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Relaxation of the lead-deficient sulfide surface layer on oxidized galena

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The surface oxidation of galena in air and in aqueous media has been investigated using electron spectroscopy and linear potential sweep voltammetry to elucidate the incongruent oxidation indicated by previous X-ray photoelectron spectroscopic studies. It has been confirmed that the initial oxidation reaction involves the removal of lead atoms from the sulfide lattice to generate a metal-deficient surface layer. It has been shown that, when the mineral is removed from the oxidizing environment, the composition of this layer relaxes slowly back towards that of the bulk mineral as a result of lead atoms diffusing from the bulk to the surface to fill metal vacancies in the sulfide lattice. The relaxation accounts for the absence of a shifted component in sulfur electron spectra from galena exposed to air or basic solutions in equilibrium with air. Correlation of the potential dependence of self-induced flotation and the extent of surface sulfur excess determined electrochemically indicates that a metal-deficiency equivalent to about half a monolayer of excess sulfur is necessary for significant flotation to be effected.

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1. Introduction

The surface oxidation of sulfide minerals has been the subject of numerous studies using a variety of investigative techniques. The interest in this reaction stems from its importance in various unit processes in the recovery of metals from sulfidic ores. In froth flotation, the products of mineral oxidation can inhibit the process [1]. Flotation of sulfide minerals can also be induced in the absence of collectors by exposure to oxidizing environments [2]. The potential dependence of self-induced flotation has been determined for a number of systems and the onset of flotation shown to occur at potentials corresponding to mineral oxidation [2]. Good correlations have been obtained between the flotation potentials and the redox values for oxidation of the particular sulfide to elemental sulfur [3].

X-ray photoelectron spectroscopic (XPS) investigations of the exposure of sulfide minerals to oxidizing environments [4, 5] have demonstrated that the initial oxidation product is not sulfur in the elemental form. The binding energy and volatility of the surface species were found to differ significantly from those of S°. It was concluded that the first stage of oxidation involves progressive removal of metal atoms leaving metal-deficient sulfides with sulfur lattices little altered from the original structure. Sulfide surface layers with stoichiometries well outside the range of established, stable bulk phases were identified. Elemental sulfur was detected on sulfide mineral surfaces, but only under conditions corresponding to higher oxidation potentials than those at which oxidation commenced.

Galena was found [2, 6] to display the same general characteristics as other sulfides with respect to self-induced flotation. However, XPS studies [7–10] of the initial oxidation of galena on exposure to air under ambient conditions, or to alkaline solutions in equilibrium with air, revealed the formation of lead hydroxide before any new sulfur environments were evident. These studies included examination of galena oxidation using an electron take-off angle of 15° to enhance the contribution of photoelectrons from the surface region [10]. It was proposed that lead hydroxide is formed by the reaction:

$$\mathrm{PbS} + 1/2\,x\mathrm{O}_2 + x\mathrm{H_2O} \longrightarrow \mathrm{Pb}_{1-x}\mathrm{S} + x\mathrm{Pb(OH)_2} \tag{1}$$

and that the associated lead-deficient phase, $\mathrm{Pb}_{1-x}\mathrm{S}$, is not evident in the sulfur photoelectron spectra because lead atoms migrate from the bulk of the mineral to maintain a low level of metal-deficiency in the oxidation product.

The conditions under which the above oxidation characteristics of galena were observed are expected to correspond to those under which self-induced flotation occurs. This appears to indicate that only a small degree of metal-deficiency at a galena surface is required to render the mineral hydrophobic. Such behaviour would differ from that observed with other sulfide minerals. Analogous studies on chalcopyrite

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[11], pyrrhotite [12, 13] and pentlandite [14] indicate that the degree of metal-deficiency is significant under conditions where effective self-induced flotation takes place. Furthermore, minerals such as pyrrhotite, that exhibit a degree of metal-deficiency in the natural condition (up to 14% iron-deficient compared with stoichiometric FeS [15]), require oxidation to a more metal-deficient surface for self-induced flotation to develop.

To elucidate the distinctive behaviour of galena, further electrochemical and XPS experiments have been carried out on the surface oxidation of the mineral in air and in aqueous media. The findings of these investigations are presented in this paper.

2. Experimental details

2.1. *Mineral source*

Large, natural crystals of galena were obtained from the Zinc Corporation Ltd mine at Broken Hill, Australia. They contained, calculated on an atomic basis, 99.3% PbS with minor elements, 0.2% Sb, 0.1% Cu, 0.06% Ag and 0.03% Bi, present as sulfides.

