

Mineralogical and geochemical studies on pyrite and chalcopyrite oxidations in the Sarcheshmeh copper mine tailings

Sajjad Jannesar Malakooti^{1,2}, Mohammad Noaparast³, Saied Ziaeddin Shafaei Tonkaboni³, Faramarz Doulati Ardejani³, Esmaeil Soleimani⁴, Esmat Esmaeilzadeh⁵

¹ Mining Engineering Department, Islamic Azad University, Science & Research Branch, Tehran, Iran. S.jannesar114@gmail.com

² Mineral Processing Engineering Department, Islamic Azad University, Langaroud Branch, Gilan, Iran.

³ School of Mining, College of Engineering, University of Tehran. Fdoulati@ut.ac.ir

⁴ Faculty of Chemistry, Shahrood University of Technology, Iran.

⁵ National Iranian Copper Industries Company (NICICO.).

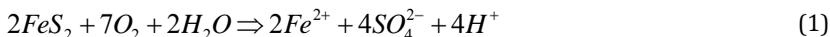
Abstract

This paper compare pyrite and chalcopyrite oxidation and related environmental problems associated with the sulphide mine tailings produced by the copper processing plant at Sarcheshmeh copper mine in Kerman, Iran. These tailings are rich in sulphide minerals particularly pyrite and chalcopyrite. Oxidation of these minerals produces the well-known problem of acid mine drainage. In this research, a depth sampling was conducted over the tailings materials. Two vertical trenches (A and B) were excavated in tailings from the surface to a depth of 4.2 m. Samples were collected from the surface and various depths in each trench with a spacing of 0.3 m. The samples were analysed for total concentrations of 62 elements, paste pH, SO₄²⁻, CO₃²⁻, and HCO₃⁻. The results show that pyrite and chalcopyrite oxidation in tailings materials have lowered the pH of the tailings to a range varied between 2.9 and 3.5. The oxidation process caused elevated concentrations of SO₄, Fe and trace elements. The results of such investigations can be used for designing an effective environmental management program.

Keywords: tailings disposal site, pyrite, chalcopyrite oxidation, acid mine drainage, AMD, Sarcheshmeh copper mine.

Introduction

Pyrite is commonly associated with coal and metal ore deposits. Pyrite oxidation and the factors affecting the kinetics of oxidation reaction (O₂, Fe⁺³, temperature, pH, Eh, and the presence or absence of microorganisms) have been the focus of extensive studies because of their importance in both environmental remediation and mineral separation by flotation (Buckley and Woods, 1987; Brown and Jurinak, 1989; Evangelou and Zhang, 1995). Comprehensive reviews of pyrite oxidation and acid mine drainage generation are given by Lawson (1982), Pyrite tends to oxidise when the mineral surface is exposed to an oxidant and moisture, either in oxygenated or anoxic systems, depending on the oxidant.

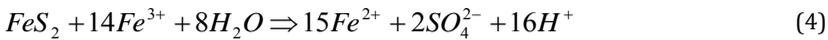


The second reaction is ferrous iron oxidation to ferric iron (Eq. 2) in which one mole of acid is consumed.



Oxidation of ferrous iron (Fe^{2+}) to ferric iron (Fe^{3+}) is chemically slow in low pH values. However, it may be biologically catalysed by the bacteria *Thiobacillus ferrooxidans* (Singer and Stumm, 1970).

The third reaction is ferric iron hydrolysis (Eq. 3) in which Fe^{3+} is precipitated as amorphous ferric hydroxide. Eq. 3 produces three moles of acid as a by product. The formation of ferric iron hydroxide precipitates is a pH dependent reaction. For pH values greater than 3.5, the system is saturated with respect to $Fe(OH)_3$, and amorphous iron hydroxide mineral tends to precipitate (Eq. 3). When pH is less than 3.5, the system is under saturation with respect to $Fe(OH)_3$, and a significant amount of Fe^{3+} can remain in the solution phase to react with pyrite to release additional Fe^{2+} , SO_4^{2-} and H^+ (Eq. 4).

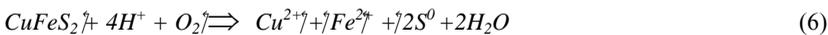


Galena and chalcopyrite are commonly associated with acid-generating minerals, such as pyrite and pyrrhotite. Ferric sulphate acid solutions, generated by the oxidation of iron sulphides can enhance the oxidation of lead and copper-bearing sulphide minerals (Jennings et al. 2000; Nowak and Laajalehto 2000; Shapter et al. 2000).

