Supplementary materials



Figure S1 XRD analysis of the original chalcopyrite

The XRD patterns were collected on a Bruker D8 (BrukerAXS, Germany) using Cu K_{α} radiation (λ =1.5406 Å) at 40 kV and 40 mA in the 2 θ range of 10°–90°. The results of the XRD analysis show that the phase of the original mineral is mainly composed of chalcopyrite, with some galena.





The result in Figure S2 shows the surface morphology of the original chalcopyrite.



Figure S3 Taxonomy of the top 20 species at the species level



Figure S4 Leaching of chalcopyrite by mixed microorganisms with leaching parameters characterized by $[Cu^{2+}]_{aq}$ (a), pH curves (b), microbial growth curves (c), $[S^T]_{aq}$ curves (d), $[Fe^T]_{aq}$ and $[Fe^{2+}]_{aq}$ curves (e) and ORP curves (f)(The Bio¹ and bio¹_adjust groups refer to the microbial community from a different site (the mining area of Xikuangshan (XKS), Hunan Province, China) compared with that from the Dabaoshan (DBS) mine site in the main text)

Figure S5 Selected SEM images of chalcopyrite residues on day 12 (a) and day 24 (b) from the Bio_adjust group or on day 12 (c) and day 24 (e) from the Bio group

Figure S6 XRD patterns (a) and Raman (b) and FTIR (c) spectra of chalcopyrite residues leached by mixed microorganisms with or without acidification

Figure S7 The microbial community characterized by a Venn diagram of the OTU distribution (a), taxonomy of the top 10 species at the phylum level (b), and taxonomy of the top 10 species at the genus level (c)

		Binding energy/eV		Chemical state
Spectral peak	This study	Reference	- FWHM	
Fe(2p3/2)	708.5	708.55 (TABELIN et al [1], 2020)	2.5	Fe(III)—S
Fe(2p3/2)	709.25	709.3 (BRION [2], 1980)	2.5	Fe(II)—O
Fe(2p3/2)	709.88	709.7 (WANG et al [3], 2022) 3		Fe(II)—O
Fe(2p3/2)	710.67	710.69 (SILVA et al [4], 2018) 2.11		Fe(III)—O
Fe(2p3/2)	711.3	711.3 (NEAL et al [5], 2001)	2.77	Fe(III)—O
Fe(2p3/2)	711.6±0.1	711.6 (WANG et al [3], 2022) 2.5		Fe(III)—O
Fe(2p3/2)	712.11	712.1 (BINDER [6], 1973)	3	Fe(II)—S
Fe(2p3/2)	712.30±0.1	712.35 (TABELIN et al [1], 2020)	2.5	Fe(III)—O
Fe(2p3/2)	713.6±0.1	713.6 (WANG et al [3], 2022)	2.5	Fe(III)—S—O
Fe(2p3/2)	714.4±0.1	714.5 (TABELIN et al [1], 2020)	2.5	Fe(III)—S—O
Fe(2p3/2)	715.2±0.1	715.5 (OUYANG et al [7], 2014)	2.9	Fe(III)—S—O
Fe(2p3/2)	715.64	715.64 (TABELIN et al [1], 2020)	3	Fe(III)—S—O
S(2p3/2)	160.7±0.1	160.7 (KARTIO et al [8], 1997)	1.32	PbS
S(2p3/2)	161.2	161.2 (MANOCHA and PARK [9], 1977)	1.32	PbS
S(2p3/2)	161.28	161.28 (ZHANG et al [10], 2021) 1.7		S^{2-}
S(2p3/2)	161.5	161.5 (WANG et al [3], 2022)	1.7	S^{2-}
S(2p3/2)	162.3	162.3 (NIE et al [11], 2019)	1.7	${ m S}_2{}^{2-}$
S(2p3/2)	162.7	162.7 (PERRY and TAYLOR [12], 1986)	1.7	\mathbf{S}^{2-}
S(2p3/2)	163.15±0.1	163.1 (YU et al [13], 1990) 1.7		\mathbf{S}^{0}
S(2p3/2)	163.37±0.1	163.3 (ZHANG et al [10], 2021)], 2021) 1.7	
S(2p3/2)	163.8	163.8 (Hyland and Bancroft [14], 1989)	1.7	Sn^{2-}
S(2p3/2)	163.9	164 (SHUL'GA et al [15], 1995)	1.7	\mathbf{S}^{0}
S(2p3/2)	164.3	164.3 (ZHANG et al [10], 2021)	1.7	S^0
S(2p3/2)	165.7±0.1	165.9 (LIU et al [16], 2018) 1.7		SO3 ²⁻
S(2p3/2)	167.31	167.2 (TURNER et al [17], 1980)		SO_3^{2-}
S(2p3/2)	168.4	168.3(PRATT et al [18], 1994) 1.65		SO_4^{2-}
S(2p3/2)	168.6±0.1	168.7(LINDBERG et al [19], 1970) 1.7		SO_4^{2-}
Cu(2p3/2)	932±0.1	931.96(JIA et al [20], 2020)	1.42	CuFeS ₂
Cu (2p3/2)	932.8±0.1	932.7(PERRY and TAYLOR [12], 1986)	2.29	Cu ₂ S
Cu(2p3/2)	933.06	933.2(SCHÖN [21], 1973) 1.88		Cu(II)-O
Cu(2p3/2)	933.3	933.3(JOLLEY et al [22], 1989) 1.87		Cu(II)-O
Cu(2p3/2)	934.6	934.6(PARMIGIANI et al [23], 1992)	3	Cu(II)-O
Cu(2p3/2)	935±0.1	935(NEFEDOV et al[24], 1980)	2.5	Cu(II)-S
Cu(2p3/2)	935.5±0.2	935.5(NEFEDOV et al [25], 1977) 2.21		Cu(II)