2.2. *Electrochemical investigations*

A rotating disc electrode, prepared from a specimen of the mineral using the procedure described previously [16], was employed for the electrochemical investigations. The exposed surface area of the galena was 0.22 cm^2. A fresh surface was produced on the electrode before each run by wet grinding on P 1000 grade silicon carbide paper; the electrode was then thoroughly washed with distilled water. For experiments in which exposure to air was examined, the water on the surface was removed with a filter paper.

Potentials were measured against a saturated calomel reference electrode (SCE) and converted to the standard hydrogen electrode (SHE) scale, assuming the SCE has a potential of 0.245 V vs SHE. All potentials are reported on the SHE scale. The potential was controlled by a Utah 0152 potentiostat programmed with a Utah 0151 sweep generator. Current–potential and current–time curves were recorded on a Yew 3086 X–Y recorder.

Voltammetry was carried out in buffer solutions of pH 4.6, 8.0 and 9.2. The compositions of these solutions were: 0.5 mol dm^{-3} sodium acetate; 0.5 mol dm^{-3} acetic acid (pH 4.6): 0.05 mol dm^{-3} boric acid; 3.9 × 10^{-3} mol dm^{-3} sodium hydroxide; 0.05 mol dm^{-3} sodium sulfate (pH 8.0); and 0.05 mol dm^{-3} sodium tetraborate (pH 9.2).

The real surface area of the galena electrode was determined from the charge passed in establishing a monolayer of ethyl xanthate on the galena surface. The anodic peak that appears on voltammograms for galena in xanthate solution has been assigned [17] to a one electron charge transfer chemisorption reaction. This peak occurs prior to reaction with the mineral to produce a lead xanthate phase. The charge associated with the peak in 10^{-2} mol dm^{-3} xanthate was found to be 305 μC cm^{-2}; this value corresponds to a roughness factor of 3.37. The monolayer charge for a two electron process, such as the reduction of S to H_2S and of PbO to Pb, was therefore taken as 610 μC cm^{-2}.

2.3. *Electron spectroscopy*

Single crystal mineral specimens of dimensions 8 mm × 8 mm × 3 mm were cleaved in air to create pairs of fresh, predominantly {100}, 8 mm × 8 mm surfaces. These surfaces were exposed to air under ambient conditions for periods of 3 to 6 h. The specimens were either (i) inserted into the nitrogen atmosphere of the spectrometer chamber and, within 5 min, cooled to ~150 K before the pressure was reduced below 10^{-2} Pa, or (ii) inserted into the nitrogen atmosphere of a glove box attached to the spectrometer preparation chamber and stored under flowing nitrogen for up to 12 h before examination. During determination of spectra at 10^{-7}–10^{-8} Pa, the specimens were maintained at ~150 K to avoid the loss of any elemental sulfur that may have been present.

After initial examination, specimens were allowed to warm to ambient temperature before being withdrawn into the glove box where they were immersed in deoxygenated 0.1 mol dm^{-3} acetic acid (about pH 3) for periods of 10 s to 2 min (depending on the extent of previous air exposure). The specimens were washed thoroughly with deoxygenated water prior to reintroduction into the spectrometer, and again cooled to 150 K before being subjected to high vacuum.

Electron spectra were obtained with a Vacuum Generators ESCA 3 spectrometer using nonmonochromatized MgK_α radiation (10 kV, 10 mA), an electron take-off angle of 45°, an analyser pass energy of 20 eV and a slit width of 2 mm. Under these conditions, the 4f$_{7/2}$ photoelectron peak from gold metal had a width of 1.05 eV and a binding energy of 84.0 eV. Each spectrum shown has been normalized by the difference between the maximum and minimum number of counts.

3. Results and discussion

3.1. *Exposure to air*

The S 2p/Pb 4f, C 1s and O 1s photoelectron spectra, and Pb(NOO)/S(LMM) X-ray excited Auger electron spectra, for fracture surfaces exposed to air under ambient conditions for 3 h were comparable with those observed previously after similar treatment [7–10]. Air exposure for this period resulted in an obvious broadening of the Pb 4f peaks on the high binding energy side (Fig. 1(a)) due to a component shifted 1 eV to higher binding energy that can be assigned to hydrated lead oxide (or hydroxide) formation. However, there was no discernible change in the