The oxidation of chalcopyrite in the presence of ferric ions under acidic conditions can be expressed as:



Hiroyoshi et al. (1997) monitored the oxygen consumption, sulphur formation, total iron, and Fe (II) concentrations at different pH levels during the oxidation of chalcopyrite. On the basis of the reaction products formed, it was concluded that ferrous ions catalysed the oxidation by dissolved oxygen in an acidic medium:



The dissolution of chalcopyrite can be also influenced strongly by galvanic effects. The presence of pyrite or molybdenite in association with chalcopyrite can cause accelerated rates of chalcopyrite dissolution (Dutrizac and MacDonald, 1973), whereas the presence of iron-rich sphalerite and galena can slow the dissolution reaction. AMD is usually characterised with high concentrations of Fe, SO_4 and low pH. It can carry potentially toxic metals and other dissolved materials away from the tailings dam site (Williams 1975). AMD has a detrimental effect on surface waters, groundwater aquifers and soils (Walter et al. 1994 a). Many physical, chemical and biological processes are involved in the oxidation of sulphide minerals and AMD generation including oxygen availability within the tailings materials, type of sulphide mineral and its content, bacterially mediated oxidation

reaction, pH-buffering reaction due to the dissolution of mineral phases, precipitation of secondary minerals, transportation of the oxidation products and their interactions with solid phase (Morin et al. 1988). Study of sulphide minerals oxidation and considering processes involved may provide useful information that can be used for development of an effective treatment scheme and environmental management program for tailings disposal sites. This paper investigates pyrite and chalcopyrite oxidation in the tailings disposal site of the Sarcheshmeh copper mine.

Methods

Site description and Sampling

Sarcheshmeh copper mine is located about 160 km southwest of Kerman, Iran. The average elevation of the mine site is 1600 m and has a latitude of 29° 58' N and a longitude of 53° 55' E. The average annual precipitation at the site varies from 300 to 550 mm. The temperature ranges from +35 °C in summer to -20 °C in winter. The area is covered with snow about 3 to 4 months per year. Altogether, twenty eight samples, 2 kg each in weight were collected in 0.5 m intervals from different depths of two trenches dug in the tailings site (Trench A: 30°, 05', 57.9" N; 55°, 50' 30.1" E and Trench B: 30°, 05', 56.4" N; 55°, 50' 32.3" E) which is located in north of the Sarcheshmeh copper mine. Two trenches had about 4.2 m depth. The samples were dried at room temperature and then sieved to obtain the particle sizes of <200 mesh. The samples were divided into two parts for mineralogical and geochemical analysis.

Pyrite and Chalcopyrite Oxidation and Mineralogical Studies

Pyrite and chalcopyrite oxidation generate AMD as a major environmental pollution source. Recent studies on sulphide minerals oxidation within the tailings materials involve inorganic/biochemical reaction approach, electrochemical reaction approach, reaction kinetics approach and computer simulation approach (Evangelou 1995). The mineralogical investigation plays an important role in sulphide minerals oxidation at the Sarcheshmeh tailings disposal site. In this paper, the geochemical and mineralogical studies were applied to consider pyrite and chalcopyrite oxidation processes. A method presented by ASTM (Gladfelter and Dickerhoof 1976; Doulati Ardejani et al. 2010; Shafaei Tonkaboni S.Z et al. 2011) was employed to determine the organic pyrite (from the non-organic pyrite). Hydrochloric Acid (HCl) was used to dissolve sulphates and then the pyrite and chalcopyrite was extracted from the remaining acidic solution using Nitric Acid (HNO₃). An AA-670 Shimadzu atomic absorption was used to measure iron and copper in solutions and the contents of pyrite and chalcopyrite that remained in the tailings particles.

As Figure 1 shows, in zones where oxygen is present in the pore spaces of wastes, pyrite and chalcopyrite remained in tailings particles. The pyrite oxidation decreased gradually from the tailings surface to a depth of about 1.8 m (Figure 1 d, left) but chalcopyrite oxidation reduced sharply to a depth of about 1.5 m (Figure 1 d, right) due to a rapid reduction in oxygen diffusion with depth.

