JOURNAL OF APPLIED ELECTROCHEMISTRY **24** (1994) 513–520

Interaction of Galena with hydrosulphide ions under controlled potentials

A.N. BUCKLEY*

CSIRO Division of Coal & Energy Technology, PO Box 136, North Ryde, NSW 2113, Australia

I.M. KRAVETS

SKB Mekhanobr, 21st Liniya 8a, VO, St. Petersburg 199026, Russia

A.V. SHCHUKAREV

Mekhanobr-Analyt, 21st Liniya 8a, VO, St. Petersburg 199026, Russia

R. WOODS

CSIRO Division of Mineral Products, PO Box 124, Port Melbourne, Victoria 3207, Australia

Received 14 July 1993; revised 1 November 1993

The surface species produced by the anodic oxidation of hydrosulphide ions at galena surfaces have been determined by X-ray photoelectron spectroscopy. Components in the S(2p) spectrum appeared at binding energies typical of sulphur atoms in an oligosulphide. The relative intensities of these components suggested that lead oligosulphides with sulphur chain lengths of up to S_4 (or S_8 if a chelate) had been formed on the mineral surface. No evidence was found for the deposition of elemental sulphur. The oligosulphide is associated with a dispersed layer of lead sulphide formed by interaction of oxidized lead species and HS^-. Investigations were also carried out on the surface oxidation of galena on exposure to air. Previous findings that the formation of lead hydroxide becomes evident from a shifted component in the Pb(4f) spectrum without any new sulphur environment being apparent from the S(2p) spectrum were confirmed. This behaviour is ascribed to diffusion of lead atoms from the bulk to maintain only a small metal deficiency in a lead-deficient sulphide layer formed concomitantly with lead hydroxide.

1. Introduction

The products of the interaction of galena surfaces with alkaline sodium sulphide solution are of interest from both practical and theoretical viewpoints. The beneficiation by flotation of oxidized base-metal ores and sulphide ores containing oxidized base metal minerals is increasingly being carried out after treating the ore with sodium sulphide [1, 2]. Crozier [2] considers "the new popularity of sulphidisation is due to the availability of reliable electrode probes that can assure the availability of sufficient sulphhydrate ion concentration for surface sulphidisation, while keeping the total NaHS concentration lower than the depression range". The concept of using electrode sensors for CPS (controlled potential sulphidization) was devised in CSIRO, Australia [3, 4]. This concept has also been developed in Russia at Mekhanobr [5] and has been applied successfully in practice to the treatment of lead–zinc and other ores.

In addition to operating as an activator for oxidized minerals and as a selective depressant for the separation of sulphide minerals, sulphur(−II) species in solution can induce flotation in the absence of conventional collectors [6, 7]. In this role, sulphur(−II) species function through reaction with oxygen to deposit sulphur on the mineral surface. Self-induced flotation of sulphide minerals, including galena, can also occur through surface oxidation [8]. Therefore, for optimization of flotation performance, it is important to know how each mineral species in a complex ore responds to the flotation environment. Galena is often one of the valuable constituents in such polymetallic sulphide ores, but its surface has yet to be fully characterized following interaction with hydrosulphide solutions.

The deposition of sulphur on to the surface of galena by oxidation of sulphur(−II) species has been compared [9] with that on gold, pyrite and chalcopyrite using the rotating ring disc electrode (RRDE) technique in order to elucidate depressant action and sulphur-induced flotation. It was shown that the reaction proceeded on each surface through oligosulphide (polysulphide) ion intermediates with

---

*Author to whom correspondence should be addressed.

0021-891X

the fraction of the current resulting in oligosulphide increasing in the order gold ≈ pyrite < chalcopyrite < galena. Depressant action was considered to involve oxidation of sulphur(−II) lowering the potential of the mineral below the value at which the surface interacts with the collector, while only proceeding to the oligosulphide ion stage. Sulphur-induced flotation occurs at low sulphur(−II) concentrations in which situation the potential increases into the region where oligosulphide ions are oxidized further to sulphur.

X-ray photoelectron spectroscopy (XPS) studies have been carried out to characterise the sulphur product of the interaction of hydrosulphide ions with gold [10], pyrite [11, 12], chalcopyrite [12], sphalerite [13] and chalcocite [14]. The initial sulphur layer on gold was found to be a gold sulphide species and this confirmed previous electrochemical findings [15] that showed the oxidation of hydrosulphide ions to give rise to an anodic prewave with a charge equivalent to a sulphur fractional surface coverage of about 0.4. Multilayer sulphur deposited on gold was found [10] to have a lower volatility and a smaller electron binding energy than bulk elemental sulphur and it was suggested that this could be due to the layer being an oligosulphide.

Support for this hypothesis has recently been provided by surface-enhanced Raman spectroscopy [16] and scanning tunneling microscopy [17]. In the latter study, sulphur was deposited electrochemically and the initial layer was identified as adsorbed monomeric sulphur with a coverage of 1/3 in a $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure with respect to the gold lattice. Multilayer deposition gave rise to arrays of rectangular close-packed structures which consisted predominantly of S_8 rings but with S–S bond distances significantly greater than those of bulk-phase polysulphur, and similar to those in oligosulphides.

