Arsenopyrite: a spectroscopic investigation of altered surfaces

S. RICHARDSON

Dept. of Geological Sciences, Aston University, Birmingham B4 7ET

AND

D. J. VAUGHAN

Dept. of Geology, The University, Manchester M13 9PL

Abstract

Surfaces of a natural sample of arsenopyrite (FeAsS) were oxidized by a range of inorganic oxidants, and the resultant surface alteration products studied using various spectroscopic techniques. The oxidants used were air during heating to relatively low temperatures (150 °C), steam, ammonium hydroxide, hydrogen peroxide, and sulphuric acid. Electrochemical oxidation in water was also undertaken. X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), and spectral reflectance measurements, were used to characterize the surface compositions. New data are proposed for the binding energies of core electrons in arsenopyrite based on the fitted XPS spectra: 706.9 eV for the Fe $2p^{3/2}$ level, 161.2 eV for the S $2p$ level, and 40.7 eV for the As $3d$ level. Spectroscopic analyses of the surfaces following oxidation indicated a range of iron oxides and hydroxides ($Fe_{1-x}O$, Fe_3O_4, Fe_2O_3, FeOOH and $Fe(OH)_3$), arsenic oxides (As_2O_3 and As_2O_5), sulphur and iron sulphates ($FeSO_4$, $Fe_2(SO_4)_3$). The relative proportions of the different phases present in the surface layer are related to the strength of the oxidant employed and, where relevant, the Eh/pH conditions prevalent during oxidation. The conclusions regarding the nature of the oxidation of arsenopyrite are discussed in relation to arsenopyrite extraction by flotation and leaching, and the breakdown of arsenopyrite in natural systems.

KEYWORDS: arsenopyrite, sulphides, surface, spectroscopy, XPS, AES.

Introduction

ARSENOPYRITE (FeAsS) is a major mineral in several ore associations, and a minor component in many others (Ramdohr, 1980; Craig and Vaughan, 1981). However, the demand for arsenopyrite as an ore is limited, since the arsenic production requirement of most countries is met by extraction from the flue dusts of smelters. From the viewpoint of both contamination of the products of processing, and environmental considerations, arsenopyrite is more often an unwanted mineral. The processes involved in arsenopyrite extraction and the efficiency of these processes are therefore important from both commercial and environmental standpoints. Foremost in these processes, is the behaviour of arsenopyrite surfaces in flotation systems. The leaching of arsenopyrite in tailings may create environmental problems and lead to the contamination of water systems by soluble arsenic species.

For these reasons, the surface characteristics are important in understanding the behaviour of arsenopyrite during processing and in oxidation. This investigation has involved the surface analysis of arsenopyrite oxidized by several inorganic oxidants.

Surface preparation

The arsenopyrite used in this investigation was from the collection of the British Museum (Natural History), catalogue number BM 1927,1624. The sample comprised several arsenopyrite crystals, of which one crystal of approximately 1 cm^3 was sliced such that the analysed surfaces were

Mineralogical Magazine, April 1989, Vol. 53, pp. 223–9

Table 1. Comparative alteration of the arsenopyrite surfaces, indicated by reflectance (R%) changes and the oxygen content of the surface estimated from Auger depth profiles. In the table, the sputter depth is determined from an estimated etch rate of 1 Å per minute.

Oxidants	Final reflectance (average*)		Auger estimation of surface oxygen, $(O/(O+Fe+As+S) \times 100)$, at a sputter depth of -		
	546nm	589nm	0Å(surface)	~30Å	~60Å
Unoxidised	51	53			
O_2/air	46	48	36	2	0
Steam	43	44	55	4	2
NH_4OH	38	40	61	10	7
H_2O_2	23	27	65	10	8
H_2SO_4	28	31	70	18	7
H_2O (0.8V)	23	24	72	25	10

* The values are an average of both R_{max} and R_{min}, and of a series of measurements.

cut in the same orientation, important in view of the effects of orientation on the spectroscopic analyses. Careful examination in polished section, along with X-ray diffraction and electron microprobe analyses show the sample to be of high purity (with atomic proportions; Fe = 32.8%, As = 31.1% and S = 36.0%, with no trace impurities). The arsenopyrite ($Fe_{0.91}As_{0.86}S$) is noted as FeAsS in the diagrams for simplicity.