The polished sections of the tailings surface show no pyrite (Figure 1 a, left) and chalcopyrite converted to covellite (Figure 1 a, right). Because of reduced oxygen

diffusion with depth of tailings, the pyrite and chalcopyrite contents increased with depth (Figure 1 b, left). Sulphide minerals can be easily recognised in the polished sections associated with a depth of 4 m (Figure 1 c, left and right), where no oxygen is available to oxidise pyrite and chalcopyrite.

It has been reported that the chalcopyrite oxidation rate increases with rising ferric iron concentration, but with an oxidation rate of 1-2 orders of magnitude less than pyrite (Rimstidt et al., 1994). Under extreme reducing conditions (depth below 1.8 m), replacement processes (most likely chalcopyrite by covellite) may take place, resulting to secondary Cu enrichments. Only secondary replacement by covellite and not by chalcocite-digenite could be expected in this zone of enrichment in the tailings disposal sites (Figure 1 b, right). This is conformed to previous observations of (Jang and Wadsworth 1994), where the replacement by covellite is the initial steps followed by chalcocite-digenite in an advanced stage.

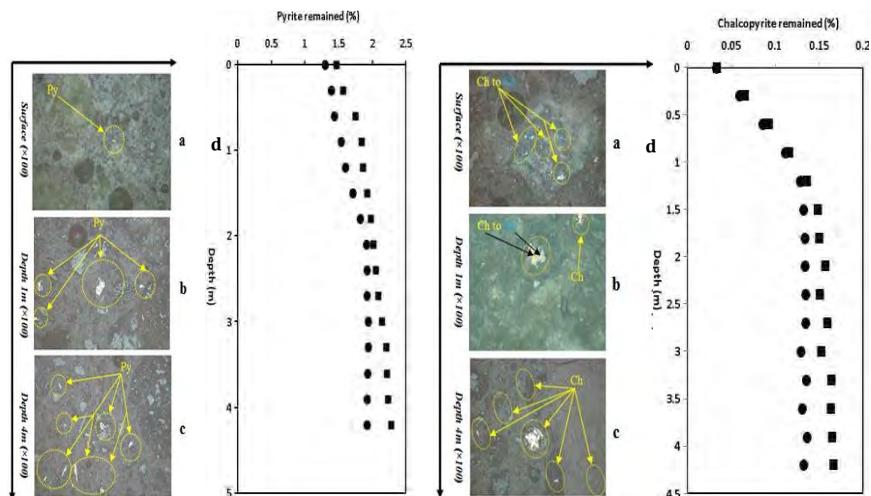


Figure 1 Polished sections of waste samples in tailings disposal site, illustrating pyrite and chalcopyrite variations with depth : (a) the tailings surface, (b) at a depth of 1 m, (c) at a depth of 4 m. Py: Pyrite, Ch: Chalcopyrite and Co: Covellite (d) Concentrations of pyrite and Chalcopyrite remained (wt %) versus depth for (●)A and (■)B profiles.

As well shown in Figure 1, the pyrite oxidation process has been more intense (20 to 30 orders of magnitude) than chalcopyrite oxidation rate. Mineralogical studies revealed that chalcopyrite converted to covellite or chalcocite in a depth of 1 m.

Geochemical studies

Pyrite and chalcopyrite oxidation and AMD generation often cause the concentrations of heavy metals to be elevated. An investigation of the geochemistry of heavy metals is important for comprehensive assessment of the potential environmental impacts of mine drainages. For this reason, a geochemical study was carried out. The samples were geochemically analysed for anions and

cations in the water laboratory of National Iranian Copper Industries Company (NICICO.). They were also analysed for trace elements (Fe, Zn, Pb, Mo, Cu, Cr, Co and Al) using combined inductively coupled plasma mass spectrometer (ICP-MS) and optical emission spectrometry (ICPOES) by the Lab West Minerals Analysis Pty Ltd., Australia, after digesting in a hot acid mixture (HF, HNO₃ and HClO₄). The analyses results are shown in Table 1.

Although not given in Table 1, the concentration of HCO₃ in the samples was very low. Carbonates were totally depleted in the tailings materials due to acid neutralisation process. The paste pH of the samples varies between 2.9 and 3.5. Low pH values and high concentrations of SO₄ and Fe in the samples describe pyrite oxidation process. SO₄ concentration in the samples varies between 538 and 2319 µg/g. The biggest concentration of sulphate was observed at a depth of 3.30 m in sampling location B. The concentrations of the most of trace elements are very high (Table 1). Pyrite oxidation at the surface layers of tailings has resulted in the elevated concentration of Fe (varies from 22900 to 53100 µg/g at a depth of 0.6 m).