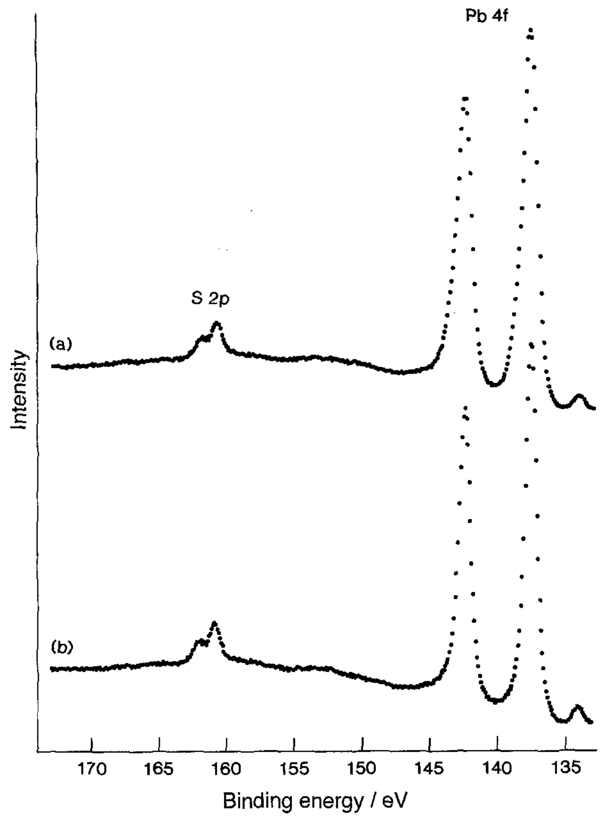

Fig. 1. S 2p/Pb 4f spectra from a cleaved galena surface: (a) exposed to air for 3 h; (b) subsequently washed with acetic acid solution under nitrogen.

S 2p spectrum from that for a fresh galena surface. Similarly, the Pb(NOO) spectrum was consistent with the formation of an appreciable concentration of a Pb/O species [18], whereas the S(LMM) spectrum was of lower intensity but indicated the absence of new sulfur species. The Pb(NOO) Auger electrons are significantly more surface sensitive than the Pb 4f photoelectrons because the kinetic energy of the former is about 90 eV compared with 1.1 keV for the latter. The corresponding C 1s spectrum revealed that very little carbonate had been formed, and the O 1s spectrum indicated that the predominant Pb/O species was hydrated oxide or hydroxide rather than unhydrated PbO.

The specimen giving rise to the spectrum in Fig. 1(a) was subsequently immersed for 10 s in deoxygenated acetic acid solution under a nitrogen atmosphere, washed with deoxygenated water and returned to the spectrometer. This treatment should have dissolved oxidized lead species, and hence eliminated the possibility that islands or patches of lead–oxygen species might mask regions of metal-deficiency. The S 2p/Pb 4f spectrum for this surface (Fig. 1(b)) was indistinguishable from that for a fresh fracture surface. In particular, the Pb 4f peaks no longer indicated the presence of lead–oxygen species and the S 2p doublet remained unchanged. The corresponding Pb(NOO)/S(LMM) spectrum, notwithstanding its overall higher background level due to surface contamination, was also indicative of unoxidized galena. It should be noted that, whereas PbS and unhydrated PbO have similar Pb 4f binding energies, their Pb(NOO) energies differ by more than 2 eV [18].

The S 2p/Pb 4f spectrum for a surface exposed to air for 6 h, but stored under flowing nitrogen for 12 h before spectroscopic examination, displayed much less Pb 4f intensity shifted 1 eV to higher binding energy than did the spectrum from the mating surface exposed to air for 3 h and examined without storage under nitrogen. In fact, the Pb 4f peaks for the former surface were barely distinguishable from those of a fresh fracture surface. This can not be due simply to the loss of water from hydrated lead oxide in the dry nitrogen atmosphere to produce PbO because a component with kinetic energy below 93 eV was absent from the $Pb(N_6O_{4,5}O_{4,5})$ spectrum [18]. Furthermore, the O 1s spectrum did not display a significant component below 531 eV that would be expected for an unhydrated oxide [19]. The overall O 1s intensity was comparable with that for the mating surface examined immediately after exposure to air for 3 h, however the majority of the intensity in the former case was at binding energies greater than 532 eV, and hence consistent with physically adsorbed species. The lower level of oxidized lead species observed after storage cannot arise from the reverse of Reaction 1 occurring in the dry nitrogen atmosphere; consideration of the thermodynamics of Reaction 1 indicates that an exceedingly low oxygen fugacity would be required for the reverse reaction to be possible. One explanation of the observed phenomenon is that dehydration of the lead hydroxide oxidation product occurs in the dry nitrogen during storage and that this process is accompanied by migration to form thicker patches covering appreciably less of the mineral surface, thereby becoming barely detectable by XPS. The time-dependence of the electron spectra from oxidized galena might explain the considerable variation in the extent of oxidation that has been deduced from XPS investigations [7, 9, 20].

The specimen stored under nitrogen following exposure to air for 6 h was immersed in acetic acid solution to search for any manifestation of oxide removal. Immersion times of 10 s and 2 min were investigated, followed by washing with water. In neither case, however, was any influence on the S 2p spectrum discernible.