Table S1 XPS data and chemical states of the leaching residues

Sample		Percentage of S 2p combination/at.%				
		\mathbf{S}^{2-}	${ m S}_2{ m 2}^{-}$	\mathbf{S}^{0}	SO3 ²⁻	SO_4^{2-}
Bio_adjust	Day 6	22.7	25.2	12.2	5.1	34.8
	Day 12	17.9		31.6	4.6	45.9
	Day 18	4.9		25.6	2.0	67.5
	Day 24	2.7		13.0	2.0	82.3
Bio	Day 6	37.3		15.0	9.1	38.6
	Day 12	43.7		26.3	5.8	24.2
	Day 18	24.5		31.3	9.2	35.0
	Day 24	18.8	—	29.9	11.1	40.2
Abio_adjust	Day 24	21.7		28.9	5.6	43.8
Abio	Day 24	24.4		29.9	8.2	37.5

Table S2 Fitted results of S 2p XPS spectra

Table S3 Fitted results of Cu 2p XPS spectra

Sample		Percentage of Cu 2p combination/at.%				
		CuFeS ₂ (Cu—S)	Cu ₂ S	Cu—O	Cu—S	
	Day 6	42.1	35.1		22.9	
Die adjust	Day 12	35.5	43.7		20.7	
Bio_adjust	Day 18		61.8		38.2	
	Day 24	_	73.2		26.8	
	Day 6	57.6		22.34	20.1	
Die	Day 12	47.8		31.17	21.0	
B10	Day 18	35.5		28.01	36.5	
	Day 24	21.0		52.90	26.1	
Abio_adjust	Day 24		64.3		35.7	
Abio	Day 24		49.7		50.3	

Table S4 Fitted results of Fe 2p XPS spectra

Sample		Percentage of Fe 2p combination/at.%					
		Fe(III)—S	Fe(II)—O	Fe(III)—O	Fe(II)—S	Fe(III)—S—O	
Bio_adjust	Day 6			68.1	_	31.9	
	Day 12		15.6	56.8		27.6	
	Day 18			69.3		30.7	
	Day 24			66.8		33.2	
Bio	Day 6	18.5		51.4		30.1	
	Day 12			58.3	25.8	15.9	
	Day 18			38.5		61.5	
	Day 24			67.8		32.2	
Abio_adjust	Day 24	10.5		52.8	_	36.7	
Abio	Day 24	16.6			51.2	32.2	