Conclusion

Pyrite and chalcopyrite oxidation resulted AMD production in the Sarcheshmeh copper mine tailings disposal site. A mineralogical and geochemical study was carried out to investigate pyrite oxidation and chemically characterise the tailings materials. The results show that the pyrite oxidation in tailings materials has lowered the paste pH of the tailings to a range between 2.9 and 3.5. Chalcopyrite oxidation was lower than that of pyrite. Oxidation process produced high concentrations of SO₄²⁻, Fe and trace elements. The results further show that the concentration of HCO₃⁻ in the samples was very low. The acid released from sulphide minerals oxidation has depleted carbonate minerals in the tailings materials, so the concentration of CO₃²⁻ was very low. Bentonite or clays covers can be used to control AMD production in old tailings. For new tailings, the disposal site base can be covered by a liner in order to prevent pollutants transportation to the groundwater aquifer. The result of such investigations would of course provide appropriate remediation plans to prevent metal inputs to soil and water resources.

Table 1 Major and trace elements concentrations in the Sarcheshmeh copper mine tailings ($\mu\text{g/g}$).

Samples no.	SO₄²⁻	Mg²⁺	K⁺	Ca²⁺	Al	Co	Cr	Cu	Mo	Pb	Zn	Fe
Location A (Depth in m)												
A30	844	18.50	58.0	28.80	85257	34.0	44	1294.8	173.0	36.4	272.3	53100
A60	866	18.60	84.3	30.40	85212	33.2	48	1203.7	94.6	39.7	210.2	49000
A90	874	18.80	42.0	32.40	82299	18.8	63	782.4	122.0	30.1	107.0	37800
A120	928	13.90	59.3	45.60	75676	24.8	29	1446.0	159.0	46.4	200.3	31900
A150	901	19.00	28.8	32.00	74905	24.3	28	1681.9	181.0	50.8	186.0	27800
A180	699	20.00	76.8	22.80	83324	24.9	26	1110.1	77.9	41.9	150.8	34200
A210	863	21.90	39.8	26.40	80134	19.4	31	1190.6	94.0	47.8	129.1	30700
A240	808	22.80	43.7	38.40	80083	23.8	34	1245.4	113.9	53.9	152.2	35100
A270	1106	11.50	23.0	31.20	81371	37.4	39	1163.7	74.5	27.9	188.5	44200
A300	835	18.50	22.3	30.40	80067	28.3	29	912.9	66.1	43.3	146.7	34000
A330	715	9.40	23.0	22.80	78473	22.5	24	781.4	82.5	36.9	154.2	30600
A360	915	20.40	28.7	31.20	85062	31.7	43	1306.5	74.8	34.3	244.9	48000
A390	1024	18.30	13.7	25.60	82926	32.2	46	1158.3	62.6	36.3	135.2	43300
A420	105	32.40	11.2	30.40	79578	34.9	53	1049.1	92.4	51.3	133.5	43100
Location B (Depth in m)												
B30	538	27.00	34.2	31.2	89998	28.4	42	1196.2	144.6	48.8	221.1	38600
B60	923	20.40	28.4	22.80	8109	35.4	57	2174.3	137.7	48.5	230.7	44600
B90	721	20.20	34.4	24.00	84042	33.2	51	1310.4	96.7	38.0	205.5	41900
B120	570	24.50	40.6	30.40	82052	26.6	48	1263.2	94.9	38.8	186.7	34700
B150	728	18.50	26.3	15.20	76154	21.6	33	1100.2	129.2	35.1	164.9	27600
B180	607	18.50	17.9	15.20	73080	27.3	27	1774.9	183.8	45.1	224.1	27000
B210	653	10.80	24.7	12.40	76787	29.8	27	1606.6	109.8	41.8	178.5	30700
B240	634	22.60	100.	38.80	73184	23.6	23	1374.3	82.8	34.9	146.0	29400
B270	558	22.80	100.	23.20	76877	18.2	31	1263.8	93.0	46.7	122.6	29700
B300	687	21.10	100.	23.20	75662	23.5	27	1072.1	84.3	53.5	147.6	29400