In air and water, arsenopyrite is slow to oxidize, so oxidants were used to accelerate the rates of oxidation and to exemplify the changes in character of the surface during oxidation in aqueous media under various pH and Eh conditions and in oxygen/air during heating at relatively low temperatures. The strengths of the oxidants and the length of exposure were based on previous unpublished work concerning the surface oxidation of pyrite, pyrrhotine, and chalcopyrite. The oxidants used were: (1) air (furnace at 150 °C); (2) steam for 2 hours; (3) 10 M NH_4OH for 30 minutes; (4) 25 vol. % H_2O_2 for 20 minutes; (5) 3 M H_2SO_4 for 30 minutes; (6) an electrochemical potential of 0.8 V in water.

Optical properties

Arsenopyrite is moderately bireflectant in most orientations in plane polarized reflected light. However, the sections were prepared in orientations showing no measurable birereflectance. Quantitative measurement of reflectance was carried out on a Reichert reflex spectral microphotometer using a WTiC standard, as approved by the Commission on Ore Microscopy of the International Mineralogical Association. The technique of using reflectance measurements to indicate the degree of oxidation has to be treated with caution, since the change in reflectance will be affected by the character of the oxidized phases on the surface, and the degree of scattering of light caused by the formation of the oxidized layer. However, the final reflectance measured is consistently proportional to the depth of oxidation as determined by spectroscopic techniques. Data on the oxidized surfaces for two of the COM standard wavelengths, 546 nm and 589 nm, are included in Table 1.

Auger electron spectroscopy

Auger electron spectroscopy (AES) can provide analyses of the elemental surface compositions to a depth of approximately 10 Å. The technique, and its applications to mineralogy have been discussed in Berry and Vaughan (1985) and Vaughan and Tossell (1986).

To produce Auger electrons, the core levels of elements are excited by the primary ejection of an electron as a consequence of electron bombardment of the surface. This leaves the core in an excited state, which relaxes when an electron from an outer orbital fills the vacancy with the associated photoemission of a quantized Auger electron, leaving the element in a doubly-ionized state.

The Auger spectra in this investigation were recorded using a Kratos XSAM 800 XPS/Auger spectrometer. The spectra were obtained in differentiated form after a primary electron beam excitation of 3 keV. By combining AES with argon ion sputtering (i.e. the mechanical erosion of the surface using argon ions), an elemental profile with depth can be obtained. The sputtering in this investigation was achieved using a Kratos Minibeam 1 ion gun with a 5 keV voltage and 1 μA cm^{-2} sample current, producing an estimated sputter rate of 1 Å min^{-1}.

The interpretation of the data in terms of the oxygen content of the surfaces at set sputter depths is included in Table 1. Oxygen was chosen to show the character of the surface because of its incorporation in most of the oxidation products. The sulphur concentration, interpreted from the differentiated Auger spectra, tends to be inversely proportional to the oxygen concentration. However, because sulphur may form as one of the oxidation products, the relationship between sulphur and oxygen concentration with respect to oxidation is not a simple inverse relationship. Auger data indicate the formation of an oxidized surface that diminishes rapidly, both chemically and in magnitude, within 30 Å of the surface. The oxygen detected below this sputter depth is of low concentration, and may be due to mixing with the surface components and an uneven surface removal during sputtering.

X-ray photoelectron spectroscopy

X-ray photoelectron spectra were also recorded using a Kratos XSAM 800 XPS/Auger spectrometer, with Mg–*Kα* X-rays as the exciting radiation. X-ray Photoelectron Spectroscopy (XPS) is important in the study of altered and unaltered surfaces due to its excellent surface sensitivity (of approximately 10 to 15 Å in thickness). XPS is used to provide chemical state information for surfaces.