The oxidation of hydrosulphide ions on chalcocite [14] results in the formation of copper sulphides of lower copper content. The initially deposited sulphur layers on sphalerite [13] and chalcopyrite [12] have an effective oxidation state of less than zero and behave as a metal-deficient sulphide layer similar to that created at the surface of the mineral on oxidation [13, 18, 19]. This suggests that the oxidation of hydrosulphide ion on these surfaces first results in an extension of the sulphide lattice with a separate sulphur phase only occurring for thick layers. In contrast, the initial layer of deposited sulphur on pyrite [11, 12] was found to be in the elemental form.

The nature of the sulphur deposited on galena as a result of interaction with hydrosulphide ions is also relevant to attempts to elucidate the mechanism of the surface oxidation of this mineral. Studies of the initial stages of galena oxidation by XPS [20–22] have shown that a shifted Pb(4f) intensity appears which is indicative of the development of oxidized lead species, but that no new sulphur environments become apparent. In contrast, the formation of a metal-deficient sulphide in the surface oxidation of chalcopyrite [18, 19] and pyrrhotite [23, 24] is evident from shifted components in the S(2p) spectrum. These sulphur-rich phases are important since they appear to be responsible for self-induced flotation [25].

In this communication, the results of investigations carried out to characterize the sulphur layer formed on galena are presented. A reexamination of the initial oxidation of galena in air with a spectrometer enabling the use of monochromatized X-rays, low electron take-off angle and small analysis area is also reported.

2. Experimental details

The galena investigated was prepared from large, natural crystals from the Zinc Corporation Mine, Broken Hill, NSW, Australia. Electron microprobe analyses of two of the surfaces examined by XPS indicated that the only significant impurities were 0.06% Sb at one surface, and 0.07% Sb and 0.02% Cu at the other. XRD analysis showed that the galena was not a single crystal, but the fracture surfaces were predominantly aligned in the {1 0 0} direction. The mineral studied was from the same source as that used in some previous XPS investigations [20, 22, 26, 27].

The X-ray photoelectron spectra were obtained with a Perkin–Elmer 5400 spectrometer at an operating pressure below 10^{-6} Pa and using monochromatized AlK_α radiation (600 W). Electron take-off angles of 15° and 45° were used for fracture and abraded surfaces, respectively. Pb(4f), S(2p), O(1s) and C(1s) spectra were determined at an analyser pass energy of 8.95 eV, and combined S(2p)/Pb(4f) spectra (to monitor the shape and level of the background in the S(2p) binding energy region) at a pass energy of 17.90 eV. In most cases, specimens were transferred to a precooled ($< -100^\circ$ C) sample stage in the analyser chamber within a few minutes of evacuation of the nitrogen in the sample introduction chamber, however the sample stage in the introduction chamber was only slightly below room temperature. Samples were cooled as soon as possible in order to prevent sublimation of any moderately volatile reaction products that might have been formed at the surfaces studied, and to minimize radiation-induced decomposition of reaction products.

Abraded surfaces treated with sodium sulphide solution for XPS analysis were maintained at the desired potential by means of a pH 150 (Russian) potentiostat and a Volta (Russian) Ag/AgCl, sat. KCl electrode. Experiments carried out to examine the visible surface layer used a PAR 173 potentiostat fitted with a PAR 179 coulometer. All potentials referred to in this paper are presented with respect to the SHE, assuming the Ag/AgCl electrode has a potential of −0.200 V relative to the SHE [28]. The

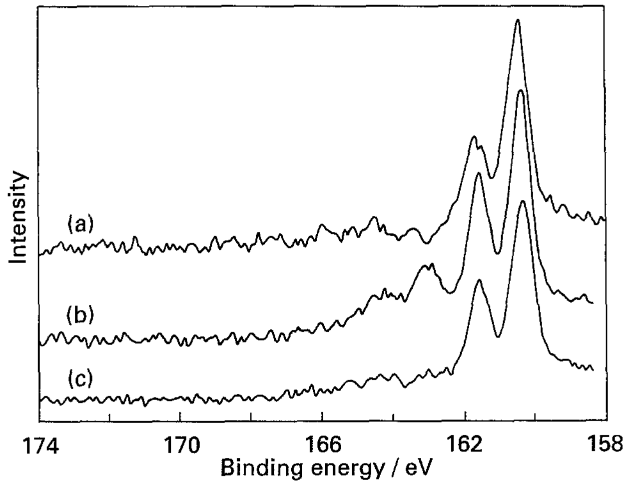

Fig. 1. S(2p) spectra from abraded galena surfaces: (a) exposed to air for < 1 min; (b) maintained at 0.200 V for 20 min in 2×10^{-3} mol dm^{-3} sodium sulphide solution at pH 9.2; (c) maintained at 0.200 V for 20 min in 2×10^{-3} mol dm^{-3} sodium sulphide solution at pH 9.2 and allowed to warm to ambient temperature within the spectrometer.

mineral sample used for these experiments consisted of a solid piece of galena mounted in resin to form a cylindrical electrode about 10 mm in diameter and 4 mm thick. A Viton O-ring of internal diameter 7 mm incorporated within a specially constructed holder restricted contact of the cylinder with the solution to the central area of one face. The faces of the cylindrical electrode were abraded under distilled water and washed immediately before mounting in the electrode assembly and subsequent insertion into the electrolytic cell containing the hydrosulphide solution which had been deoxygenated by saturation with nitrogen. The sodium sulphide solution included 0.05 mol dm^{-3} sodium tetraborate that buffered the pH to 9.2.

