Physicochem. Probl. Miner. Process. 46(2011) 263-277

journal homepage
www.minproc.pwr.wroc.pl/journal/

Physicochemical Problems
of Mineral Processing

Index No. 32213X ISSN 1643-1049

Mari LUNDSTRÖM*, Jari AROMAA**, Olof FORSÉN**

MICROSCOPY AND XRD INVESTIGATIONS OF THE PRODUCT LAYER FORMED DURING CHALCOPYRITE LEACHING IN COPPER(II) CHLORIDE SOLUTIONS

Received May 15, 2010; reviewed; accepted August 21, 2010

This study presents a microscopy investigation of chalcopyrite surface product layers formed in concentrated cupric chloride solutions, similar to those used in the HydroCopper® process. The physical appearance as well as chemical composition of chalcopyrite reaction product layer was studied as a function of pH (from 1 to 3) and leaching time. Microscopic methods, such as stereo-optical microscopy, scanning electron microscopy (SEM) analyses and X-ray diffraction analyses were applied. To study the chalcopyrite reaction product layers, mineral surface was leached either at open circuit potential (OCP) or treated by anodic polarization. It was shown that at lower pH values a gray elemental sulfur layer was the prevailing phase in the reaction product layer even with longer (22 h) leaching times. With increasing pH (up to from 2 to 3) the reaction product layer became more yellow-brown, and consisted mainly of FeOOH. However, also elemental sulfur was observed at higher pH. At pH 1 the thickness of the reaction product layer increased from ca. 1 to 9 µm with increasing leaching time up to 22 hours. At pH 2 the layer grew up to ca. 10 µm and at pH 3, up to ca. 14 µm.

keywords: chalcopyrite, chloride leaching, reaction product layer, sulphur, iron compounds

1. INTRODUCTION

Chalcopyrite, $CuFeS_2$, is the most common mineral in copper production. It is available in large quantities and with widespread distribution across the globe. There

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* Outotec Oyj, Base Metals P.O. Box 86, 02201 Espoo, Finland, mari.lundstrom@iki.fi

** Aalto University, Department of Materials Science and Engineering, P.O. Box 16200, 00076 Aalto, Finland

is a great environmental incentive to develop alternative, economically beneficial processes to produce copper from sulfide minerals. Hydrometallurgical process routes may also offer the possibility to economically utilise small ore bodies and concentrates with low metal contents. HydroCopper® (Hyvärinen et al., 2005) is a chloride based process, which operates at ambient pressure and at temperatures near to the boiling point of the solution at pH between 1.5 and 2.5. The copper (II) ion (Cu^{2+}), used as the oxidant in the process, converts the sulfur content of sulfide minerals into elemental sulfur instead of the usual sulfur dioxide. Although in a commercial process with particle collisions or a high degree mixing, chalcopyrite reaction product layer can be removed, a basic knowledge about the reaction product layer formation and composition is of a great importance.

In chalcopyrite leaching, a solid reaction product layer forms on the mineral surface. The reaction product layer on chalcopyrite has conventionally been suggested to be elemental sulfur, a polysulfide (e.g. CuS_2) or an iron precipitate (e.g. ferric oxyhydroxide or jarosite) (Hiroyoshi et al., 2004; Kinnunen et al., 2006). On a solid chalcopyrite electrode or in heap leaching, the forming layer can hinder the transfer of the metal ions into the solution. The passivation of chalcopyrite has caused problems, specifically in sulfate leaching and bioleaching. The slow dissolution kinetics of chalcopyrite has also limited the number of commercial applications of the mineral. In sulfate media, at temperatures below 110 ºC, chalcopyrite is mentioned to leach slowly, having a tendency to accumulate elemental sulfur and iron precipitate product layers, which can hinder the diffusion (Dreisinger, 2003). It has been shown, however (Lu et al., 2000), that the addition of sodium chloride to a sulfate solution (0.5 M NaCl, 0.8 M H_2SO_4, T = 95 ºC) changed the amorphous or cryptocrystalline sulfur film into a crystalline and porous sulfur layer that increased remarkably the dissolution rate of chalcopyrite.

The reaction product layer forming in ferric and copper(II) chloride solutions has generally been suggested to be a more porous sulfur layer, which does not act as a diffusion barrier, but is a less protective and easily removable layer (Table 1). Formation of interference films such as iron oxides has also been observed (Parker et al., 2003). In ferric chloride media, iron precipitates as hematite at higher temperatures (>100°C) and as akaganeite (ß-FeOOH) at lower temperatures (Riveros et al., 1997; Dutrizac et al., 1999). In the presence of hematite seed however, hematite can already form at lower temperatures.

