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Floating sulfides: activating and poisoning surfaces

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Froth flotation is the established method of mineral separation in mineral processing. The flotation behaviour of sulfide minerals can be radically modified by surface sorption of metals from complex sulfide ore pulps; this can be both beneficial (activation) and problematic (poisoning). Using XAS (REFLEXAFS), the Pb species that "poison" and the Cu species that "activate" the surface of ZnS have been determined. The Cu activation, which is vital to successful ZnS flotation, involves Cu-Zn exchange at the ZnS surface and the development of an oxidised CuS species - xanthate attaches to this species forming covellite. Pb sorbs onto the ZnS surface as an Pb-O species which subsequently reacts with xanthate to form a PbS-like species. With chalcopyrite, both Zn and Pb can poison the surface; the Pb reacts with the CuS species which develops on the oxidised CuFeS₂ surface while Zn sorbs onto the FeOOH component present on the surface.

Keywords: Flotation, Sulfides, XAS, REFLEXAFS

1. Introduction

Froth flotation is the major method of mineral separation in ore processing, and is employed to separate finely ground complex sulfide ores into pure mineral concentrates. Flotation involves a selective sorption reaction between sulfide mineral particles and organic compounds, such as xanthates, which renders the mineral hydrophobic causing it to 'float'. If the mineral surface is modified, the flotation behaviour is changed - this can be used to successfully float hydrophilic minerals but can also cause problems when it inadvertently occurs in a mineral pulp (causing poisoning of the surface). In flotation plants, sphalerite (ZnS) is floated by activation with CuSO₄, but in polymetallic ores, Pb sorption onto the sphalerite is a major cause of flotation inefficiency. Chalcopyrite (CuFeS₂) has an inherent self-flotability but this is lost if Pb and Zn are present in solution.

In this investigation, fluorescence REFLEXAFS (reflection EXAFS) was used to study the environment of Cu and Pb sorbed onto the surface of sphalerite, and Zn and Pb sorbed onto the surface of chalcopyrite, with the aim of understanding the observed behaviour in flotation circuits and experimental studies. This technique involves directing the X-ray beam to hit the specimen at half the 'critical angle' (approximately 100 mdeg), at which the penetration depth is < 50 Å, and thus the technique is 'surface sensitive' (Greaves, 1991).

2. Experimental

For REFLEXAFS, ca. 2.5 x 8 cm slices of synthetic ZnSe, both synthetic ZnS and natural (Zn,Fe)S and polycrystalline CuFeS₂

were polished to optical flatness. The ZnSe and ZnS samples were first immersed in either 0.5 mol solution of CuSO₄ for 1 minute or 5 x 10⁻³ mol. lead nitrate solution for 10 minutes. The CuFeS₂ samples were first immersed in 5 x 10⁻³ mol. of either zinc or lead nitrate solution for 10 minutes at a pH of 5.5 where Zn²⁺/Pb²⁺ are the dominant species. The samples were then either analysed immediately or further reacted with 1g/200ml sodium isopropyl xanthate, [C₃H₇OCS₂Na, (Na⁺PrX)], for 10 minutes at pH 10, then analysed. The samples were rinsed with water after each immersion.

The XAS data were collected using the Synchrotron Radiation Source (SRS) at the CCLRC Daresbury Laboratory, UK (full details of experimental setup can be found in Patrick *et al.*, 1998). The spectra were calibrated, normalised and background subtracted to an edge step of unity using the Daresbury Laboratory programs EXCALIB and EXBACK (Diakun *et al.*, 1984). EXAFS data analysis was performed using the Daresbury program EXCURV92 (Binsted *et al.*, 1991).

3. Results and discussion

3.1 Activation of sphalerite

Analysis of the Cu K-edge fluorescence REFLEXAFS spectra (Table 1, Figures 1 & 2) produced from ZnSe treated with CuSO₄ reveal the Cu is bonded to the host selenium atoms, and oxygen. Data from activated ZnS reveals a similar picture with 3 S and 1 O atoms bonded to the Cu, lending credibility to the use of the ZnSe as an analogue. The best fit for the data from the (Zn,Fe)S is also 3 S and 1 O but the fit for 2 S and 2 O was very similar. In all cases these Cu-O, Cu-S and Cu-Se distances are typical for compounds of these elements.