3. Results and discussion

3.1. *Reference spectra*

The shape of the background in the S(2p) region for galena is quite complex, largely because of the Pb(4f) energy loss spectrum. Nevertheless, on balance the S(2p) spectrum is preferred over the S(2s) for obtaining chemical information because the 2p doublet peaks are significantly narrower and more intense than the 2s peak, and a change in the apparent intensity ratio of the 2p doublet components can be a sensitive indicator of the presence of a low intensity doublet at higher binding energy. However the S(2p) and Pb(4f) spectra from galena surfaces can only be interpreted correctly if due consideration is given to the shape of the background. Accordingly it is necessary to determine the S(2p) and Pb(4f) spectra and their associated backgrounds for essentially unaltered galena for comparison with spectra from hydrosulphide-treated surfaces, and for surfaces allowed to oxidize in air.

Reference spectra were determined for fresh galena surfaces prepared by fracture, by dry abrasion in air, and by wet abrasion in air followed by washing with distilled water, and insertion into the spectrometer within 1 min of exposure. Some oxidation at the abraded surfaces could be detected from the O(1s) and C(1s) spectra, nevertheless the S(2p) spectra were essentially the same as those from fresh fracture surfaces. A very small component arising from lead–oxygen species was evident in the Pb(4f) spectrum from the dry abraded surface, but these species were not detectable in the case of surfaces which were washed after wet abrasion.

Figure 1(a) shows the S(2p) spectrum from a galena surface immediately after wet abrasion. A broad, low intensity hump between 163 and 167 eV, presumably due to a feature in the Pb(4f) energy loss spectrum, is present in the background on the high binding energy side of the S(2p) peak. The Pb : S intensity ratio for this surface, estimated by assuming straight line backgrounds beneath the Pb(4f) and S(2p) peaks, by using the Perkin–Elmer sensitivity factors, and by assuming, implicitly, a homogeneous surface layer, was 1.1 : 1. The deviation of this ratio from unity probably reflects inadequate assumptions concerning the shapes of the backgrounds as well as some lead enrichment at the surface in response to the presence of oxygen at the surface [20, 29].

3.2. *Surfaces treated with hydrosulphide solution*

Abraded galena surfaces were examined by XPS after immersion in 2×10^{-3} mol dm^{-3} or 2×10^{-4} mol dm^{-3} sodium sulphide solution at pH 9.2 under controlled potential. In each case the electrode was held initially at −0.4 V (typically for 4 min) to remove any oxidation products formed during the brief exposure to air that occurred between abrasion and insertion into the electrochemical cell. The products of surface oxidation are known [30] to be reduced under these conditions but the potential applied was insufficiently negative to allow cathodic reduction of the mineral lattice [30]. The potential was then increased to the desired value for a period of up to 20 min, after which the electrode was removed rapidly from the hydrosulphide solution, washed with distilled water in air, and transferred to the spectrometer.

The S(2p) spectrum from a galena surface maintained for 20 min in 2×10^{-3} mol dm^{-3} hydrosulphide solution at 0.200 V (Fig. 1(b)) exhibits new intensity shifted to higher binding energy from the doublet due to galena. The high binding energy component accounts for about 30% of the total S(2p) intensity, and therefore would represent more than a monolayer if the sulphur were present as a uniformly deposited cover. The S(2p) spectrum cannot be fitted adequately with only one doublet in addition to that for the galena substrate; two additional doublets are required (Fig. 2) shifted by 1.25 eV and 2.65 eV from the galena $2p_{3/2}$ binding energy of 160.35 eV, with linewidths of 0.8 eV and 0.95 eV, and accounting for 10% and 20% of the total S(2p) intensity, respectively. The Pb : S atomic ratio at the treated surface was 0.85 : 1 which represents a significant enrichment in sulphur compared with a fresh surface.

A binding energy of 163.0 eV (the component shifted by 2.65 eV) is too low to arise from elemental sulphur; in fact the linewidth of the fitted component (0.95 eV) is too low for the spectrum to be consistent with even a very low concentration of elemental sulphur to be present. The binding energy for elemental sulphur, deposited on pyrite from hydrosulphide solution in relatively thick layers, but which nevertheless exhibited no measurable charging, was 163.6 eV relative to Au(4f)$_{7/2}$ = 83.9 eV [12]. At Mekhanobr, the binding energy for a solid piece of natural elemental sulphur has been measured at 163.8 eV relative to C(1s) = 284.6 eV for adventitious carbon. Szargan *et al.* [31] reported a value of 164.1 eV for elemental sulphur deposited on pyrite, and Bancroft and coworkers quote values of 163.7 eV and 164.0 eV [32, 33]. Thus a binding energy of 163.0 eV is at least 0.6 eV less than the value for elemental sulphur; consequently the species present at the surface cannot be sulphur with an effective oxidation state of zero.

