates in this oxidation step. Schematic representation of the reactions that took place in these three stages:



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ИССЛЕДОВАНИЕ ОКИСЛЕНИЯ МИНЕРАЛОВ ПРИ ХРАНЕНИИ И ТРАНСПОРТИРОВКЕ МЕДНОГО КОНЦЕНТРАТА

После периода хранения и транспортировки общая масса медного концентрата увеличивается, а содержание меди в нем снижается. По этой причине был изучен химический механизм окисления. Были определены основные компоненты, такие как медь, железо и сера, и были измерены Т0 воздуха, влажность и рН образца для определения потенциала окисления. Опыты проводили в самые жаркие месяцы с мая по сентябрь, а интенсивность процесса окисления и механизм реакций определяли по изменению рН концентрата.

Ключевые слова: медь, медный концентрат, окисление, сульфидные минералы, рН.