Electrochemical studies were carried out with the objective of elucidating the incongruent oxidation of galena indicated by the XPS investigation. Galena surfaces exposed to air were examined by cathodic stripping of the oxidized layer in tetraborate solution of pH 9.2. This solution was selected since the solubility of lead oxide is a minimum close to that pH value [21]. Figure 2 presents voltammograms obtained after different exposure times, with the potential sweep being applied immediately after inserting the electrode into the electrochemical cell.

It can be seen that a peak develops between −0.5 and −0.6 V and increases with exposure time. This peak can be assigned to the reduction of lead(II) oxide or hydroxide to lead metal [22]. The potential

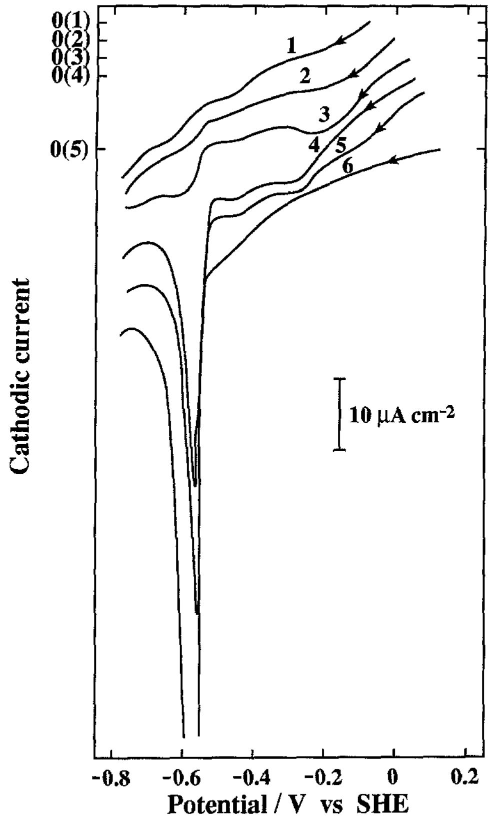

Fig. 2. Voltammograms for negative-going potential scans at 10 mV s^{-1} for galena in pH 9.2 solution after exposure to air for (1), 0, (2) 20, (3) 55, (4) 150, (5) 210 and (6) 600 min. Peak current for (6) was 150 mA cm^{-2}.

at which the peak appears suggests that the actual species reduced is lead borate which will be formed by reaction of lead oxide with the solution as a result of the lower solubility of the borate.

The appearance of a lead oxide peak substantiates the XPS findings. If equal quantities of lead and sulfur oxidation products were present on the mineral surface, cathodic stripping would give rise to a peak at about −0.2 V [22] corresponding to the process:

$$\mathrm{Pb}_{1-x}\mathrm{S} + x\mathrm{Pb(OH)}_2 + 2xe^- \longrightarrow \mathrm{PbS} + 2x\mathrm{OH}^- \qquad (2)$$

The formation of PbO in excess of oxidized sulfur species could be explained by incongruent oxidation, or by loss of sulfur to the atmosphere. The formation of SO_2 has been proposed [23] to explain the appearance of oxidized lead products without the detection of any associated nonsulfide sulfur during galena oxidation. However, the evolution of SO_2 during the reaction of lead sulfide with oxygen is expected only at elevated temperatures [24]. Another potential route for sulfur loss would be oxidation to lead thiosulfate which is unstable and might decompose to yield PbS and SO_3. Thiosulfate has been shown [22] to be a product of galena oxidation in aqueous solutions. However, as concluded previously [7], any sulfur oxides would be expected to react with the lead hydroxide formed concomitantly on the surface, as does atmospheric CO_2; these oxides would then be retained at the surface and be detected in the sulfur spectrum. In fact, no sulfur–oxygen species are evident in the spectra shown in Fig. 1. Previous studies of the exposure of galena to air [7] have shown sulfate to appear only after a few days.

Although the electrochemical and electron spectroscopic results are in agreement with respect to lead hydroxide being the major product, they appear to differ with respect to altered sulfur environments. A peak at about −0.2 V in Fig. 2 is indicative of a sulfur species reacting with lead oxide or hydroxide to reform PbS, such as Reaction 2. When stripping was carried out in an acetate buffer of pH 4.6, following 10 s rapid rotation of the electrode to dissolve lead oxide, the sulfur peak was still apparent. For example, the charge passed in reducing the sulfur to H_2S after 4 h exposure was found to be 350 μC cm^{-2}. This corresponds to a metal-deficient sulfide having about 0.6 of a monolayer of sulfur in excess of the number of lead atoms present.