A binding energy of 163.0 eV is consistent with sulphur in a severely metal-deficient sulphide lattice, however the fitted component at this binding energy has a relatively narrow linewidth and therefore would not be representative of a range of electronic environments. A range of environments is usually encountered in such a metal-deficient sulphide phase, for example, that observed at the surface of oxidized chalcopyrite [18, 19].

The binding energy and the linewidth of both the component at 163.0 and that at 161.6 eV are consistent with sulphur environments in metal oligosulphides. S(2p) spectra from oligosulphides of copper [34], platinum [34, 35], and rhodium [35], revealed different electron binding energies for the structurally distinct sulphur atoms in the oligosulphido ligands. The binding energy of sulphur atoms bonded to the metal was in the range 161.5–162.0 eV and similar to that for the corresponding metal sulphide. Sulphurs two and three atoms remote from the metal atom were found to have 2p binding energies about 1 eV and about 1.5 eV greater. These findings suggest two possible interpretations of the shifted components in the hydrosulphide-treated galena spectrum in terms of a lead oligosulphide. First, the sulphur atom bonded to lead could have a binding energy similar to that in galena and the S(2p) components shifted by 1.25 eV and 2.65 eV arise from sulphur environments one and two or three sulphur atoms remote from the metal atom, respectively. Four sulphur atoms must be considered since the ratio of the intensities of the two shifted components was 1 : 2. Thus the spectrum shown in Fig. 1(b) and Fig. 2 can be rationalized by the bonding of predominantly S$_4$ oligosulphide monodentate ligands to the lead atoms in the galena surface. It is also consistent with the formation of chelate rings with S$_8^{2-}$ ions acting as bidentate ligands. An alternative explanation is possible because the S(2p)$_{3/2}$ binding energy for galena is unusually low (160.4 eV) and, since a binding energy of 161.6 eV is similar to that in the oligosulphides studied [34, 35], the doublet shifted by 1.25 eV may be more indicative of sulphur atoms bonded to the metal. If this second explanation is correct, the lead oligosulphide would be composed of either predominantly S$_3$ monodentate, or S$_6$ bidentate ligands.

The Pb(4f) spectrum corresponding to the S(2p) spectrum in Fig. 1(b) was not discernibly different from that for unoxidized galena. This indicates not only that any part of the mineral surface not covered by adsorbed oligosulphide was not oxidized, but also that the Pb(4f)$_{7/2}$ binding energy for the lead oligosulphide was essentially the same as that for galena. This is in agreement with the Cu(2p)$_{3/2}$ binding energy for [Cu$_3$(S$_4$)$_3$]$^{3-}$ being similar to that for Cu$_2$S [34], and the Pt(4f)$_{7/2}$ binding energy for [Pt(S$_5$)$_3$]$^{2-}$ being similar to that for PtS$_2$ [35].

The majority of the sulphur deposited on to the surface of the galena electrode was lost to the vacuum when the specimen was allowed to warm to ambient temperature within the analyser chamber of the spectrometer (Fig. 1(c)), however at least some of this loss may have been stimulated by the X-ray irradiation and not merely been the result of the vacuum. Comparison of Fig. 1(c) with Fig. 1(a) indicates that some of the component shifted by about 1.2 eV is retained at the surface at ambient temperature. A lower volatility for sulphur atoms nearer to lead

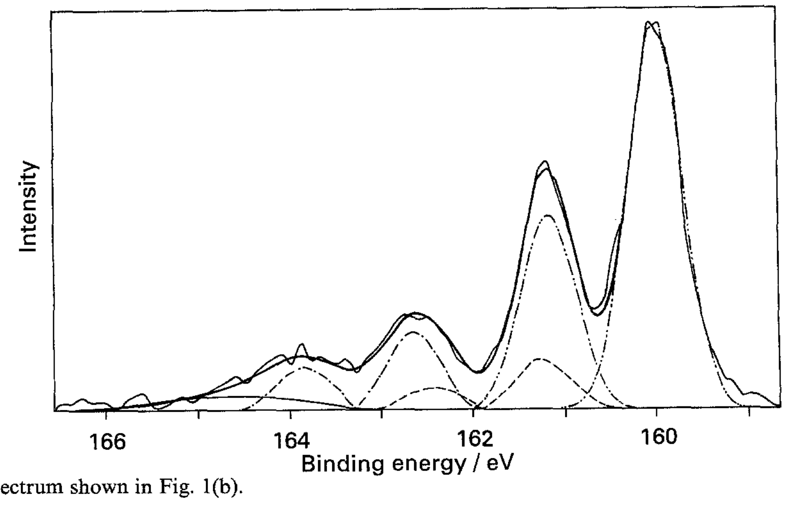

Fig. 2. Fitting of the spectrum shown in Fig. 1(b).

atoms is in agreement with previously observed behaviour for other sulphide mineral systems [19]. The Pb : S atomic ratio for the surface at ambient temperature was 1.1 : 1, consistent with loss of the majority of the deposited sulphur. As expected, the Pb(4f) spectra from the surface before and after warming were indistinguishable.