This article presents microscopy and XRD investigations of the chalcopyrite reaction product layer, formed in concentrated cupric chloride solution, [NaCl] = 250 - 280 g/dm^3, [Cu^{2+}] = 17.9 - 30 g/dm^3 and T = 85 - 90°C. The topic has been studied earlier (Lundström et al., 2005; 2008; 2009), but this article aims to give a deeper microscopic view on the composition of the reaction product layer formed on stationary chalcopyrite in copper(II) chloride solution.

Table 1. Reaction product layers forming on chalcopyrite in ferric and cupric chloride solutions

LAYER	SOLUTION	T, ºC	SOURCE
Elemental sulfur	0.5 – 1.0 M $FeCl_3$, 1 M HCl	40 – 80	(Havlík et al., 1995)
Intermediate sulfides	1.0 M $FeCl_3$, 0.2 M HCl	3.5 – 45	(Havlík et al., 1995)
Amorphous non-stoichiometric, S_4 predominating	0.4 M $FeCl_3$, 1.0 M HCl		(Mikhlin et al. 2004)
Fine grained sulfur mat with globules and sulfur crystals (8h), sulfur globules with small porosity (24h), partly protective	0.1 M $FeCl_3$, 0.3 M HCl	95	(Dutrizac, 1990)
Sulfur formation at crystal boundary sites and fractures. Interference films (iron oxides, sulfates) removing sulfur.	0.03 M $FeCl_3$, 0.1 M HCl		(Parker, 2005)
Porous non-protective sulfur	0.02 - 0.50 M $FeCl_3$, 1 M HCl, 3 M NaCl	96	(Palmer et al., 1981)
Porous elemental sulfur	1.0 M $CuCl_2$, 0.2 M HCl	90	(Hirato et al., 1987)
Elemental sulfur	0.1– 0.5 M $CuCl_2$, 0.1 M HCl, 4 M NaCl	65– 104	(Bonan et al., 1981)

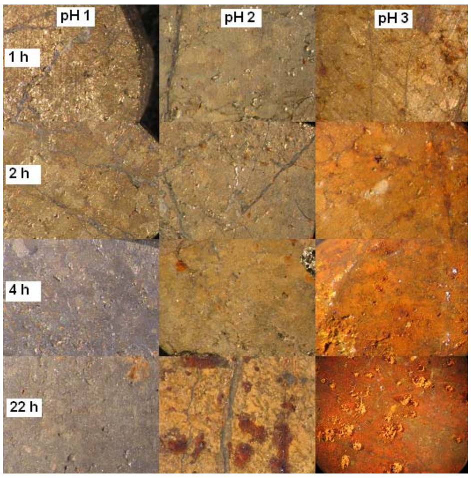


Fig. 1. Reaction product layer with respect to pH from 1 to 3 and leaching time from 1 to 22 h [NaCl] = 280 g/dm^3, [Cu^{2+}] = 30 g/l, T = 90°C

2. MATERIALS AND METHODS

2.1. CHALCOPYRITE MINERAL

The chalcopyrite used was from two sources: (i) chalcopyrite mineral used to make cubic chalcopyrite samples was from North America, samples obtained from a local Finnish gemstone shop, (ii) chalcopyrite mineral used to make electrodes originated from Pyhäsalmi mine, Finland. The average composition of the chalcopyrite in Pyhäsalmi concentrate is Cu 34.3%, Fe 30.4%, S 34.9%, Zn 0.04% and Ag 0.02%. However, no concentrate was used, but the chalcopyrite samples were chosen carefully from the liberated grains. The chosen chalcopyrite samples, examined both using microscope and visually, did not contain other phases on the polished electrode surface. The average elemental composition of samples used was analyzed with SEM/EDS from eight North American samples (in wt. %: Cu 34.5 ± 0.8, Fe 30.2±0.5 and S 35.9±1.0) and six Finnish samples (in wt. %: Cu 33.4 ± 0.2, Fe 30.5±0.8 and S 36.0±0.7). The analyzed compositions were near to the theoretical composition of chalcopyrite (i.e., Cu 34.6t, Fe 30.4 and S 34.9).