Table 1

Summary of Cu K-edge fluorescence REFLEXAFS data of Cu sorbed onto ZnSe, ZnS and (Zn,Fe)S flat surfaces.

Sample	Type (angle, mdeg)	Atom	CN	r(Å)	2σ ² (Å ²)	Fit (R)
ZnSe + Cu	REFLEXAFS (125)	O	1	1.95	0.044	42.3
		Se	3	2.36	0.018	
ZnSe+Cu+ Na ⁺ PrX, pH10	REFLEXAFS (140)	S	1	2.21	0.008	39.1
		Se	3	2.39	0.031	
ZnS + Cu	REFLEXAFS (110)	O	1	2.07	0.030	32.8
		S	3	2.25	0.018	
ZnS+Cu + Na ⁺ PrX, pH10	REFLEXAFS (120)	S	4	2.25	0.021	41.8
		S	1	2.70	0.032	
(Zn,Fe)S+Cu 8Mol.% FeS	REFLEXAFS (130)	O	1	2.05	0.036	44.7
		S	3	2.25	0.020	
(Zn,Fe)S+Cu+ Na ⁺ PrX, pH 10.2 8Mol.%FeS	REFLEXAFS (140)	S	4	2.22	0.022	60.1
		S	1	2.75	0.012	

Footnote to Table 1: Angle is angle of incidence φ for REFLEXAFS. Atom is the type of scatterer, CN (±20%) is number of scatterers, at distance r (±0.02 Å, inner shells, ±0.05 Å outer shells), with Debye-Waller factor 2σ² (±20%).

The addition of Na⁺PrX to the ZnSe samples at pH 10, 'displaces' the oxygen to give an average copper coordination of 1 S and 3 Se atoms. The data from the ZnS and (Zn,Fe)S samples are comparable, except that they have a significant Cu-S distance of ca. 2.73 Å. Interpretation of the data suggest the formation of a CuS-like surface species, as identified in a study of amorphous CuS species (Patrick *et al.* 1997).

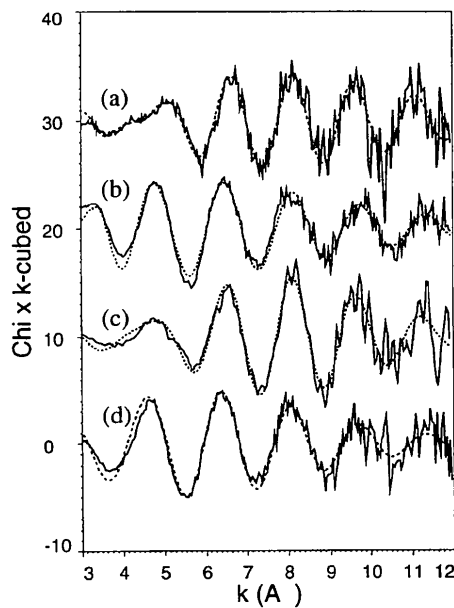


Figure 1

Cu K-edge fluorescence REFLEXAFS spectra (solid lines) and theoretical fits (broken lines) corresponding to the analyses in table 2 and 3 of a) ZnSe + Cu; b) ZnS + Cu; c) ZnSe + Cu + Na¹PrX, (pH 10); d) ZnS + Cu + Na¹PrX, (pH 10).