A galena electrode, maintained for 20 min in 2×10^{-4} mol dm^{-3} hydrosulphide solution at 0.200 V, gave rise to virtually the same S(2p) spectrum as that for the more concentrated solution shown in Fig. 1(b). The S(2p) spectrum determined at $< -100°$ C from a surface maintained for only 5 min in 2×10^{-4} mol dm^{-3} hydrosulphide solution at 0.200 V was similar to that in Fig. 1(c). Thus, not only was there a lower sulphur coverage, but the oligosulphide produced had a shorter chain length (about S_2 if monodentate or S_4 if bidentate). The fact that the chain length is less for the surface polarized for the shorter time suggests that the sulphur is more likely to be deposited as individual atoms than as oligosulphide ions.

The anodic charge passed suggests that a multilayer of sulphur would have been formed. During the controlled potential period in 10^{-3} mol dm^{-3} hydrosulphide solution, the current was initially 310 μA cm^{-2} and fell to 130, 70, 50 and 40 μA cm^{-2} after 30 s, 1 min, 5 min and 20 min, respectively. This corresponds to about 60 mC cm^{-2} and, if all the charge resulted in sulphur deposition, then, assuming the deposition of a monolayer of sulphur requires 0.23 mC cm^{-2} [36] and that the roughness factor of the abraded surface was 6.5 [37], the equivalent of about 40 layers of sulphur atoms would have been deposited. In the 2×10^{-4} mol dm^{-3} hydrosulphide solution, the observed currents were 50 μA cm^{-2} initially dropping to 15 μA cm^{-2} after 1 min and 8 μA cm^{-2} after 10 and 20 min. The equivalent sulphur coverages after 5 and 20 min, making the same assumptions as described above, would be about 3, and 10 atomic layers, respectively.

Furthermore, visible examination of the electrode that had been held for 20 min in 10^{-3} mol dm^{-3} HS$^-$ showed a clear change in reflectivity both before and after the recording of spectra that suggested a substantial alteration of the mineral surface. The change appeared to be greater than was accounted for by the oligosulphide layer revealed by XPS and more consistent with the charge passed in depositing the layer. To explore this apparent discrepancy, further electrochemical investigations of the PbS/HS$^-$ system were carried out. The surface of a galena electrode was examined after being held at different potentials in the range -0.15 to 0.2 V in pH 9.2 solution containing 10^{-3} mol dm^{-3} HS$^-$ until an anodic charge of 60 mC cm^{-2} had been passed. At potentials below about 0.1 V, no change in the appearance of the surface was discernible, whereas, at more positive potentials, a change in optical reflectivity was evident and this became more distinct with increase in potential.

A galena electrode was held at 0.2 V in pH 9.2 solution containing 10^{-3} mol dm^{-3} HS$^-$ until 150 mC cm^{-2} of anodic charge had been passed. After washing and drying the electrode, transparent adhesive tape was attached to the surface. On withdrawal, the dark layer responsible for the reflectivity change had been transferred to the tape. Scanning electron microscopic examination of this layer showed it to consist of highly dispersed material together with coherent fragments of galena. Microprobe analysis of both these constituents showed them to be PbS with a Pb : S ratio of 1 : 1 within the accuracy limits of the probe. As expected from this analysis, the dispersed material was found to be insoluble in a range of organic solvents.

The potential at which the dark surface layer begins to appear coincides with that for the onset of anodic oxidation of galena. The latter reaction commences at about 0 V at pH 9.2 and increases rapidly above about 0.2 V [30]. Polarization of a galena electrode at 0.2 V in tetraborate solution in the absence of HS$^-$ did not result in a discernible change in the mineral surface and hence the change in reflectivity must involve interaction with HS$^-$.

Oxidation of galena in alkaline media results in lead being extracted from the mineral surface to form an overlayer of lead–oxygen species, leaving a metal-deficient sulphide [20]. It is suggested that the overlayer reacts with HS$^-$ to form a dispersed PbS layer. In addition, the excess sulphur left in the galena lattice could become involved in the oxidation of HS$^-$ in the same manner as surface intermediates in the oxidation of HS$^-$ to oligosulphide ions on gold or sulphide minerals [9]. This reaction could be represented by:

$$y\mathrm{Pb}_{1-x}\mathrm{S} + z\mathrm{HS}^- + z\mathrm{OH}^- \longrightarrow y(1-x)\mathrm{PbS} + \mathrm{S}_{xy+z}^{2-} + z\mathrm{H_2O} + 2(z-1)e^- \quad (1)$$

The overall mechanism is essentially one of oxidation of HS$^-$ to oligosulphide ions coupled with reconstruction of the mineral surface. The bulk of the charge passed at 0.2 V would be accounted for by this process with only a fraction arising from the formation of a surface lead oligosulphide. The latter species might be formed on the dispersed PbS as well as at the unaltered galena surface, so that not all of the lead oligosulphide would necessarily be detectable by XPS.