2.2. ELECTROCHEMICAL SETUP

In anodic polarization experiments of chalcopyrite electrodes a standard three-electrode electrochemical cell with a thermostated water jacket was used. Chalcopyrite electrodes were polarized from OCP to 1.2 V vs. SHE at pH 1.5 and pH 3. The solution contained [NaCl] = 250 g/dm^3, [Cu^{2+}] = 17.9 g/ dm^3 and T = 85°C. The electrolyte solution was stirred with a magnetic stirrer at 500 rpm. No purging of gases was done. The counter electrode was a platinum sheet, the reference electrode was saturated Ag/AgCl (REF201, Radiometer Analytical, France) placed in a sintered glass tube containing a gel of agar powder, potassium chloride and distilled water. The reference electrode junction was positioned in an external beaker and connected to the cell via a liquid bridge and a Luggin capillary.

2.3. STEREO-OPTICAL MICROSCOPY

For the Stereo-optical microscopy analysis, twelve cubic chalcopyrite samples (1 cm^3) were leached at OCP for 1, 2, 4 and 22 hours at pHs 1, 2 and 3 ([NaCl] = 280 g/ dm^3, [Cu^{2+}] = 30 g/dm^3 and T = 90°C). pH was varied by addition of HCl and NaOH. The solution was stirred at 500 rpm and the samples were placed into a mesh basket to be able to avoid collisions. After determined leaching time, each sample was rinsed with deionised water, then ethanol and then dried. The sample surfaces were photographed with a Leica MZ6 stereomicroscope and were later cast in epoxy resin for cross-sectional analysis using the SEM line scan analysis.

2.4. SEM ANALYSIS

For the SEM analysis, two type of samples were used (i) cubic samples leached at OCP and (ii) anodically polarized chalcopyrite electrodes. The cubic samples (i) were rinsed, dried and cast in epoxy resin and polished to give a cross-section of the leached surface. To enhance conductivity, the samples were coated with carbon by vapour deposition. A LEO 1450 SEM/Oxford Instruments® INCA EDS was used to analyze the structure and composition of the reaction product layer. The anodically polarized electrodes (ii) were coated by carbon as such and analyzed. Additionally one cross-sectional analysis was carried out from a polarized chalcopyrite electrode. These were analyzed at Outotec Research Centre with a Cambridge S360 scanning electron microscope equipped with and Oxford INCA EDS analyzer.

2.5. X-RAY DIFFRACTION ANALYSES

Samples for X-ray diffraction analyses were treated similar to those used in the Stereo-optical microscopy analysis. Three cubic chalcopyrite samples (1 cm^3) were leached at OCP for 22 hours at pH 1, 2 and 3 ([NaCl] = 280 g/dm^3, [Cu^{2+}] = 30 g/dm^3 and T = 90°C). After leaching, the samples were washed and dried and forwarded to Outotec Research in Pori, Finland, for analysis. There the reaction product layer formed was separated from the mineral sample by careful scraping with a scapel blade and the sample was analyzed by XRD.

3. RESULT AND DISCUSSION

3.1. STEREO-OTICAL MICROSKOPY

Twelve cubic chalcopyrite samples (1 cm^3) were leached in a copper(II) chloride solution for 1, 2, 4 and 22 hours at pH 1, 2 and 3. The sample surfaces were photographed with a Leica MZ6 stereomicroscope. Figure 1 shows the photographs of the chalcopyrite surface after leaching for 1 to 22 hours at pH from 1 to 3. It can be seen that at pH 1 the chalcopyrite surface becomes grayer with increasing time, suggesting the presence of elemental sulfur on the mineral surface. At pH 2, the surface becomes more yellow, even brown, with increasing time. At pH 3, the chalcopyrite surface becomes more yellow-orange with increasing time. Goethite (α-FeOOH) has been shown to be a strong yellowish brown, akaganeite (β-FeOOH) a strong brown, lepidocrocite (γ-FeOOH) a moderate orange and hematite (α-Fe_2O_3) a moderate reddish brown (Scheinost et al., 1999). Thus, the presence of FeOOH with increasing pH can be suggested.

3.2. SCANNING ELECTRON MICROSCOPY ANALYSES

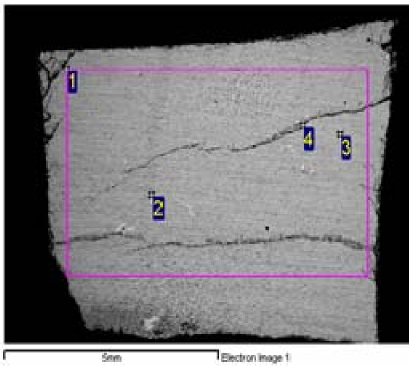
SEM analyses were firstly (area analyses, point analyses) carried out on chalcopyrite electrode surfaces, which had been anodically polarized from OCP to

1.2 V vs. SHE at pH 1.5 and at pH 3 (Figs. 2–4). Additionally, one cross-sectional analysis (Fig. 5) was carried out from a polarized chalcopyrite electrode. Furthermore, twelve cubic chalcopyrite samples were analysed using line scan analysis (Figure 6).

