STUDY OF THE EFFECT OF CHALCOPYRITE AND PYRITE MINERALS ON THE OXIDATION OF COPPER SULFIDE CONCENTRATE

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Abstract

Changes in the weight of copper concentrate from oxidation and a decrease in copper content create economic losses. Mining plants having problems with increasing overall weight of the copper concentrate and reduction of the copper composition after a certain period of transport and handling. Trivalent iron, one of the main oxidizing factors of the copper concentrate, is a strong oxidizer that oxidized copper sulfide minerals as well as other minerals in the concentrate, which is formed by the oxidation of pyrite. Generally, mass change can occur during electron transition and phase transfer. Therefore, the chemical mechanism, oxidation process, and content alteration of the main components in copper concentrate were studied in this study in order to solve and define those problems. To study the real condition of the copper concentrate oxidation, the oxidation process of the copper concentrate was studied under 3 conditions such as in the shadow, in the sun, and the storage. Mongolian National Standard and International standards (MNS2078:1984, ISO 10258:2018) and XRD, AAS, ICP analysis were used to study the main components of the copper concentrate. By the study on the oxidation of copper concentrate at the mine site, copper was decreased by 0.77-0.85%, and iron was reduced by 0.30-0.64%. As a result of the oxidation study of concentrate that is kept in the mining site, temperature, relative humidity, and pH were highly correlated with concentrate oxidation.

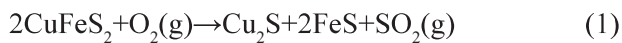**Key words:** copper concentrate, chalcopyrite, pyrite, oxidation

1. Introduction

Copper, iron, and sulfur that are the main components of the copper concentrate mostly exist as sulfide minerals such as chalcopyrite ($CuFeS_2$), chalcocite (Cu_2S), covellite (CuS), pyrite (FeS_2), enargite (Cu_3AsS_4) in the copper concentrate. Also, quartz usually exists as accompanied minerals in the copper concentrate. Copper mineralization can be occurred in 3 regions. Primary sulfide ore region: In a depth of 1-5 km from ground, pressure of 2000-3000 bar, temperature of 200-300°C, the primary sulfide ore forms. Main ore minerals include: chalcopyrite ($CuFeS_2$), bornite (Cu_5FeS_4), tennantite ($Cu_{12}As_4S_{13}$), pyrite (FeS_2), enargite (Cu_3AsS_4), galena (PbS), tetrahedrite ($Cu_{12}Sb_4S_{13}$) and sphalerite (ZnS). Oxidized ore: By a react of atmosphere precipitation's oxygen and carbon dioxide, in a normal pressure and temperature, primary sulfide dissolve to a liquid form by a oxidation. Secondary sulfide ore region: Ore minerals will be oxidized by oxygen enriched atmosphere precipitation while its seeping through ore's body and will be utilized all its oxygen consumption when it connects to ground water. Copper sulfate which has converted into liquid form will transmit to ground water and in this region copper sulfate will interact with primary sulfide ores to form secondary sulfide ores such as covellite (CuS), bornite (Cu_5FeS_4), chalcocite (Cu_2S) (Erdenechimeg, 2019). Oxidation process of enargite in air is slow. Even though oxidation process of enargite is slow in acidic and neutral condition, it can be fastened in the presence of iron ion and bacteria (Chandra and Gerson, 2010). From table we can clearly see secondary ore has greater copper value than primary sulfide copper ore holds mainly chalcopyrite, pyrite, arsenopyrite and enargite. Chemical features of this minerals are directly referred to mass alteration Generally, mass change can be observed in the open system due to the following cases: breaking of bonds which always absorbs energy and increases mass, the formation of bonds which always releases energy and decreases mass, and the transformation of existing bonds which is really the excitation and de-excitation of the system to different states (Luo; Fernflores, 2017; Oku, 2009; Winterberg, 2015). Thus, open system mass
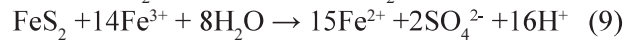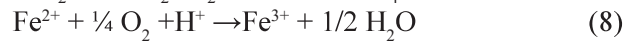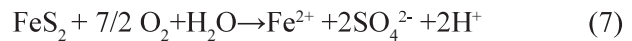
change can be observed from oxidation products of irreversible oxidation with atmosphere air taking part in it. Oxidation research of main components of copper concentrates has much carried. Under normal conditions, oxidation studies of the main components of copper concentrate are rare. According to a study copper sulfide, ferric oxide and ferric sulfate have made from chalcopyrite which oxidized by oxygen. In addition, it is possible to extract geotite accompany by water and oxygen (Xiong, 2018).