The suggested explanation of the experimental observations is not inconsistent with the results of previous RRDE studies. Oligosulphide ion formation accounted for 20% and 10% of the total current for galena in 1×10^{-3} and 2×10^{-4} mol dm^{-3} HS$^-$, respectively, at 0.2 V on a 10 mV s^{-1} potential scan when the electrode was rotated at 70 Hz [9]. Also, the current arising from oxidation of HS$^-$ on galena under these conditions was inhibited at potentials above 0.1 V, but that from oligosulphide ion formation was unaffected. Thus, the proportion

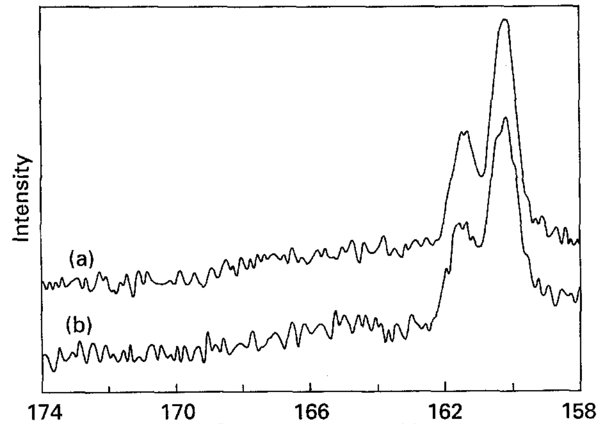

Fig. 3. S(2p) spectra from galena fracture surfaces determined at < −100° C and with an electron take-off angle of 15°: (a) exposed to air for 15 min; (b) exposed to air for < 1 min.

of the charge due to oligosulphide ion formation is expected to increase significantly with time when an electrode is held at a constant potential.

A comparison was made in the introduction between XPS studies of sulphur(−II) oxidation on gold [10], pyrite [11, 12], chalcopyrite [12], sphalerite [13] and chalcocite [14]. Chalcocite represents a special case since there are a series of stable phases of higher sulphur content that can be formed. Of the others, the XPS studies suggest that involvement of the mineral in the sulphur(−II) oxidation reaction to form a metal-deficient sulphide or oligosulphide rather than elemental sulphur increases in the order pyrite < gold < chalcopyrite < galena. This order is similar to that for the formation of oligosulphide ion intermediates [9] of gold ≈ pyrite < chalcopyrite < galena.

3.3 *Sulphur product of the oxidation of galena surfaces on exposure to air*

As discussed elsewhere [19–22], although there is clear evidence for the formation of lead hydroxide or hydrated lead oxide during the initial stage of the oxidation of galena surfaces on exposure to air under ambient conditions or to alkaline aqueous solutions in equilibrium with air, a concomitantly formed sulphur oxidation product has not been detected by XPS. New sulphur species were identified on galena only after extended exposure to air, or oxidation in acid solutions where the lead product is soluble. Interpretation of spectra under the latter conditions was complicated due to minor elements in the galena becoming concentrated in the surface region [20].

It has been assumed [19–22] that the initial oxidation reaction results in the formation of a metal-deficient sulphide, analogous to the oxidation behaviour exhibited by other sulphide minerals [18, 19, 23, 24]:

$$PbS + \tfrac{1}{2}xO_2 + xH_2O \longrightarrow Pb_{1-x}S + xPb(OH)_2 \quad (2)$$

The lead-deficient phase, $Pb_{1-x}S$, has not been evident in the sulphur photoelectron spectra which suggests the degree of metal-deficiency is not great. Prior electrochemical experiments [30, 38] had been consistent with the formation of elemental sulphur:

$$PbS + \tfrac{1}{2}O_2 + H_2O \longrightarrow Pb(OH)_2 + S^0 \quad (3)$$

and it is still frequently assumed that this is the species present at the mineral surface after limited oxidation [39, 40].

The initial oxidation of galena on exposure to air has been reexamined due to the controversy regarding the identity of the products of this process. In light of previous unsuccessful attempts to detect a sulphur product, it is clear that investigation by means of XPS would require electron spectra determined at low temperature with maximum surface sensitivity and resolution, and careful comparison of spectra from oxidized and unoxidized surfaces. As the surface sensitivity of previously reported attempts had not been maximized, usually because of spectrometer or specimen limitations [19, 20, 22], electron spectra were determined at an electron take-off angle of 15° from galena fracture surfaces before and after oxidation in air under ambient conditions. The oxidation was allowed to proceed for a period that was sufficient to give rise to a significant component in the Pb(4f) spectrum from hydrated lead oxide, but no detectable component in the S(2p) spectrum from sulphur–oxygen species such as sulphate. The use of the S(2p) spectrum for exploring sulphur species on sulphide minerals has been maintained in the present search for the sulphur product. Other workers [41, 42] have advocated the S(2s) to avoid background problems with the S(2p) spectrum. However, the appearance of new environments with small binding energy shifts is much more readily discernible from an apparent change in the ratio of the intensities of the $2p_{3/2}$ to $2p_{1/2}$ peaks and the background difficulty can be overcome by proper comparison with reference spectra.