3.2. POINT ANALYSES FOR CHALCOPYRITE ELECTRODES

The SEM images for chalcopyrite electrodes can be seen in detail in Figs. 2 - 5. The average EDS analyses from the selected area and some point analyses are presented. The EDS data (weight percentages) were normalized in order to find an empirical formula for the surface composition. The normalized mass of each element was divided by the atomic weight, giving the number of moles in the empirical formula. It must be taken into account that SEM/EDS analyses have a drop shape volume and if the surface layer is thin, it also counts the elements under the reaction product layer. However, the analyzed values before and after the polarization can be compared. The changes in composition can be used to estimate the composition of the surface product layer.

Figures 2 to 4 show the surface before and after polarization at pH 1.5 and 3. It can be seen that before polarization, the mineral composition is near to the theoretical composition of chalcopyrite (Cu:Fe:S was 5:5:11). After polarization at pH = 1.5, a slight excess of sulfur was detected (Cu:Fe:S was 5:5:12). The analysis after polarization at pH = 3 showed a dramatic change in the surface composition, no copper was detected; instead the surface was mainly composed of iron, sulfur and oxygen and (Fe:S:O:Cl was 6:12:13:1). This layer was assumed to be a hematite, goethite, or iron hydroxide type layer.

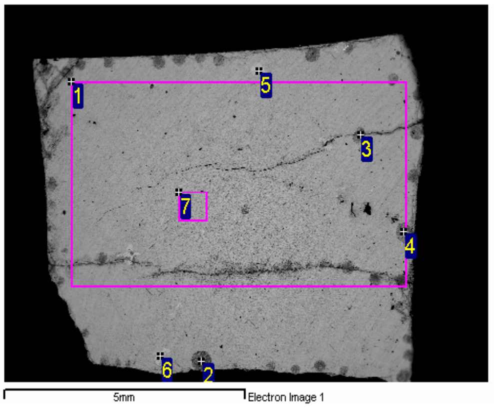


Processing option: all elements analyzed (normalized).

All results in wt. %

Spectrum	S	Mn	Fe	Cu	Zn	Total
1	36.1		30.00	33.21	0.69	100
2	34.64	0.43	8.11	1.16	55.68	100
3	34.41	0.51	12.31	7.21	45.56	100
4	34.52	0.34	7.48	0.68	56.97	100

Fig. 2. SEM images of the polished $CuFeS_2$ electrode. The area analysis of chalcopyrite sample Cu = 33.21, Fe = 30.00 and S = 36.10 (in wt. %), with small sphalerite inclusions. Ratio of elements (Cu:Fe:S) was 5:5:11 when calculated quantitatively from area 1



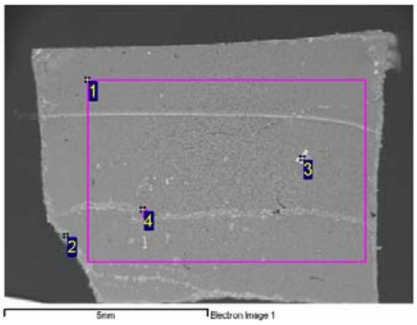
Processing option: All elements analyzed (normalized). All results in weight percent

Spectrum	O	Na	Si	S	Cl	Mn	Fe	Cu	Zn	Ag	Total
1				32.12			29.60	32.28			100
2	22.31	1.82		22.90	9.35		28.88	14.73			100
3	21.31			19.68	4.18		36.32	18.51			100
4	17.62			23.31	4.23		33.53	21.31			100
5				35.61			28.55	31.02		4.83	100
6			0.03	37.37		0.46	6.93		55.22		100
7			0.01	37.26			30.03	32.69			100

Fig. 3. SEM images of the $CuFeS_2$ electrode. The area analysis of chalcopyrite dissolved at pH 1.5 is sulfur rich, Cu = 32.38, Fe = 29.60 and S = 38.12 (in wt. %), with chlorine – oxygen rich aggregates, sphalerite and silver rich inclusion. Ratio of elements (Cu:Fe:S) was 5:5:12 when calculated quantitatively from area 1. The solution contained [NaCl] = 250 g/dm^3, [Cu^{2+}] = 17.9 g/dm^3, T = 85°C

The crosscut of anodically polarized chalcopyrite electrode (Fig. 5) showed a two phase structure forming during anodic polarization. The layer, seen in Fig.5, consisted mainly of iron and oxygen (in ratio from 1:2 to 1:3). Low concentrations of chloride and sulfur were also present in the reaction product layer, but no copper or sodium were detected.