References

- TABELIN C B, CORPUZ R D, IGARASHI T, et al. Acid mine drainage formation and arsenic mobility under strongly acidic conditions: Importance of soluble phases, iron oxyhydroxides/oxides and nature of oxidation layer on pyrite [J]. Journal of Hazardous Materials, 2020, 399: 122844. DOI: 10.1016/j.jhazmat.2020.122844.
- [2] BRION D. Etude par spectroscopie de photoelectrons de la degradation superficielle de FeS₂, CuFeS₂, ZnS et PbS a l'air et dans l'eau [J]. Applications of Surface Science, 1980, 5(2): 133–152. DOI: 10.1016/0378-5963(80)90148-8.
- [3] WANG Jun, LIU Yu-ling, LUO Wen, et al. Inhibition of humic acid on copper pollution caused by chalcopyrite biooxidation [J]. Science of the Total Environment, 2022, 851: 158200. DOI: 10.1016/j.scitotenv.2022.158200.
- [4] DA SILVA G R, ESPIRITU E R L, MOHAMMADI-JAM S, et al. Surface characterization of microwave-treated chalcopyrite [J]. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 2018, 555: 407–417. DOI: 10.1016/j.colsurfa.2018.06.078.
- [5] NEAL A L, TECHKARNJANARUK S, DOHNALKOVA A, et al. Iron sulfides and sulfur species produced at hematite surfaces in the presence of sulfate-reducing bacteria [J]. Geochimica et Cosmochimica Acta, 2001, 65(2): 223–235. DOI: 10.1016/s0016-7037(00)00537-8.
- [6] BINDER H. Investigations on the nature of the chemical bonds in iron-sulphur compounds using X-ray photoelectron spectroscopy [J]. Zeitschrift f
 ür Naturforschung B, 1973, 28: 255–262.
- [7] OUYANG Bing-jie, LU Xian-cai, LIU Huan, et al. Reduction of jarosite by Shewanella oneidensis MR-1 and secondary mineralization
 [J]. Geochimica et Cosmochimica Acta, 2014, 124: 54–71. DOI: 10.1016/j.gca.2013.09.020.
- [8] KARTIO I, WITTSTOCK G, LAAJALEHTO K, et al. Detection of elemental sulphur on galena oxidized in acidic solution [J]. International Journal of Mineral Processing, 1997, 51(1-4): 293-301. DOI: 10.1016/S0301-7516(97)00028-8.
- [9] MANOCHA A S, PARK R L. Flotation related ESCA studies on PbS surfaces [J]. Applications of Surface Science, 1977, 1(1): 129–141. DOI: 10.1016/0378-5963(77)90011-3.
- [10] ZHANG Duo-rui, CHEN Hong-rui, XIA Jin-lan, et al. Red mud regulates arsenic fate at acidic pH via regulating arsenopyrite bio-oxidation and S, Fe, Al, Si speciation transformation [J]. Water Research, 2021, 203: 117539. DOI: 10.1016/j.watres.2021.117539.
- [11] NIE Wen-shan, MAO Qi-hang, DING Yao-bin, et al. Highly efficient catalysis of chalcopyrite with surface bonded ferrous species for activation of peroxymonosulfate toward degradation of bisphenol A: A mechanism study [J]. Journal of Hazardous Materials, 2019, 364: 59–68. DOI: 10.1016 /j.jhazmat.2018.09.078.
- [12] PERRY D L, TAYLOR J A. X-ray photoelectron and Auger spectroscopic studies of Cu₂S and CuS [J]. Journal of Materials Science Letters, 1986, 5(4): 384–386. DOI: 10.1007/BF01672333.
- [13] YU Xiang-rong, LIU Fen, WANG Zhong-yan, et al. Auger parameters for sulfur-containing compounds using a mixed aluminum-silver excitation source [J]. Journal of Electron Spectroscopy and Related Phenomena, 1990, 50(2): 159–166. DOI: 10.1016/0368-2048(90)87059-W.
- [14] SHUL'GA Y M, RUBTSOV V I, VASILETS V N, et al. EELS, XPS and IR study of C60.2S8 compound [J]. Synthetic Metals, 1995, 70(1-3): 1381–1382. DOI: 10.1016/0379-6779(94)02887-5.
- [15] LIU Huan, LU Xian-cai, ZHANG Li-juan, et al. Collaborative effects of *Acidithiobacillus ferrooxidans* and ferrous ions on the oxidation of chalcopyrite [J]. Chemical Geology, 2018, 493: 109–120. DOI: 10.1016/j.chemgeo.2018.05.032.
- [16] TURNER N H, MURDAY J S, RAMAKER D E. Quantitative determination of surface composition of sulfur bearing anion mixtures by Auger electron spectroscopy [J]. Analytical Chemistry, 1980, 52(1): 84–92. DOI: 10.1021/ac50051a021.
- [17] PRATT A R, MUIR I J, NESBITT H W. X-ray photoelectron and Auger electron spectroscopic studies of pyrrhotite and mechanism of air oxidation [J]. \gca, 1994, 58(2): 827–841. DOI: 10.1016/0016-7037(94)90508-8.
- [18] LINDBERG B J, HAMRIN K, JOHANSSON G, et al. Molecular spectroscopy by means of ESCA II. Sulfur compounds. Correlation of electron binding energy with structure [J]. Physica Scripta, 1970, 1(5, 6): 286–298. DOI: 10.1088/0031-8949/1/5-6/020.
- [19] JIA Yun, WANG Shuai, MA Xin, et al. Synthesis of thioxopropanamide surfactants for studying the flotation performance and adsorption mechanism on chalcopyrite [J]. Applied Surface Science, 2020, 505: 144539. DOI: 10.1016/j.apsusc.2019.144539.
- [20] SCHÖN G. ESCA studies of Cu, Cu₂O and CuO [J]. Surface Science, 1973, 35: 96–108. DOI: 10.1016/0039-6028(73)90206-9.
- [21] JOLLEY J G, GEESEY G G, HANKINS M R, et al. Auger electron and X-ray photoelectron spectroscopic study of the biocorrosion of copper by alginic acid polysaccharide [J]. Applied Surface Science, 1989, 37(4): 469–480. DOI: 10.1016/0169-4332(89)90505-9.
- [22] PARMIGIANI F, PACCHIONI G, ILLAS F, et al. Studies of the Cu–O bond in cupric oxide by X-ray photoelectron spectroscopy and *ab initio* electronic structure models [J]. Journal of Electron Spectroscopy and Related Phenomena, 1992, 59(3): 255–269. DOI: 10.1016/0368-2048(92)87005-7.
- [23] NEFEDOV V I, SALYN Y V, SOLOZHENKIN P M, et al. X-ray photoelectron study of surface compounds formed during flotation of minerals [J]. Surface and Interface Analysis, 1980, 2(5): 170–172. DOI: 10.1002/sia.740020503.
- [24] NEFEDOV V I, ZHUMADILOV É K, KOPYTOVA T Y. Comparison of the chemical shifts of X-ray electron and Auger lines [J]. Journal of Structural Chemistry, 1977, 18(4): 549–553. DOI: 10.1007/BF00745292.