After exposure of a fresh fracture surface to air for 15 min, the Pb(4f) spectrum could be fitted with a component shifted by about 1 eV to higher binding energy, arising from the oxide species, with intensity accounting for 25% of the total Pb(4f) intensity. The corresponding S(2p) spectrum (Fig. 3(a)) not only indicated the absence of sulphur–oxygen species, but also that part of the spectrum expected to reveal the presence of a sulphur-rich phase, an oligosulphide or elemental sulphur, viz., 161–165 eV, was the same, within experimental uncertainty, as that from the unoxidized surface (Fig. 3(b)). The only discernible difference in the spectra was a slightly higher background on the *lower* binding energy side of the S(2p) doublet from the fresh fracture surface. As expected, the S(2p) and Pb(4f) spectra were unchanged after the specimen had been allowed to warm to ambient temperature *in situ*.

It could be argued that the S(2p) intensity of the sulphur-rich phase is masked by overlying lead–oxygen species. However, even if the intensity of the higher binding energy component in the S(2p) spectrum were only half that for the Pb(4f) spectrum, then still the observed S(2p) spectrum would be inconsistent with a new sulphur environment; a component shifted to higher binding energy and accounting for 10% of the total S(2p) intensity would be discernible.

Thus once again, no evidence for a sulphur-rich phase was obtained during the initial oxidation of galena on exposure to air, and the previously proposed rationalization for such an observation, in terms of lead atom migration from the bulk to the surface [20], remains plausible. A new sulphur electronic environment would only become evident after the limit of lead atom migration to the surface had been reached. The oxidative behaviour can not be explained by impurity migration since similar findings have been made with galena of 99.99% purity [43].

As pointed out in Section 1, self-induced flotation of sulphide minerals has been ascribed to the formation of sulphur-rich phases at the mineral surface [25]. The XPS results suggest that the sulphur excess at a galena surface is not large and hence that only a small change in stoichiometry is required to render the mineral floatable. It could be argued that the sulphur-excess might be greater immediately after oxidation and that subsequent lead migration results in an equilibration of the surface region before spectra are recorded. It should be emphasized that the initial products in such a mechanism cannot be elemental sulphur overlying unaltered galena. These are the thermodynamically stable phases in the lead/sulphur system, and lead would not migrate from the mineral to the sulphur phase to form metastable lead-deficient sulphide species when isolated *in vacuo*.

4. Conclusions

Lead oligosulphides are the product of the anodic oxidation of hydrosulphide ions on freshly abraded galena surfaces at potentials sufficiently high for multilayer sulphur deposition. It is suggested that the formation of an oligosulphide is associated with reconstruction of the mineral surface resulting from interaction between HS^- and the products of the oxidation of galena. No elemental sulphur was observed on this mineral.

The oligosulphide sulphur atoms have binding energies of 161.6 eV and 163.0 eV, typical of the sulphur atom binding energies in bulk copper, platinum and rhodium oligosulphides. The volatility of the sulphur atoms having the higher binding energy is greater than that for the sulphur atoms nearer to the lead atoms, in agreement with previous observations for metal-deficient sulphide surface phases. The Pb(4f) binding energy for the oligosulphide was the same as that for galena. Sulphur layers deposited at the same potential for the same and shorter periods in more dilute hydrosulphide solution suggested that the sulphur layers were deposited atom-by-atom rather than as oligosulphide entities.

Photoelectron spectra determined at a take-off angle of 15° from galena fracture surfaces exposed to air under ambient conditions confirmed the previously reported absence of new sulphur environments resulting from the formation of the lead–oxygen species. Thus, previous explanations for this observation, in terms of lead atom migration from the bulk to the surface to minimize metal-deficiency, are supported.

Acknowledgements

The CSIRO authors acknowledge financial support from the Australian Government Department of Industry, Technology and Commerce, Bilateral Science and Technology Scheme to enable a period working at Mekhanobr. Assistance in carrying out the electrochemical experiments was provided by Z. V. Skvortsova of SKB Mekhanobr, and the electrode for controlled potential treatment of the galena was constructed by W. Kennedy of the CSIRO Division of Mineral Products. Electron microprobe analyses of the galena were provided by A. Belous of Mekhanobr-Analyt and by I. R. Harrowfield of the CSIRO Division of Mineral Products.