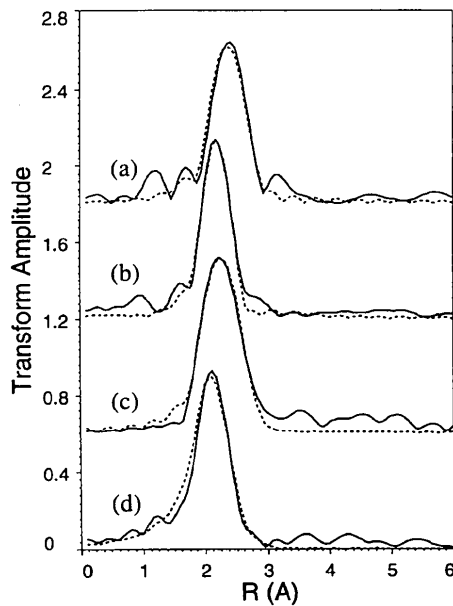


Figure 2

Fourier transforms of the Cu K-edge fluorescence REFLEXAFS spectra (solid lines) and theoretical fits (broken lines) of a) ZnSe + Cu; b) ZnS + Cu; c) ZnSe + Cu + Na¹PrX, (pH 10); d) ZnS + Cu + Na¹PrX, (pH 10).

3.2 Poisoning of sphalerite

The Pb L_{III}-edge data (Table 2) collected for the ZnS and (Zn,Fe)S samples reacted with aqueous Pb gave a best fit with Pb bonded to 2 O atoms at *ca.* 2.3 Å and 3 O atoms at *ca.* 2.5 Å, with Pb-Pb distances of 3.9 and 4.6 Å. The spectrum has the characteristics of a metal in a disordered structural environment; this is a common feature of Pb oxides. Although Pb²⁺ is the predominant species in solution at pH 5.5, the sorption process may involve the first hydrolysis product, Pb(OH)⁺, as it is more easily absorbed onto mineral surfaces.

Table 2

Pb L_{III}-edge spectra of Pb sorbed onto ZnS, and (Zn,Fe)S. (See Table 1 for definitions)

Sample	Type (angle, mdeg)	Atom	CN	r(Å)	2σ ² (Å ²)	Fit (R)
ZnS + Pb	REFLEXAFS (87)	O	2	2.29	0.073	44.5
		O	3	2.51	0.063	
		Pb	3	3.82	0.41	
		Pb	5	4.54	0.17	
(Zn,Fe)S + Pb	REFLEXAFS (85)	O	1	2.26	0.043	55.1
		O	3	2.49	0.050	
		O	2	3.12	0.050	
		Pb	4	3.81	0.047	
		Pb	6	5.35	0.027	
ZnS+Pb + Na ¹ PrX pH 7	REFLEXAFS (85)	O	2	2.50	0.68	34.8
		S	2	2.84	0.065	
		O	3	3.12	0.013	
		Pb	4	3.99	0.013	
		Pb	4	4.63	0.013	
(Zn,Fe)S + Pb + Na ¹ PrX pH 7.1	REFLEXAFS (80)	O	2	2.45	0.049	36.5
		S	3	2.84	0.041	
		O	2	3.01	0.017	
		Pb	4	4.09	0.020	
		Pb	4	4.84	0.082	

Analysis of the samples reacted with Na¹PrX indicate the presence of a more uniform Pb environment on the ZnS surfaces, which revealed two Pb-O bonds of 2.4-2.5 Å and, significantly, two S atoms at a distance of *ca.* 2.85 Å, with additional Pb shells at *ca.* 4.0 and 4.7 Å. The bond distances and spectral characteristics are consistent with the formation with of a PbX₂ species at the surface.

3.3 Poisoning of chalcopyrite

The REFLEXAFS data from the Zn sorbed on the CuFeS₂ surface (Table 3) show that, prior to xanthate addition the zinc is bonded to oxygen, with no evidence of sulfur coordination. There are additional shells of metal backscatterers at *ca.* 3.2 Å, with Fe giving a slightly better fit than Cu and Zn. On addition of Na¹PrX the spectrum changes dramatically; the analysis clearly shows sulfur in the inner coordination sphere and the best fit gives 1 oxygen at *ca.* 2.0 Å and 3 sulfurs at *ca.* 2.3 Å. A more distant metal shell (best fit with Fe) is seen at *ca.* 4.1 Å.

The data obtained from the CuFeS₂ reacted with Pb (Table 4) revealed that the inner coordination sphere comprised 2 oxygen atoms at *ca.* 2.4 Å and 3 sulfur atoms at *ca.* 2.9 Å, with a possible metal shell at *ca.* 4.8 Å. After treatment with Na¹PrX only sulfur is present in the inner coordination sphere and a metal shell could be fitted at *ca.* 4.1 Å. This metal shell is fitted best with Fe atoms although fits with Cu or Zn were virtually identical, but the fits with Pb atoms were significantly worse.