From the Belgrade University's research of chalcopyrite and pyrite oxidization, it was noted in the temperature of 100-260°C chalcopyrite oxidized and converted into secondary sulfide minerals including covellite, chalcocite, also, pyrite has transferred to ferric sulfate form. In the following condition concentrate mass loss and SO_2 gas releasing was observed (Reaction 1,2). Furthermore, concentrate mass change registered at the increased temperature of 275-393°C due to forming ferric sulfate, copper sulfate and copper oxysulfates. Stable sulfates have formed until 620°C then sudden mass loss occurred from the formation of CuO at 714-847°C (Mitovski, 2015; Mitovski, Strbac, Sokic, Kragovic, Grekulovic, 2017),

$$2CuFeS_2+O_2(g)\rightarrow Cu_2S+2FeS+SO_2(g) \qquad (1)$$
$$2FeS_2+2O_2(g)\rightarrow 2FeS+2SO_2(g) \qquad (2)$$
$$FeS+2O_2(g)\rightarrow FeSO_4 \qquad (3)$$
$$Cu_2S+SO_2(g)+3O_2(g)\rightarrow 2CuSO_4 \qquad (4)$$
$$2Cu_2S+2.5O_2(g)\rightarrow 2CuO\cdot CuSO_4 \qquad (5)$$
$$CuSO_4\rightarrow CuO+SO_3(g) \qquad (6)$$

Pyrite always coexists with nonferrous metals sulfides including chalcopyrite, sphalerite and galenite. Pyrite can be oxidized by chemical, bacterial and electrochemical mechanisms (Chiriţă and Schlegel, 2017; Zivkovic, Mitevska, and Savovicc, 1996). Pyrite oxidation velocity apparently depends on oxidizing reagent feature and bacterial activity. Bacterial oxidation occurs in pH lower than 4.5 (Perkins.E.H, Gunter.W.D, Nesbtt.H.W 1997, Chandra.A.P and Gerson.A.R, 2010). Iron(II), iron(III) components, thiosulfate and sulfate compose from pyrite oxidation also, solid compositions are possible to give sulphur, iron(II) hydroxide, iron(III) hydroxide, geotite and magnetite (Perkins, Gunter, Nesbtt, and St-Arnaud, 1997; Goh, Buckley, Lamb, Rosenberg, and Moran, 2006). Oxygen and iron(III) are the most essential factor for pyrite oxidization. Mainly iron carries sulfide oxidization. Pyrite oxidizes from iron(III) and this process originates from either pyrite transference into iron(II), sulfate forms and the

further oxidization of iron(II) to iron(III) by oxygen influence. Reaction 7-9 (Goh, Buckley, Lamb, Rosenberg, and Moran, 2006).

$$FeS_2 + 7/2\ O_2+H_2O\rightarrow Fe^{2+} +2SO_4^{2-} +2H^+ \qquad (7)$$
$$Fe^{2+} + ¼\ O_2 +H^+ \rightarrow Fe^{3+} + 1/2\ H_2O \qquad (8)$$
$$FeS_2 +14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} +2SO_4^{2-} +16H^+ \qquad (9)$$

In the neutral (pH=6-7) condition Fe(II) rapidly oxidizes to Fe(III) and in acidic condition (pH<4) Fe(II) is relatively slow to transfer but Thiobacillus ferrooxidans bacteria increases following reaction rate (Chandra, and Gerson, 2010; Perkins, Gunter, Nesbtt, and St-Arnaud, 1997).

Melanterite forms due to the oxidation of pyrite. As the oxidation of pyrite with the melanterite which is the iron hydroxide has occurred in the presence of oxygen, the content of the melanterite was decreased and iron hydroxide which is the ferrihydrite was created and precipitated. But, 1.6 mg of pyrite was oxidized, the amount of iron hydroxide was reached the saturated value and oxygen was used sufficiently and decreased. On the other hand, the oxidation process can be occurred until a certain period (Goh, Buckley, Lamb, Rosenberg, and Moran, 2006).