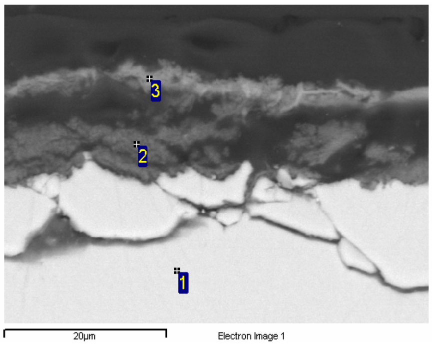
The SEM images of the chalcopyrite electrode surface (Fig. 2) showed an indication of excess sulfur at lower pH and of iron, oxygen and sulfur at higher pHs (Figs. 3 and 4). However, the potentials in the anodic polarization experiment were high (1.2 V vs. SHE) and were not directly related to chalcopyrite dissolution at OCP.



Processing option: all elements analyzed (normalized). All results in weight percent

Spectrum	O	P	S	Cl	Fe	Cu	Zn	Total
1	22.41		38.76	3.74	33.61	2.48		100
2	22.50		23.27	5.97	34.12	14.14		100
3	3.61		33.64		7.88		54.87	100
4	17.88	0.55	30.62	2.79	33.42	14.75		100

Fig. 4. SEM images of the $CuFeS_2$ electrode. The area analysis of chalcopyrite dissolved at pH 3.0 is iron-oxygen rich, Cu = 2.48, Fe = 33.61, S = 38.76 and O = 22.41 (in wt. %), with small chlorine excess Ratio of the elements at pH 3 Fe:S:O:Cl was 6:12:13:1. The solution contained [NaCl] = 250 g/dm^3, [Cu^{2+}] = 17.9 g/dm^3, T = 85°C



Processing option: all elements analyzed (normalized). All results in weight percent

Spectrum	O	Si	P	S	Cl	Fe	Cu	Total
1				35.96		30.89	33.15	100
2	36.24	0.76		3.22	9.99	53.39		100
3	37.52	1.52	0.44	2.50	7.80	50.23		100

Fig. 5. A crosscut-section SEM picture of an $CuFeS_2$ electrode made at Outotec Research Oy after anodic polarization at pH 3. The solution had [NaCl] = 250 g/dm^3, [Cu^{2+}] = 17.9 g/dm^3, T = 85ºC

3.3. LINE SCAN FOR CUBIC SAMPLES

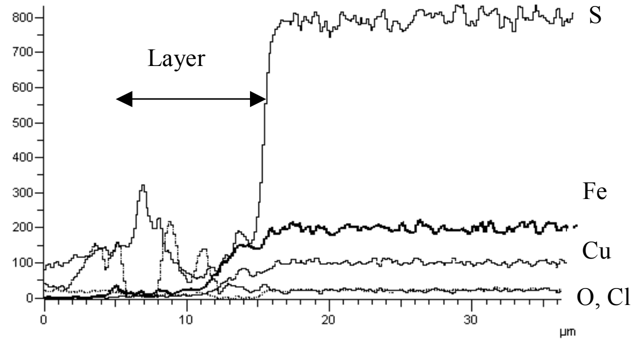
To get a better crosscut-section examination of the reaction product layers on stationary chalcopyrite formed at OCP, SEM analyses were carried out on the leached cubic samples (Fig. 1). Originally, an elemental analysis of the reaction product layer was carried out using point analysis. However, it was observed that the reaction product layer was only ≤5 μm thick at leaching times ≤4 h, which made it difficult to make a point analysis of the reaction product layer. Also, when polishing the sample leached at pH 1, grey particles were observed in the epoxy and the polishing wheel, indicating that the grey reaction product layer formed at pH 1 was easily removable. For that reason, the line scan was applied.

The line scan was used to give a better indication of the thickness and the composition of the reaction product layer for all samples. The thickness of the layer was determined following the pulse signals – epoxy resin gives either very low signals (as in Fig. 6 at pH 3 for 22 hour) or O and Cl pulses if air bubbles or Cl resins are present (as in Fig. 6 at pH 1 for 22 hours). The base material chalcopyrite gives pulses of S, Fe and Cu. If the chalcopyrite sample was fragile or uneven, the base material did not give even pulses (as in Fig. 6 at pH 2 for 22 h).