Samples no.	SO₄²⁻	Mg²⁺	K⁺	Ca²⁺	Al	Co	Cr	Cu	Mo	Pb	Zn	Fe
B330	2319	25.20	100.	34.80	72366	35.5	35	1328.7	83.9	28.8	174.9	44200
B360	644.0	16.30	100.	34.00	73266	26.4	27	1240.6	84.6	42.7	143.4	34000
B390	801.0	19.70	250.	30.40	77591	17.6	21	658.7	55.6	44.7	115.4	22900
B420	725.0	15.10	100.	22.80	82080	30.2	35	1270.4	89.7	48.8	246.1	41800

References

- Brown AD and Jurinak J J (1989) Pyrite oxidation in aqueous mixtures. *J. Environ. Qual.* 18, 545-550.
- Buckley AN, and Woods R W (1987) The surface oxidation of pyrite. *Appl. Surf. Sci.* 27: 437-452.
- Doulati Ardejani F, Jodeiri Shokri B, Bagheri M, Soleimani E (2010) Investigation of pyrite oxidation and acid mine drainage characterization associated with Razi active coal mine and coal washing waste dumps in the Azad shahr–Ramian region, northeast Iran. *Environ Earth Sci.* 61: pp. 1547–1560.
- Dutrizac JE, and Mac Donald RJC (1973) The effect of some impurities on the rate of chalcopyrite dissolution. *Can. Metall. Quart.* 12(4), 409–420.
- Evangelou VP and Zhang Y L (1995) A review: pyrite oxidation mechanisms and acid mine drainage prevention. *Crit. Rev. Environ. Sci. Technol.* 25(2), 141-199.
- Gladfelter WL, Dickerhoof DW (1976) Use of atomic absorption spectrometry for iron determinations in coals. *Fuel* 55 (4): pp. 360—361.
- Hiroyoshi N, Hirota M, Hirajima T, and Tsunekawa M (1997) A case of ferrous sulfate addition enhancing chalcopyrite leaching. *Hydrometallurgy* 47: pp. 37—45.
- Jang, HJ, and Wadsworth ME (1994) Kinetics of hydrothermal enrichment of chalcopyrite. In: C.N. Alpers and D.W. Blowes (Editors), *Environmental Geochemistry of Sulfide Oxidation*. ACS Symposium Series. American Chemical Society, Washington, DC, pp. 661.
- Jennings SR., Dollhopf DJ, and Inskeep WP (2000) Acid production from sulfide minerals using hydrogen peroxide weathering. *Appl. Geochem.* 15, 247-255.
- Lowson RT (1982) Aqueous oxidation of pyrite by molecular oxygen. *Chem. Rev.* 82, 461-497.
- Morin KA, Cherry JA, Dave NK, Lime TP, Vivjurka AJ (1988) Migration of acidic groundwater seepage from uranium-tailing impoundments, 1. Filed study and conceptual hydrogeochemical model. *J Contaminant Hydrogeology* 2: pp. 271-303.
- Nowak P, and Laajalehto K (2000) Oxidation of galena surface-an XPS study of the formation of sulfoxy species. *Appl. Surf. Sci.* 157, 101–111.
- Rimstidt JD, Chermak, JA, and Gagen PM (1994) Rates of Reaction of Galena, Spalerite, Chalcopyrite, and Asenopyrite with Fe(III) in Acidic Solutions. In: C.N. Alpers and D.W. Blowes (Editors), *Environmental Geochemistry of Sulfide Oxidation*. ACS Symposium Series. American Chemical Society, Washington, pp. 2—13.
- Shapter JG, Brooker MH, and Skinner WM (2000) Observation of oxidation of galena using Raman spectroscopy. *Int. J. Min. Process.* 60: pp. 199—211.
- Singer PC, Stumm W (1970) Acid mine drainage, rate determining step: *Science* 167: pp. 1121—1123.
- Shafaei Tonkaboni SZ, Jannesar Malakooti S, Doulati Ardejani F, Singh R, Soleimani E, Noaparast M, and Naseh R (2011) Pyrite oxidation in the Sarcheshmeh copper mine tailings dam, Kerman, Iran. *IMWA* 2011, 59—63.
- Walter AL, Frind EO, Blowes DW, Ptacek CJ, Molson JW (1994a) Modelling of multicomponent reactive transport in groundwater, 1. Model development and evaluation. *Water Resour Res* 30 (11): pp. 3137—3148
- Williams RE (1975) *Waste production and disposal in mining, milling, and metallurgical industries*. Miller-Freeman Publishing Company, San Francisco, California, pp. 485.