Besides pyrite oxidation, sulphur will be oxidized into intermediate components then to sulfate and polysulfate. Thiosulfate and sulfide from sulfate oxidation are easily form sulfates to help the reaction of final product formation (Perkins, Gunter, Nesbtt, and St-Arnaud, 1997; Steger, and Desjardins, 1978).

2. Materials - Methods

2.1 Sampling and preparation of copper concentrate:

To study the oxidation mechanism of copper concentrate under external conditions and environmental impact, one type of copper concentrate sample from the mining site was located under three different conditions (in the shadow, in the sun, in the storage) and each was sampled after various pre-selected time intervals, such as 0, 13, 27, 41, 62, 77, 91 and 104 days. On 2018.05.15, 2t samples were produced and preserved as in the shadow (Sample 1), under the direct sunlight (Sample 2) and in the storage (Sample 3).

We used samples of fresh concentrate from the factory. Prior to each analysis, chemical analyzes were performed after the concentrate samples were dried at 105 ° C for two hours.

2.2 Chemical analysis methods of concentrate samples

The pH, total iron, total copper, sulfur, arsenic contents were determined for the copper concentrate samples. Humidity composition was measured from standard methodology of ISO 10251:2006, MNS 2078:1984 and ISO 10258:2018 are standard methods used to measure the overall amount of iron and copper. Total copper and iron were determined by the titrimetric method. Overall Sulphur studied by mass difference method with a standard methodology of ISO 334:2013, burning copper concentrate for 2 hours at 800°C, then leached in hydrochloric acid, next added barium chloride to precipitate and filtered it. Arsenic contents were controlled using standardized instruction methods BSZ-2017/01. After leaching the arsenic contents with the aqua regain warm water bath approximately for 90 minutes, the arsenic contents were determined by AAS measurement.

3. Results and discussion

3.1 Main content of copper concentrate components

On 2018.05.15 the first sampling was brought from the mining site and was dried at 105^{0}C for almost 2 hours. The humidity and main components of samples, that are copper, iron, sulfur also pH, arsenic contents were determined on various pre-selected time intervals, such as 0, 13, 27, 41, 62, 77, 91 and 104 days by following the standardized methods. Total copper, iron contents of concentrate samples are shown in Figure 1 and Figure 2.
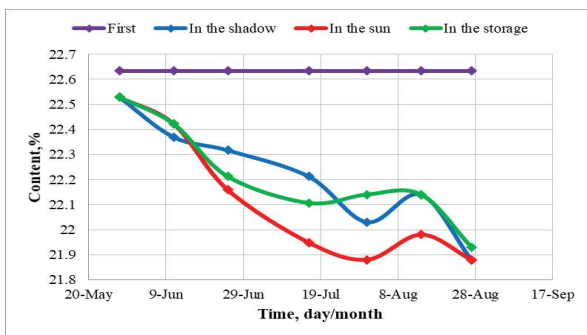

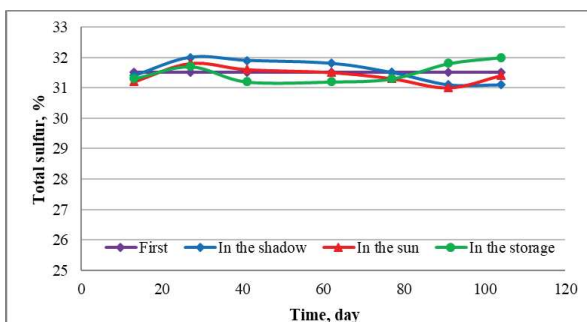**Fig 1.** Total copper contents of concentrate samples