The X-ray photoelectron effect involves the ejection of electrons as a result of bombardment with Mg–*Kα* X-radiation. The core electrons for example, are emitted with quantized kinetic energies, and these kinetic energies can be used to calculate the binding energies of electrons at particular energy levels in the solid. The binding energies can be used to indicate the chemical phases present in the material (surface layer) being studied (Briggs and Seah, 1983). Mineralogical applications have been discussed by Berry and Vaughan (1985). The use of sputtering to analyse chemical surfaces with depth, as with AES, is not possible due to the chemical reduction of surface components, as indicated for sulphides by Tsang *et al.* (1979).

In this investigation, the spectra obtained were fitted using a non-linear least-squares fitting procedure. New data for selected energy levels in arsenopyrite are proposed. These, and previous data for peak positions and linewidths are included in Table 2. Additional data for the iron oxides and hydroxides (McIntyre and Zetaruk, 1977; Harvey and Linton, 1981; Mills and Sullivan, 1983), sulphates (Frost *et al.*, 1974; Limouzin-Maire, 1981) and arsenic oxides (Bahl *et al.*, 1976; Wagner *et al.*, 1979) were also used during this study.

The arsenopyrite surfaces were orientated. This is important since it removes the possibility of differences in the spectra being due to the crystallographic orientation. This effect, and the effect of crystallographic orientation on the nature of oxidation are topics requiring further detailed investigation.

In Fig. 1, two Fe $2p$ spectra are illustrated. The upper spectrum shows the unoxidized arsenopyrite, from which a Fe $2p^{3/2}$ binding energy of 706.9 eV was fitted. The lower spectrum, for steam-oxidized arsenopyrite, indicates the presence of phases with higher binding energy Fe $2p^{3/2}$ electrons. These are interpreted as various iron-containing oxidized phases, the values being consistent with a range of iron(II) and (III) oxides and hydroxides, with associated oxysulphates. The overlapping of the peak envelopes for the oxides and hydroxides, as indicated in Table 2, makes it more expedient to fit the peaks in terms of the iron(II) and (III) oxidation states, rather than assign them to simple oxides and hydroxides. The same fitting procedure was used with the oxygen 1*s* spectra.

The determination of the peak area due to the sulphate in the Fe $2p^{3/2}$ and S $2p$ spectra is difficult because, although the peak positions have been defined previously in work by Frost *et al.* (1974) and Limouzin-Maire (1981), the Fe $2p^{3/2}$ spectrum in this region, and to a lesser extent the Fe^{3+} region, is affected by shake-up lines from the compounds with lower binding energies. The shake-up lines are prominent satellites caused, in this case, by the paramagnetic state of the Fe(II) and Fe(III) in the surface. In the Fe $2p^{3/2}$ spectra, the $Fe_2(SO_4)_3$ peak was fitted at 714.6 eV, which has consequently been found to be slightly high. The use of a lower value does not alter the peak area calculation significantly. A more accurate assessment of the molecular proportion of sulphates in the surface can be obtained using the

Table 2. X-ray photoelectron data: The binding energies (B.E.) and peak widths for relevant energy levels.

Compound	B.E. (eV)	Linewidth (eV)	Compound	B.E. (eV)	Linewidth (eV)
	Fe 2p 3/2			O 1s	
FeAsS	706.9	0.9	$Fe_{1-x}O$	530.0	0.7
$Fe_{1-x}O$	709.5	1.3	$Fe_3O_4(2+)$	530.0	0.7
$Fe_3O_4(2+)$	709.5	1.3	$Fe_3O_4(3+)$	531.4	1.1
$Fe_3O_4(3+)$	710.8	1.5	Fe_2O_3	531.4	1.1
Fe_2O_3	711.0	1.5	FeOOH (O)	530.0	0.7
FeOOH	711.0	1.5	FeOOH (OH)	531.4	1.1
$Fe(OH)_3$	711.0	1.5	$Fe(OH)_3$	531.4	1.1
$FeSO_4$	712.3	1.8	$FeSO_4$	532.6	1.3
$Fe_2(SO_4)_3$	714.6	1.8	$Fe_2(SO_4)_3$	532.9	1.3
Fe^{2+}	709.8	1.4	As_2O_3	531.0	1.1
Fe^{3+}	711.0	1.6	As_2O_5	531.4	1.1
	S 2p			As 3d	
FeAsS	161.2	0.9	FeAsS	40.7	1.2
sulphur	162.5	1.2	As_2O_3	42.7	1.4
$FeSO_3$	165-6	1.4	As_2O_5	44.3	1.4
$FeSO_4$	168.0	1.4			
$Fe_2(SO)_3$	168.2	1.4			