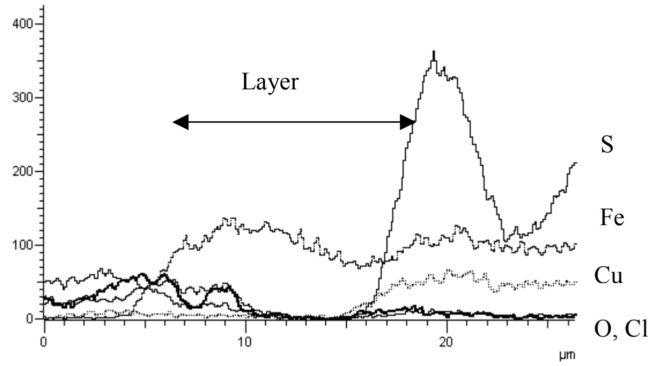
Between the epoxy and the base chalcopyrite material there was a reaction product layer, which gave pulses of the elements present in the layer. The thickness of the layer was also estimated based on this. It must be noted that the number of pulses does not directly describe the concentration of a certain element, but the trends in the number of pulses indicate if the concentration of an element at a certain point is increasing or decreasing. Figure 6 shows the line scans of samples at pH 1, 2 and 3 after 22 hours leaching. Line scans were also carried out at each pH after 1, 2 and 4 hours of leaching. The curves on the base materials side from top to bottom are S, Fe, Cu, O and Cl.

It was observed that the reaction product layer at pH 1 gave pulses for sulfur and grew from a thickness of ca. 1 μm to ca. 9 μm. At pH 2, for t = 1-2 hours sulfur pulses and sulfur together with iron and oxygen pulses (t from 4 to 22 h) were found, the thickness increasing from ca. 1 μm to ca. 10 μm. At pH 3, there were indications for both oxygen and iron for all times measured and the layer thickness increased from ca. 1 μm to ca. 14 μm. At all pH values the chalcopyrite reaction product layer thickness (from 9 to 14 μm) after 22 hours of leaching was 5 to 8 times higher than the layer thickness of 1.7 μm, reported by Parker (2005) in 0.1 M HCl solution after 22 hours of leaching at the OCP.

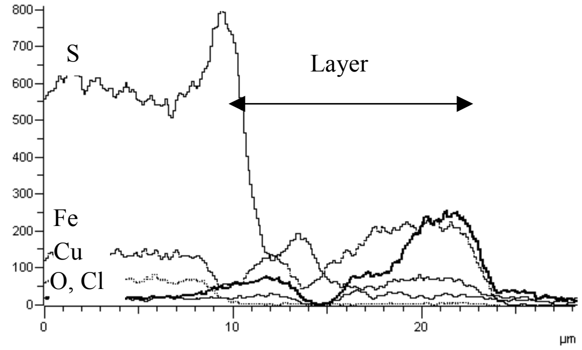
Line scans agreed with the earlier SEM study for polarized chalcopyrite electrodes (Fig. 2 to Fig. 5). At pH 1, only sulfur pulses were observed at the reaction product layer, but no iron or oxygen. This suggests the presence of S^0 (Fig. 6, pH 1). At pH 2, sulfur pulses were observed at short leaching times (≤2 h), but also iron and oxygen pulses for leaching times longer than 2 hours (Fig. 6, pH 2). At pH 3, strong oxygen and iron peaks were observed in the reaction product layer, and the presence of sulfur also became evident with increasing leaching time, t = 22 h.



pH 1, 22h



pH 2, 22h



pH 3, 22h

Fig. 6. SEM analysis of chalcopyrite samples. Line scan of the polished $CuFeS_2$ samples, leached at pHs 1 – 3 for 22 hours in [NaCl] = 280 g/dm^3, [Cu^{2+}] = 30 g/dm^3 and T = 90ºC. The curves on the base materials side from top to bottom are S, Fe, Cu, O and Cl. The side of the chalcopyrite base material varies: on the right at pH 1 and 2, and on the left at pH 3

3.4. X-RAY DIFFRACTION ANALYSES

To confirm the presence of phases on the chalcopyrite surface, X-ray diffraction (XRD) analyses were carried out on the reaction product layers formed on cubic (1 cm^3) chalcopyrite samples leached at the OCP. Figure 7 shows that after 22 hours leaching at pH 1, the reaction product layer consisted of elemental sulfur and a trace amount of goethite (analyzed as α-$Fe_2O_3 \cdot H_2O$). At pH 2 the amount of FeOOH (ß-FeOOH, akaganeite) had increased, and S^0 was still present. At pH 3 (Fig. 8), the reaction product layer consisted of FeOOH (akaganeite $Fe^{3+}O(OH)$, synthetic) and there were indications of S_8, where sulfur forms an eight-membered ring of sulfur atoms (Dreisinger, 2003). Also chalcopyrite was detected in all XRD analyses.