Fig 2. Total iron contents of concentrate samples

As shown in the Figures the copper content of the primary concentrate sample reached 22.54%. In summer weather after 104 days of oxidation, the copper content of the concentrate samples has decreased by 0.83% in the shadow, 0.85% in the sun, 0.77% in the storage respectively. The iron content after 104 days of oxidation has decreased by 0.30% in the shadow, 0.64% in the sun, 0.47% in the storage. In other words, the total copper content has by approximately 0.77-0.85% and the total iron content by approximately 0.30-0.64% decreased after the copper concentrate oxidation. Arsenic and sulfuric contents in the copper concentrate under the three conditions have not shown much variable difference by each measuring days Figure 3.
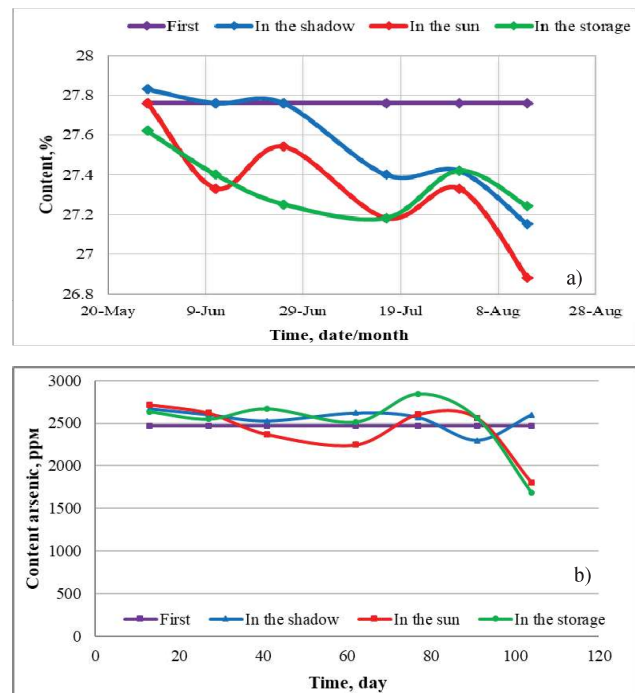

Fig 3. a) Arsenic contents of copper concentrates b) Sulfuric contents of copper concentrates under the three conditions

In Figure 4, it can be seen the relativity of weather and the relative humidity. During the temperature of 20^{0}C-26^{0}C, there is no significant increase in the graph. On the other hand, as time passes the relative humidity increases by 14-60%, due to the fact that copper contents are negatively correlated to the iron contents. In other words, by increasing humidity the amount of contents decreases. As shown in Figure 4 the increase of relative humidity turns pH into acidity. Sulfuric acid is created as a result of oxidation of copper concentrate, the more it oxidizes the more it becomes acidic. In other words, relative humidity and average atmospheric temperature seem to be negatively related to changes in the total iron and
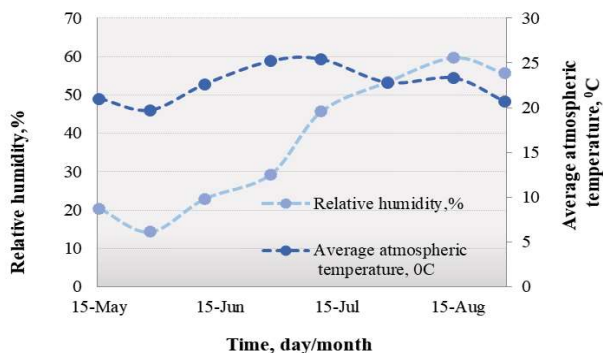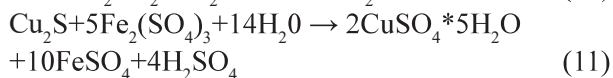
copper content over time.

Fig 4. The correlation between temperature and relative humidity

Fig 5. pH of copper concentrate samples

In determining the pH of these samples, as shown in Figure 5, the initial pH was 4.42, but became more acidic over time, reaching pH = 3.13 by day 104, which became more acidic over time under the influence of sulfuric acid, a by-product of oxidation. This is done according to the following reactions (Perkins, Gunter, Nesbtt, and St-Arnaud, 1997; Goh, Buckley, Lamb, Rosenberg, and Moran, 2006; Steger, and Desjardins, 1978; Kaur and Schoonen, 2017).

$$2CuFeS_2+O_2=Cu_2S+2FeS+SO_2 \qquad (10)$$
$$Cu_2S+5Fe_2(SO_4)_3+14H_2O \rightarrow 2CuSO_4*5H_2O +10FeSO_4+4H_2SO_4 \qquad (11)$$
$$2FeS_2 + 7O_2 + 2H_2O \rightarrow 2FeSO_4 + 2H_2SO_4 \qquad (12)$$