Table 3

Zn K-edge REFLEXAFS spectra of the surface of CuFeS₂ reacted with Zn(NO₃)₂ (See Table 1 for definitions)

Sample	Type (angle, mdeg)	Atom	CN	r(Å)	2σ ² (Å ²)	Fit (R)
CuFeS ₂ + Zn pH 5.5	REFLEXAFS (115)	O	4	2.00	0.013	71.6
		Fe	4	3.18	0.031	
CuFeS ₂ + Zn + Na ⁱ PrX pH 10.2	REFLEXAFS (115)	O	1	1.97	0.003	31.5
		S	3	2.33	0.011	
		Fe	4	4.14	0.049	

Table 4

Pb L_{III} edge REFLEXAFS spectra of the surface of CuFeS₂ reacted with Pb(NO₃)₂ (See Table 1 for definitions)

Sample	Type (angle, mdeg)	Atom	CN	r(Å)	2σ ² (Å ²)	Fit (R)
CuFeS ₂ + Pb pH 5.5	REFLEXAFS (115)	O	3	2.37	0.045	51.4
		S	2	2.91	0.043	
		Fe/Cu ¹	4	4.75	0.044	
CuFeS ₂ + Pb + Na ⁱ PrX, pH 10.2	REFLEXAFS (90)	S	4	2.71	0.046	62.6
		Fe	4	4.07	0.050	

¹ The addition of this shell improved the fit but the data quality may not justify the addition of the extra parameters.

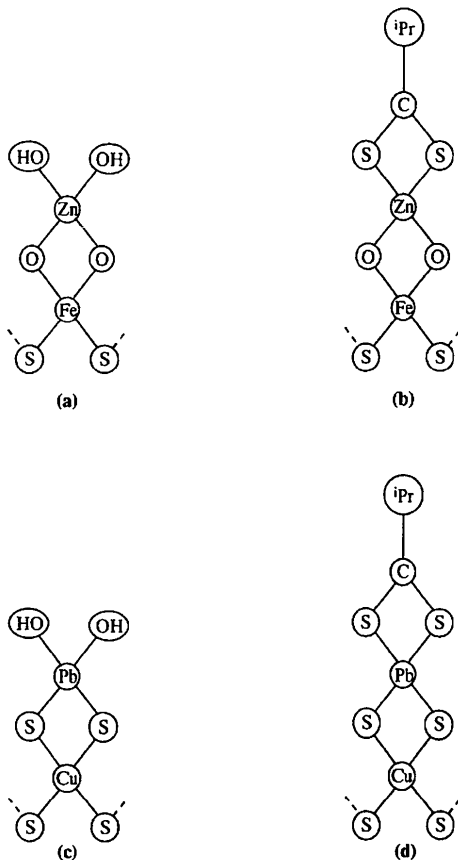
Studies of the surface of chalcopyrite show that the main species present are CuS (responsible for the self-flotability of chalcopyrite) and a Fe(OH)_x-type species. Our data indicates that the Fe(OH)_x species is the site of Zn sorption (Figure 3). The appearance of S bonded to the Zn on the addition of NaⁱPrX shows that the xanthate sulfur displaces oxygen, although some Zn-O bonds are retained. The Pb bonds directly to the S atoms on the mineral surface, thus rendering the hydrophobic areas of the CuFeS₂ surface hydrophilic. When xanthate is added, it preferentially reacts with the Pb-O species by displacing the oxygen and these areas become hydrophobic again. Thus, the loss in self flotability of chalcopyrite would be much less affected by Zn than by Pb sorption.

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**Figure 3**

A schematic representation of the environments of Zn and Pb on the surface of chalcopyrite. (a) CuFeS₂ + Zn (b) CuFeS₂ + Zn + NaⁱPrX (c) CuFeS₂ + Pb (d) CuFeS₂ + Pb + NaⁱPrX.