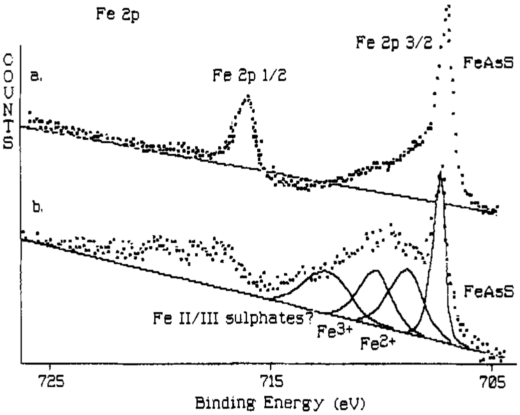

FIG. 1. X-ray photoelectron Fe $2p^{3/2}$ spectra for (*a*) unoxidized arsenopyrite and (*b*) steam-oxidized arsenopyrite.

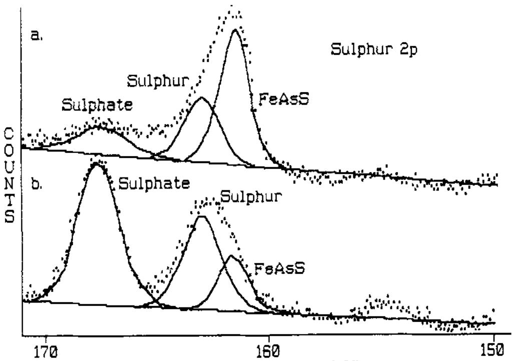

FIG. 2. X-ray photoelectron sulphur 2*p* spectra obtained following (*a*) furnace oxidation and (*b*) sulphuric acid oxidation.

sulphur 2*p* and the arsenic 3*d* spectra. Fig. 2 shows the sulphur 2*p* spectra for arsenopyrite oxidized by heating in oxygen/air (150 °C) and by sulphuric acid. The expected enhancement of sulphate peaks in the sulphuric acid oxidized sample is evident. It is also possible to determine the proportion of sulphur (0) in the surface from the S 2*p* spectra. This is inferred to arise as a result of elemental sulphur formation on the oxidized arsenopyrite surfaces.

The arsenic 3*d* spectra, shown in Fig. 3, indicate the formation of arsenic(III) species in the altered surfaces, and in the case of sulphuric acid, the additional presence of arsenic(V) species. The formation of arsenic oxides due to heating in oxy-

Table 3. Estimated percentages of phases present in the 10-15 Å surface layer of oxidised arsenopyrite, derived from x-ray photoelectron data.

Compound	Oxidants					
	O_2/air 150°C 3 days	steam 2hr	NH_4OH 10M 30 min	H_2O_2 25 vol 20 min	H_2SO_4 3M 30 min	H_2O 0.8 V 20 min
$FeSO_4/Fe_2(SO_4)_3$	9	13	9	18	14	18
As^{5+}					21	
As^{3+}	7	11	15	18	11	26
Fe^{3+} oxides/	12	18	22	27	24	25
Fe^{2+} hydroxides	16	22	23	17	17	18
Sulphur	21	15	12	11	9	9
FeAsS	35	21	19	9	4	4

gen/air is expected. However, the formation of arsenic oxides during oxidation in solutions in the proportions detected is surprising, considering their very high solubilities. Wedepohl (1978) cites solubility values of 20.5 gl^{-1} for arsenic(III) oxide, and an even higher solubility for arsenic(V) oxide. A possible explanation for the unexpected insolubility of the arsenic compounds is the potential for arsenite and arsenate formation. In Fig. 3, at increased binding energies, the Fe 3*p* spectrum is also seen. As the oxidation, indicated by the concentration of the arsenic oxides, increases there is a shift in the Fe 3*p* peak maximum to higher binding energies, consistent with the oxidation of iron. The resolution of the Fe 3*p* electron binding energies is less defined than the Fe 2*p* binding energies, due to the greater delocalization of electrons in the 3*p* energy level of iron.