Such a sulfur product would be expected to give rise to a shifted component in the sulfur spectrum. The reason for the absence of such a component became apparent when it was noted that the charge associated with the reduction of the sulfur oxidation product diminished if the electrode was left immersed in the electrolyte for a period prior to the stripping voltammogram being recorded. This indicated that, when the electrode was removed from the oxidizing environment, lead atoms continued to diffuse to fill the vacancies that had been formed in the mineral lattice at the surface by the oxidation process.

3.2. *Anodic oxidation in aqueous solutions*

In order to explore how rapidly the surface composition can relax, the changes in sulfur coverage with time were determined following anodic oxidation in pH 9.2 or 4.6 solution. Figure 3 shows cathodic stripping voltammograms after holding at 0.25 V in pH 9.2 solution for 200 s to oxidize the surface, followed by

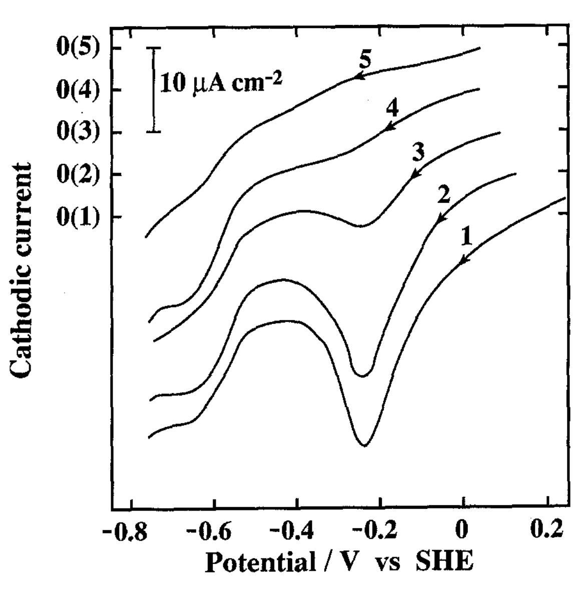

Fig. 3. Voltammograms for negative-going potential scans at 10 mV s^{-1} for galena in pH 9.2 solution after holding at 0.25 V for 200 s followed by standing at open circuit for (1) 0, (2) 2, (3) 5, (4) 10 and (5) 20 min.

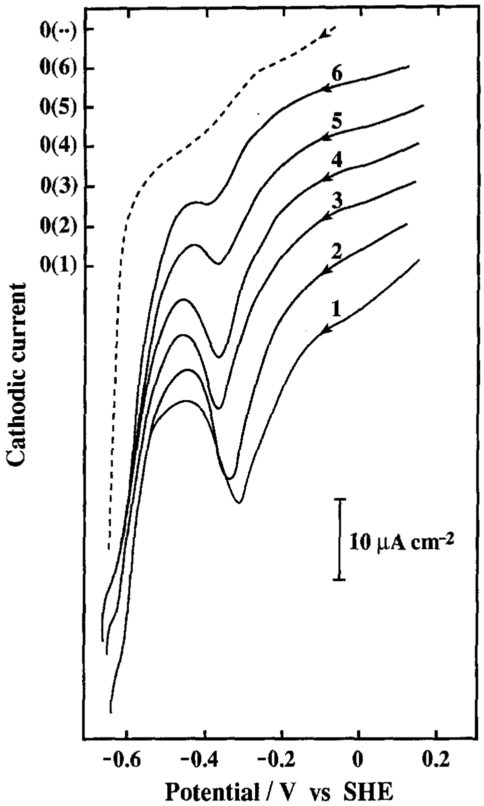

Fig. 4. Voltammograms for negative-going potential scans at 10 mV s^{-1} for galena in pH 4.6 solution after holding at 0.30 V for 20 s with rotation at 10 Hz followed by standing at open circuit for (1) 0, (2) 2, (3) 5, (4) 10, (5) 20 and (6) 40 min. The dashed curve is from a fresh galena surface.

different periods at open circuit. No current can flow during the latter condition and the solution does not contain any species that would be expected to interact with the oxidized surface. The cathodic peak at pH 9.2 is due to Reaction 2 and integration of the charge indicates that anodic treatment had established close to a monolayer of excess sulfur in the surface region. It can be seen from Fig. 3 that the excess sulfur decreases with time on open circuit to be negligible after 20 min.

Figure 4 shows analogous voltammograms for anodic oxidation for 20 s at 0.30 V in pH 4.6 solution with the electrode rotated at 10 Hz to disperse the lead ions produced in association with the sulfur product. Cathodic reduction of the surface layer at this pH is expected to proceed by:

$$\mathrm{Pb}_{1-x}\mathrm{S} + 2x\mathrm{H}^+ + 2x\mathrm{e}^- \longrightarrow (1-x)\mathrm{PbS} + x\mathrm{H_2S} \qquad (3)$$

The anodic treatment effected at pH 4.6 was also found to yield the order of a monolayer of excess sulfur at the surface. Following the deposition period, the rotation was stopped and then the electrode held for different periods at open circuit. It is clear from Fig. 4 that, as at pH 9.2, the quantity of excess sulfur at the surface diminished with time and that only a small amount remained after 40 min.