With increasing pH, iron forms various iron oxide or iron oxide-hydroxide compounds. The XRD spectrum agreed with that of goethite (pH 1), ß-FeOOH (pH 2) and synthetic akaganeite (pH 3), generally discussed as FeOOH. This is intended to describe more of an iron compound, where iron is present as a trivalent species with two oxygen atoms and one hydrogen atom, than the exact phase structure. Earlier (Dutrizac and Riveros, 1999; Riveros and Dutrizac, 1997) in ferric chloride media, FeOOH was found to occur in the form of ß-FeOOH (akaganeite).

4. CONCLUSIONS

The analyses indicate that during copper(II) chloride leaching of chalcopyrite elemental sulfur is the main reaction product at pH = 1 and iron compounds at pH = 3. Microscopic observation suggests formation of elemental sulfur at pH = 1, and at pH = 2 and 3 formation of FeOOH. The SEM surface analysis showed slight excess of sulfur at pH = 1.5 (Cu:Fe:S was 5:5:12). At pH = 3 the surface was mainly iron, sulfur and oxygen (Fe:S:O:Cl was 6:12:13:1). This layer was assumed to be hematite, goethite, or iron hydroxide. Crosscut section analysis confirmed a two-phase layer, consisting of mainly of iron and oxygen in ratio 1:2 to 1:3.

Based on SEM line scan analysis of reaction product layers only sulfur was observed at pH = 1 and the thickness of the layer increased from ca. 1 µm to 9 µm within 22 hours. At pH = 2 there was sulfur at leaching times 1 – 2 h with iron and oxygen after 4 - 22 h. The thickness increased from ca. 1 µm to 10 µm. At pH = 3 there was oxygen and iron for all times measured and the layer thickness increased from ca. 1 µm to 14 µm.

The X-ray analysis showed that at lower pH the reaction product layer consisted of elemental sulfur and a trace amount of goethite. With increasing pH the amount of FeOOH increased, but sulfur was still present.

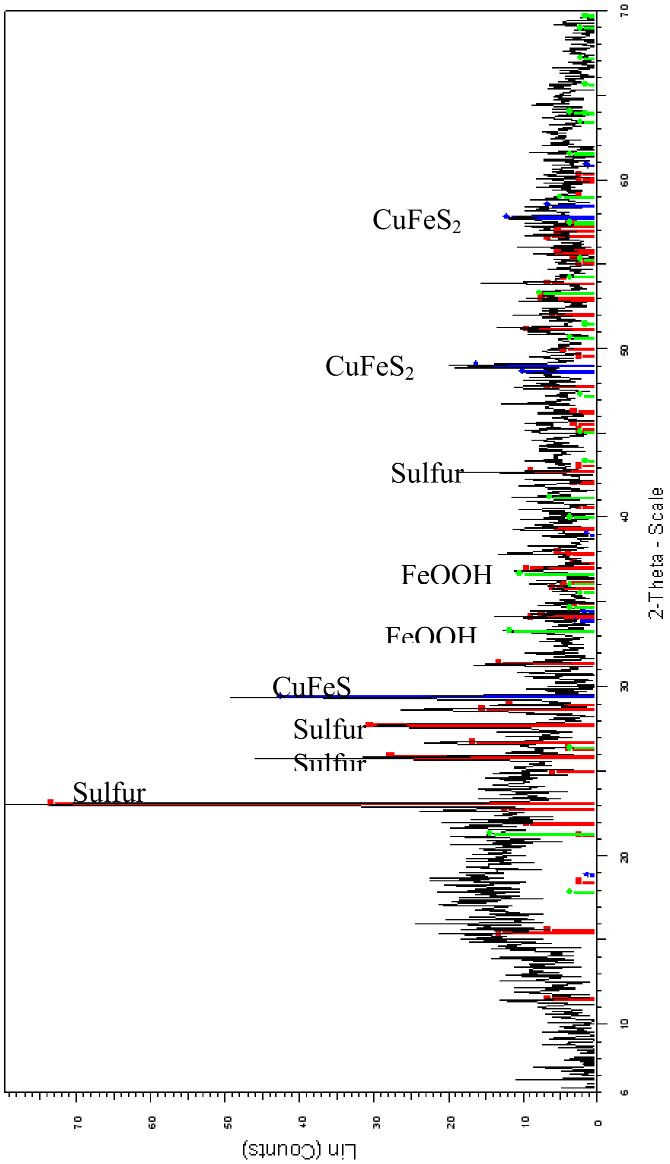


Fig. 7. XRD spectrum and analysis of the chalcopyrite reaction product layer after leaching at pH 1 for 22 hours at OCP. Solution had [NaCl] = 280 g/dm^3, [Cu^{2+}] = 30 g/dm^3 and T = 90°C