Surface analysis

By using the XPS peak areas for the surface compounds, the approximate percentages of the phases present in the analysed surfaces can be estimated. These approximations are shown in Table 3.

The iron oxides/hydroxides have been grouped together in this table although separated in terms of the oxidation state of iron. It is probable that in the oxidized surfaces, the Fe^{2+} species predominate as a component of magnetite, Fe_3O_4. In less oxidized surfaces, the Fe^{2+} oxide component is greater than that of Fe^{3+}, suggesting the presence of wüstite, $Fe_{1-x}O$. Where the Fe^{3+} ion predominates in an aqueous environment, it will be easily hydrated and is likely to precipitate as iron(III) hydroxides and a form of FeOOH, rather than iron(III) oxide, although this is the most stable phase. Iron(III) oxide would be expected as the major iron(III) phase in the surface in oxygen/air during heating at low temperatures.

In the oxidized surfaces, arsenic(III) species are major components, which indicates that the rate of formation of the oxidized arsenic phase is greater than the dissolution of arsenic from the surface. The formation of arsenic(V) species is limited to oxidation in sulphuric acid, and can be explained in terms of Eh/pH diagrams, where the field of stability of As_2O_5 is limited to low pH and high Eh.

A major phenomenon in the surface oxidation concerns the inter-relationship between the sulphur species. In general, the formation of oxysulphates increases with the apparent depth of oxidation as determined by reflectance and AES techniques. Conversely, the presence of sulphur is inversely proportional to the depth of oxidation. It could be inferred that sulphur is the initial product of arsenopyrite oxidation and that the sulphur is being progressively oxidized, although sulphites would then be expected to form in measurable quantities. The Eh/pH conditions of the oxidation appear to have a considerable effect on the sulphur species forming in the surface, and these conditions also suggest that the arsenopyrite oxidizes directly to sulphates.

Conclusions

Arsenopyrite is stable in air and in water at room temperature. In acid and alkaline environments arsenopyrite surfaces oxidize fairly rapidly, but to a limited depth into the surface. The products of oxidation are for the most part uniform, with the variations in surface compositions produced by different aqueous oxidants the result of

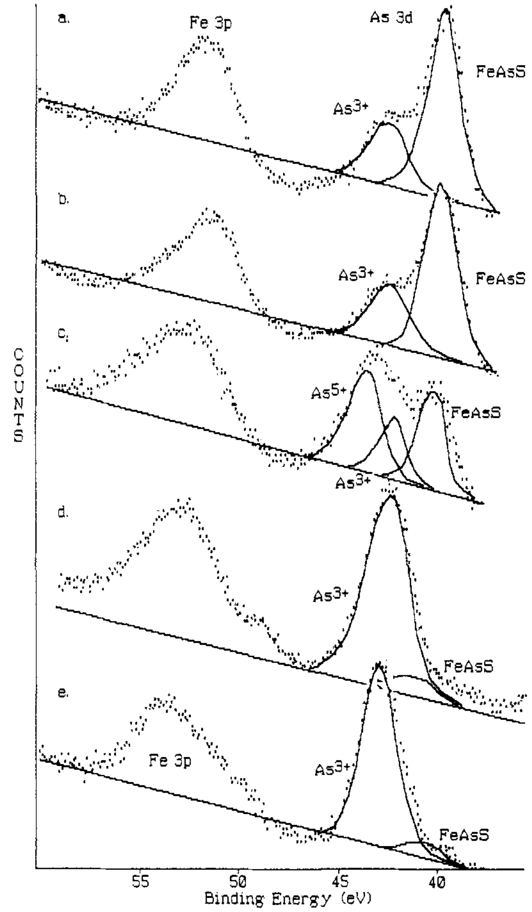

FIG. 3. Comparative X-ray photoelectron spectra for fitted As 3*d* and unfitted Fe 3*p* obtained following (*a*) furnace oxidation, (*b*) steam oxidation, (*c*) sulphuric acid oxidation, (*d*) electrochemical oxidation, and (*e*) hydrogen peroxide oxidation.

the particular Eh/pH conditions. Although the arsenic compounds expected to form have a high solubility, they are prevalent in the altered surfaces. This may be due to the reaction rate being faster than that of dissolution, or it could be due to the arsenic compounds forming in the subsurface below the oxidizing interface. The formation of ferrous and ferric arsenites or arsenates may account for the unexpected solution characteristics.