The diffusion of lead within the galena structure to fill vacancies at the surface should occur during the anodic treatment as well as at open circuit. Thus, a metal-deficient surface should develop only when the rate of removal of lead atoms exceeds that of their diffusion from the underlying mineral. To examine this aspect, the charge passed in creating a metal-deficient layer in pH 4.6 solution was determined by stepping the potential to 0.25 V and recording the current during the 200 s it was held at this value. Integration of the current–time curve showed that a charge of 1.14 mC cm^{-2} had been passed. A negative-going potential scan was then applied and a charge of 400 μC cm^{-2} found to be associated with the peak arising from Reaction 3. This corresponds to 35% of the charge passed in establishing the layer. Thus, more than half the lead vacancies in the surface layer had been filled by metal atoms diffusing from underlying mineral during the deposition period.

An experiment was carried out in which the same anodic treatment was applied as in Fig. 4 (20 s at 0.30 V and 10 Hz), the electrode held for 40 min at open circuit to allow the surface to relax, and the anodic treatment applied again. The resulting surface also contained about a monolayer of excess sulfur. When a further 40 min rest period was introduced before the stripping voltammogram, the excess surface sulfur had only been decreased by about one half. Repeating this treatment with a third anodic treatment again resulted in monolayer coverage. On leaving such a surface for a further 40 min at open circuit, no significant change in the quantity of excess sulfur occurred. Two important points can be made from these observations. Firstly, the conclusion is confirmed that the changes observed following periods at open circuit result from diffusion of lead ions within the electrode and not from interaction of the sulfur product with the solution. Secondly, only a limited number of lead atoms in the mineral are available for equilibration with the surface within a time-frame of the order of an hour.

It can be seen from Fig. 4 that, in addition to the peak near −0.4 V, a shoulder appears in the region of −0.6 V after holding at 0.30 V. The current flow at the negative potential limit arises from the following process:

$$\mathrm{PbS} + 2\mathrm{H}^+ + 2\mathrm{e}^- \longrightarrow \mathrm{Pb} + \mathrm{H_2S} \qquad (4)$$

It is suggested that the shoulder observed after oxidation arises from reduction of the altered galena that underlies the oxidized layer. This sublayer will contain fewer lead atoms than the original composition as a result of lead atoms moving into the overlying metal-deficient surface layer formed by the oxidation process.

3.3. *Oxidation in aqueous solution in equilibrium with air*

Previous XPS studies of galena oxidation [7] showed that an altered sulfur environment developed when galena was immersed in acetic acid solution in equilibrium with air. Interpretation of these spectra was complicated due to minor elements in the galena becoming concentrated in the surface region.

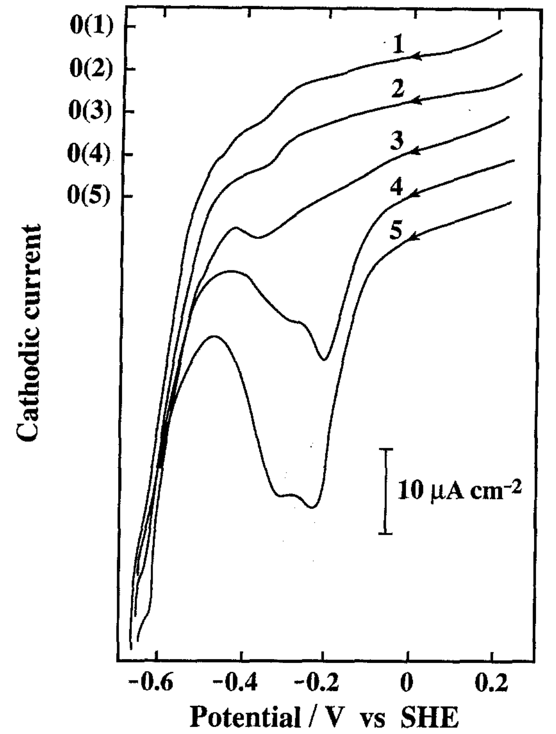

Fig. 5. Voltammograms for negative-going potential scans at $10\,\mathrm{mV\,s^{-1}}$ for galena in pH 4.6 solution after immersion in pH 4.6 solution in equilibrium with air for (1) 20, (2) 45, (3) 100, (4) 130 and (5) 210 min.