3.2 Results of x-ray diffraction analysis (XRD)

The chemical analysis was confirmed by X-ray diffraction and the results are shown in Figure 6 and Figure 7 for oxidized and non-oxidized samples.
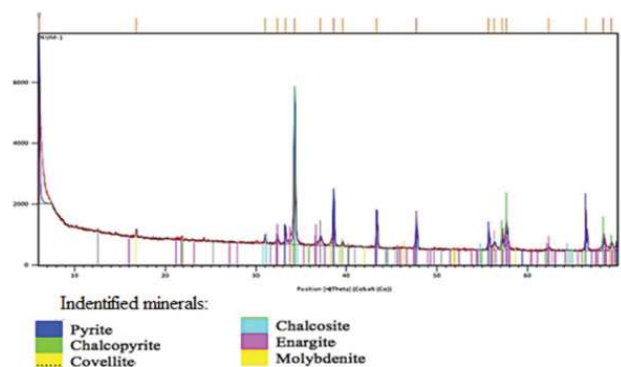

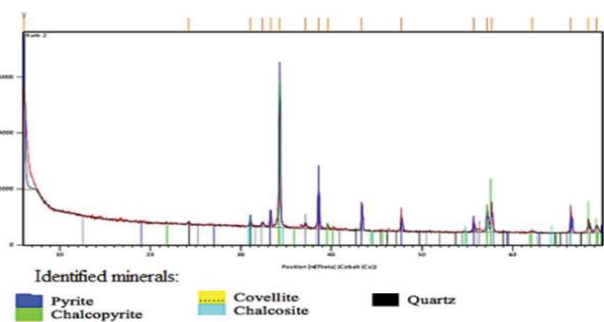Fig 6. X-ray diffraction pattern of the oxidized sample

Fig 7. X-ray diffraction pattern of the non-oxidized sample

According to the results of X-ray structural analysis, the concentrate mainly contains pyrite, chalcopyrite, covellite, chalcocite, and molybdenite. Mineral analysis of oxidized and non-oxidized copper concentrate, transformation, and comparison of X-ray diffraction is shown in Figure 8. Oxidized and non-oxidized copper concentrate's mineral analysis, transformation, transfer x-ray diffraction comparison was shown in Figure 8. Therefore, oxidized and non-oxidized copper concentrate's mineral composition differential XRD x-ray diffraction was sketched from America, Canada mineralogy administration's official "RRUFF INFO" database which includes more than 2000 mineral samples. Otherwise, after identifying minerals by θ degree, 13 types of minerals that can define oxidation process possibility x-ray diffraction has piled up on Figure 3.8 one by one. As shown in the figure, in the oxidized sample (sample 2), intensities of secondary sulfides such as chalcocite (Cu_2S), pyrrhotite ($Fe_{1-x}S_2$), chalcanthite ($CuSO_4*5H_2O$), paraquimbite ($Fe_2(SO_4)_2*9H_2O$), covellite (CuS) and szomolnokite ($FeSO_4*H_2O$) were increased.
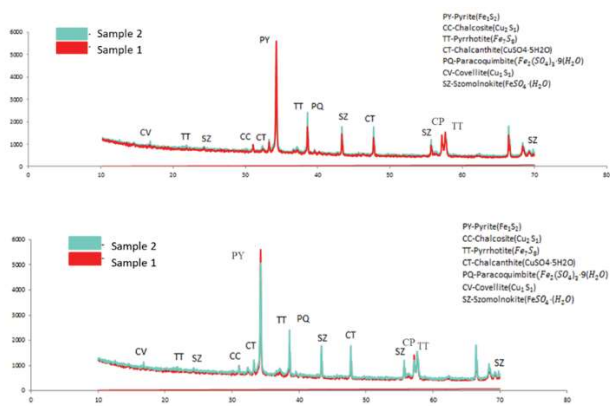
Fig 8. X-ray diffraction of the minerals phase transition in the oxidized (Sample 2) and non-oxidized samples (Sample 1)

4. Conclusions

As a result of the study of the oxidation of concentrate stored at a mining site, temperature, relative humidity and pH are highly dependent on the oxidation of the concentrate. In all three conditions, the total copper content decreased by 0.77-0.85% and the total iron content decreased by 0.3-0.64%, and the concentrate stored in the sun was more oxidized than the concentrate stored in other conditions.

The results of X-ray diffraction analysis showed that the primary sulfide minerals were reduced in the oxidized concentrate. However, the increased content of secondary sulfide minerals, iron, and copper sulfate minerals in the oxidized concentrate indicates that there is a phase transition between sulfide minerals in the concentrate due to oxidation.

Funding

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