References

[1] A. M. Marabini and G. Rinelli, *in* 'Advances in Mineral Processing, a Half-Century of Progress in Application of Theory and Practice' (edited by P. Somasundaran), AIME, Littleton CO (1986) pp. 269–288.
[2] R. D. Crozier, 'Flotation: Theory, Reagents and Ore Testing', Pergamon Press, Oxford (1992) 356 pp.
[3] M. H. Jones and J. T. Woodcock, *Proc. Australas. Inst. Min. Metall.* **266** (1978) 11.
[4] *Idem, Int. J. Miner. Process.* **6** (1979) 17.
[5] V. I. Revnivtsev, G. N. Mashevsky, A. M. Kokorin, O. V. Laubgan, T. O. Nichiporenko, M. L. Khanin and G. I. Shorsher, *in* 'Proc. XVIIth International Mineral Processing Congress, Dresden, Germany' (1991) pp. 295–305.
[6] G. W. Walker, C. P. Walters and P. E. Richardson, *in* 'Proc. Int. Symp. Electrochemistry in Mineral and Metal Processing' (edited by P. E. Richardson, S. Srinivasan and R. Woods), Electrochem. Soc, Pennington, NJ, **84-10** (1984) pp. 202–218.
[7] G. W. Heyes and W. J. Trahar, *in* 'Proc. Int. Symp. Electrochemistry in Mineral and Metal Processing' (edited by P. E. Richardson, S. Srinivasan and R. Woods), Electrochem. Soc, Pennington, NJ, **84-10** (1984) pp. 219–232.
[8] W. J. Trahar, *in* 'Principles of Flotation: The Wark Symposium' (edited by M. H. Jones and J. T. Woodcock), Australasian IMM, Melbourne (1984) pp. 117–135.
[9] R. Woods, D. C. Constable and I. C. Hamilton, *Int. J. Miner. Process.* **27** (1989) 309.
[10] A. N. Buckley, I. C. Hamilton and R. Woods, *J. Electroanal. Chem.* **216** (1987) 213.
[11] A. N. Buckley, R. Woods and H. J. Wouterlood, *Aust. J. Chem.* **41** (1988) 1003.
[12] J. J. McCarron, G. W. Walker and A. N. Buckley, *Int. J. Miner. Process.* **30** (1990) 1.
[13] A. N. Buckley, R. Woods and H. J. Wouterlood, *Int. J. Miner. Process.* **26** (1989) 29.
[14] J. Gebhardt, J. J. McCarron, P. E. Richardson and A. N. Buckley, *Hydrometallurgy* **17** (1986) 27.
[15] I. C. Hamilton and R. Woods, *J. Appl. Electrochem.* **13** (1983) 783.
[16] X. Gao, Y. Zhang and M. J. Weaver, *Langmuir* **8** (1992) 668.
[17] *Idem, J. Phys. Chem.* **96** (1992) 4156.
[18] A. N. Buckley and R. Woods, *Aust. J. Chem.* **37** (1984) 2403.

[19] A. N. Buckley and G. W. Walker, *in* 'Proc. XVI Int. Miner. Process. Congress' (edited by K. S. E. Forssberg), Elsevier, Amsterdam (1988) pp. 589–599.
[20] A. N. Buckley and R. Woods, *Appl. Surf. Sci.* **17** (1984) 401.
[21] G. W. Walker, P. E. Richardson and A. N. Buckley, *Int. J. Miner. Process.* **25** (1989) 153.
[22] A. N. Buckley and K. W. Riley, *Surf. Interface Anal.* **17** (1991) 655.
[23] A. N. Buckley and R. Woods, *Appl. Surf. Sci.* **22/23** (1985) 280.
[24] *Idem, ibid.* **20** (1985) 472.
[25] A. N. Buckley, I. C. Hamilton and R. Woods, *in* 'Developments in Mineral Processing: Vol. 6, Flotation of Sulphide Minerals' (edited by K. S. E. Forssberg), Elsevier, Amsterdam (1985) pp. 41–60.
[26] A. N. Buckley and R. Woods, *Int. J. Miner. Process.* **28** (1990) 301.
[27] *Idem, Colloids Surf.* **53** (1991) 33.
[28] R. G. Bates, 'Determination of pH, Theory and Practice', Wiley, New York (1964).
[29] K. Laajalehto, R. StC. Smart, J. Ralston and E. Suoninen, *Appl. Surf. Sci.* **64** (1993) 29.
[30] J. R. Gardner and R. Woods, *J. Electroanal. Chem.* **100** (1979) 447.
[31] R. Szargan, S. Karthe and E. Suoninen, *Appl. Surf. Sci.* **55** (1992) 227.
[32] M. M. Hyland and G. M. Bancroft, *Geochim. et Cosmochim. Acta* **53** (1989) 367.
[33] J. R. Mycroft, G. M. Bancroft, N. S. McIntyre, J. W. Lorimer and I. R. Hill,. *J. Electroanal. Chem.* **292** (1990) 139.
[34] S. C. Termes, A. N. Buckley and R. D. Gillard, *Inorg. Chim. Acta* **126** (1987) 79.
[35] A. N. Buckley, H. J. Wouterlood, P. S. Cartwright and R. D. Gillard, *ibid.* **143** (1988) 77.
[36] I. C. Hamilton and R. Woods, *J. Appl. Electrochem.* **13** (1983) 783.
[37] R. Woods, *J. Phys. Chem.* **75** (1971) 354.
[38] P. E. Richardson and E. E. Maust Jr, *in* 'Flotation: A. M. Gaudin Memorial Volume' (edited by M. C. Fuerstenau), AIME/SME, New York, NY (1976), Vol. 1, pp. 364–392.
[39] M. K. Y. Rao and K. A. Natarajan, *Int. J. Miner. Process.* **29** (1990) 175.
[40] Feng Qiming, Xu Si and Chen Jin, *in* 'Proc. First Int. Conf. Modern Process Mineral. Min. Process.', Beijing (1992) pp. 508–512.
[41] P. W. Page and L. B. Hazell, *Int. J. Miner. Process.* **25** (1989) 87.
[42] K. Laajalehto, P. Nowak and E. Suoninen, *ibid.* **37** (1993) 123.
[43] P. E. Richardson, R.-H. Yoon, R. Woods and A. N. Buckley, *ibid.*, in press.