However, the binding energy corresponding to the altered sulfur environment was too low to arise from elemental sulfur.

Stripping voltammograms for a galena electrode after immersion for different periods in acetate solution of pH 4.6 are presented in Fig. 5. It can be seen that a cathodic peak develops at −0.3 V which is the same potential at which sulfur is removed from the metal-deficient sulfide formed potentiostatically at this pH (see Fig. 4). At the longer immersion times, however, a second peak also appears with a peak potential close to −0.2 V. This indicates the appearance of a new sulfur-containing phase that is more readily reducible than the metal-deficient lead sulfide formed under the conditions explored in the previous sections. One possible explanation of this feature is that it arises from a copper sulfide species at the surface; copper is a minor component of the galena under investigation and previous XPS investigations [7] have shown that it concentrates at the surface during treatment in acetic acid solution. In support of this assignment of the additional cathodic peak to reduction of a copper sulfide is the observation that the reduction of the metal-deficient copper sulfide formed by anodic oxidation of chalcopyrite gave rise to a cathodic peak at about −0.2 V in pH 4.6 solution [5].

3.4. *Correlation of galena oxidation with self-induced flotation*

Guy and Trahar [6] investigated the potential dependence of the self-induced flotation of galena in pH 8 solution. In their experiments, they adjusted the potential by the addition of redox reagents to the pulp and, when a stable potential was achieved, determined the flotation recovery with nitrogen as the carrier gas. Recovery data as a function of potential were reported for 1 min flotation.

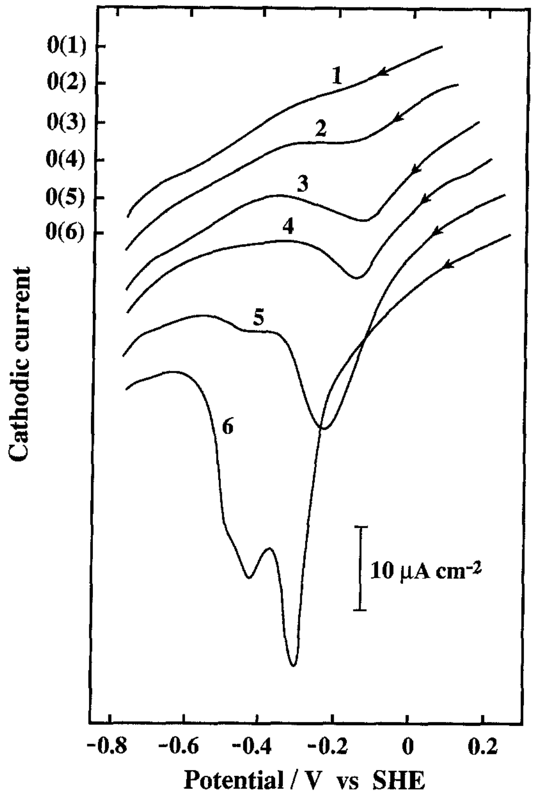

Fig. 6. Voltammograms for negative-going potential scans at $10\,\mathrm{mV\,s^{-1}}$ for galena in pH 8.0 solution after holding for 1 min with rotation at 10 Hz at (1) 0.15, (2) 0.20, (3) 0.25, (4) 0.30, (5) 0.35 and (6) 0.40 V.

To simulate the flotation conditions used by Guy and Trahar [6], the potential of a galena electrode was stepped to values in the range investigated by those authors and held at the set value for 1 min with the electrode rotated at 10 Hz to disperse soluble reaction products. The rotation was then stopped and a negative-going potential scan applied immediately. The resulting voltammograms are shown in Fig. 6. These curves are analogous to those obtained under the other conditions investigated. After being held at potentials below 0.35 V, a single cathodic peak appears between −0.15 and −0.3 V, depending on the potential of anodization; the peak can be assigned to Reaction 2 or 3. For potentials $\geqslant 0.35$ V, a second peak becomes apparent at about −0.45 V. This peak arises from the reduction of lead oxide to lead. As discussed above for galena surfaces exposed to air, the lead oxide species reduced to the metal must be in excess of the sulfur species since equal quantities would give a single peak due to Reaction 2. The formation of excess lead oxide species can be explained by some galena being oxidized to thiosulfate ions which would be lost to the solution phase.

$$2\mathrm{PbS} + 7\mathrm{H_2O} \longrightarrow 2\mathrm{Pb(OH)_2} + \mathrm{S_2O_3^{2-}} + 10\mathrm{H^+} + 8\mathrm{e^-} \qquad (5)$$