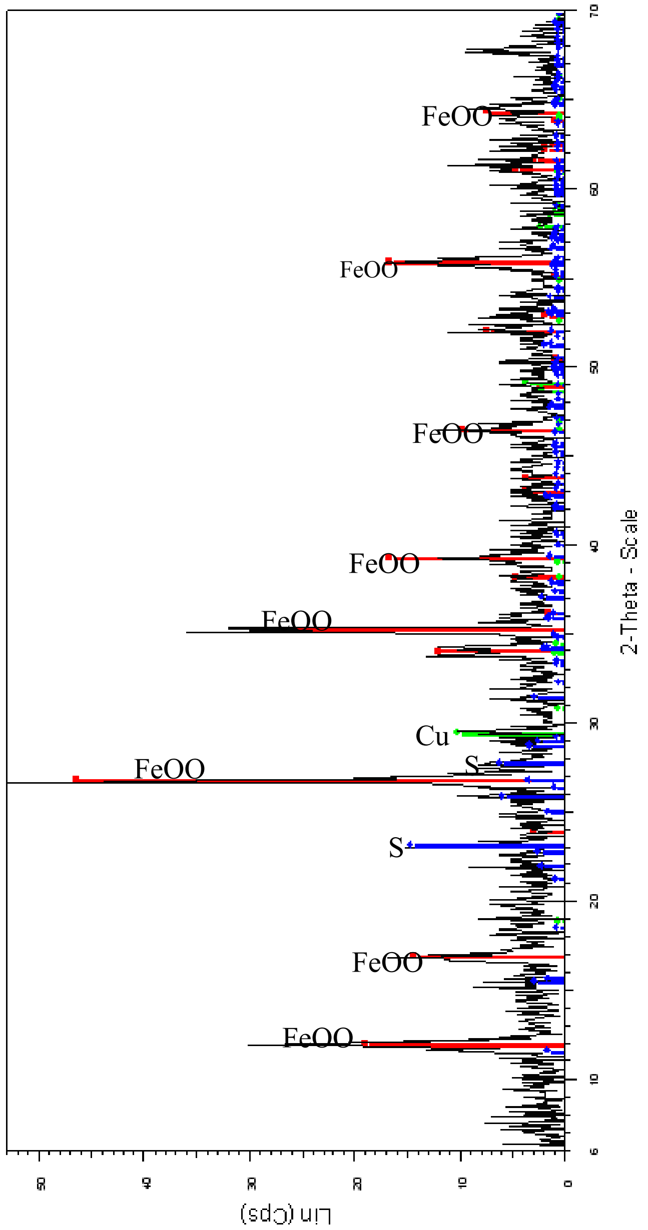


Fig. 8. XRD spectrum and analysis of the chalcopyrite reaction product layer after leaching at pH 3 for 22 hours at OCP. Solution had [NaCl] = 280 g/dm^3, [Cu^{2+}] = 30 g/dm^3 and T = 90°C

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W pracy przedstawiono badania mikroskopowe warstw powierzchniowych na chalkopirycie utworzonych w stężonych roztworach chlorku miedzi(II), które stosuje się w procesie HydroCopper®. Badano fizyczną postać oraz skład chemiczny produktów reakcji na chalkopirycie jako funkcji pH (od pH 1 do 3) oraz czasu ługowania. Zastosowano metody mikroskopowe takie jak stereo-optyczną, scanningowo-electronową (SEM) oraz rentgenowską. W celu zbadania produktów reakcji, powierzchnia mineralna była ługowana przy otwartym obwodzie potencjału (OCP) lub traktowana przez anodową polaryzację. Wykazano, że przy niskich wartościach pH dominującą wśród produktów reakcji fazą jest szara siarka elementarna istniejąca nawet po długich (22 godziny) czasach reakcji. Wraz ze wzrostem pH (do 2 lub 3) produkty reakcji stawały się bardziej zółto-brązowe i składały się głównie z FeOOH, jednakże siarkę elementarną obserwowano także przy wyższych pH. Przy pH 1 grubość warstwy wzrastała do około 1 -9 µm i rosła wraz z czasem ługowania do 22 godzin. Przy pH 2 grubość warstwy rosła do około 10 µm, a przy pH 3 do około 14 µm.

słowa kluczowe: chalkopiryt, ługowanie chlorkowe, produkty reakcji, siarka, związki żelaza