The surface characterization of arsenopyrite subject to oxidation is important in its applications to flotation methods of extraction. In order to deduce the possible surface interactions with flotation reagents, further analysis is required. However, the present investigation on the oxidation of arsenopyrite surfaces indicates that the concentration of sulphur in the surface layer can be influenced by chemical conditions and may be important in this respect.

Consideration must be given to the disposal of arsenopyrite tailings, since this investigation has shown that in solutions of low pH, such as those found in tailings dumps, arsenopyrite will oxidize rapidly, and water percolating through the dumps will subsequently dissolve soluble arsenic oxides. The involvement of other sulphides likely to be present in dump materials will be important in the generation of sulphuric acid and lowering of the pH, thus further increasing the formation of soluble arsenic oxides. If the run-off enters the drainage system it will result in serious local pollution of the environment.

Acknowledgements

The authors would like to thank Mr A. Abbot, and the Dept. of Electrical and Electronic Engineering and Applied Physics, Aston University, for help in obtaining the XPS and Auger spectra. The British Museum (Natural History) is thanked for supplying the arsenopyrite sample. Financial support from NATO (Grant 833/83 to D. J. Vaughan and J. Tossell) is gratefully acknowledged, as is the provision of a Studentship by the University of Aston to S. Richardson.

References

Bahl, M. K., Woodall, R. O., Watson, R. L. and Irgolic, K. J. (1976) Relaxation during photoemission and LMM auger decay in arsenic and some of its compounds. *J. Chem. Phys.* **64**, 1210–18.

Berry, F. J. and Vaughan, D. J. (1985) *Chemical bonding and spectroscopy in mineralogy*. Chapman and Hall, London.

Briggs, D. and Seah, M. P. (1983) *Practical surface analysis by Auger and X-ray photoelectron spectroscopy*. Wiley.

Craig, J. R. and Vaughan, D. J. (1981) *Ore microscopy and ore petrography*. Wiley.

Frost, D. C., Leeder, W. R. and Tapping, R. L. (1974) X-ray photoelectron spectroscopic study of coal. *Fuel* **53**, 206–11.

Harvey, D. T. and Linton, R. W. (1981) Chemical characterisation of hydrous ferric oxides by X-ray photoelectron spectroscopy. *Anal. Chem.* **53**, 1684–8.

Limouzin-Maire, Y. (1981) Etude par spectroscopie ESCA de sulfures et sulfates de manganese, fer, cobalt, nickel, cuivre et zinc. *Bull. Chim. Soc.* (France), Pt 1, 340–3.

McIntyre, N. S. and Zetaruk, D. G. (1977) X-ray photoelectron spectroscopic studies of iron oxides. *Anal. Chem.* **49**, 1521–9.

Mills, P. and Sullivan, J. (1983) An XPS study of the bonding of core level electrons in iron oxides. *J. Phys. D. Appl. Phys.* **16**, 723–32.

Ramdohr, P. (1980) *The ore minerals and their intergrowths* (2nd ed.) Pergamon Press.

Tsang, T., Coyle, G. J., Adler, I. and Yin, L. (1979) XPS studies of ion bombardment damage of iron–sulphur compounds. *J. Electron Spectroscopy and related phenomena* **16**, 389–96.

Vaughan, D. J. and Tossell, J. A. (1986) Interpretation of the Auger electron spectra (AES) of sulfide minerals. *Phys. Chem. Min.* **13**, 347–50.

Wagner, C. D., Gale, L. H. and Raymond, R. H. (1979) Two dimensional chemical state plots: A standardised data set for use in identifying chemical states by X-ray photoelectron spectroscopy. *Anal. Chem.* **51**, 466–82.

Wedepohl, K. H. (ed.) (1978) *Handbook of Geochemistry*, II/3, Arsenic 33-H-1, Springer-Verlag, Berlin.

[*Manuscript received 17 March 1988*]