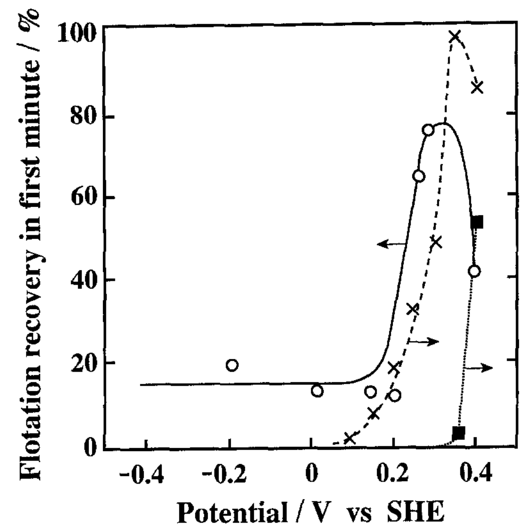

Fig. 7. Potential dependence of flotation recovery of galena at pH 8 in absence of collectors from ref. 6. (○); coverage of excess sulfur after holding at set potential in pH 8.0 solution for 1 min derived by integration of charges on voltammograms in Fig. 6 (×); coverage of lead hydroxide derived similarly (□).

Reaction 5 has been shown [22] to occur in aqueous solutions, particularly at elevated potentials.

The cathodic charges derived by integration of the currents on the voltammograms in Fig. 6 were converted to equivalent fractional surface coverages as before. These values are compared in Fig. 7 with the self-induced flotation data reported by Guy and Trahar [6] for the recovery after 1 min. It can be seen that there is a good correlation between the onset of effective flotation and of the generation of a sulfur-rich surface and this substantiates the conclusion [6] that self-induced flotation arises from oxidation of the mineral. The data in Fig. 7 indicates that a significant degree of metal deficiency in the surface, equivalent to about half a monolayer of excess sulfur, is necessary for significant flotation to be effected. It is also evident that the extent to which oxidation occurred in the investigations described in the previous sections is of the same magnitude as is required for self-induced flotation.

It can also be seen from Fig. 7 that the fall in flotation recovery above 0.3 V correlates with the appearance of more lead oxide than excess sulfur at the mineral surface. This substantiates the conclusion [6] that the fall in recovery in this potential region arises from oxidation of galena to thiosulfate. It has been established [25] that the presence of metal hydroxides interferes with the floatability of sulfides.

The extent of the oxidized layer was found to be significantly diminished when the galena electrode was subjected to a period at open circuit. Sulfur coverages after 10 and 20 min at open circuit are compared in Fig. 8 with those observed when the stripping sweep was applied immediately after anodization. It can be seen that the degree of sulfur-excess at the surface is rapidly decreased when the oxidizing driving force is removed, with the rate of decrease depending on the initial surface coverage. As before, this behaviour is explained by diffusion of lead atoms into the surface layer from the underlying mineral. Such surface relaxation would imply that the self-induced floatability of galena could be removed simply by changing the carrier gas from air to nitrogen, provided oxygen is the potential determining species. Clearly, a reversal in floatability would not occur if other redox couples are present that could poise the potential in the flotation region. In this regard, galena differs from minerals such as chalcopyrite for which the oxidized surface remains unless it is introduced into a reducing environment.

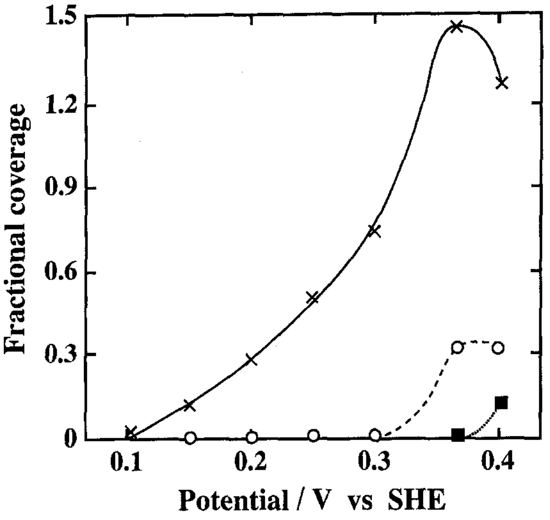

Fig. 8. Potential dependence of coverage of excess sulfur on galena after holding at set potential with rotation at 10 Hz for 1 min followed by standing on open circuit for (×) 0, (○) 10 and (□) 20 min.

3.5. *Nature of the surface sulfur species*

Lead sulfide is stable over a narrow range of composition, varying ±0.1% from PbS [15, 26]. Variations from a 1:1 stoichiometry involve the introduction of sulfur or lead vacancies which create free electrons or positive holes, respectively [26]. The presence of impurity atoms can enhance the carrier density by an order of magnitude over that for pure PbS [26]. Minor elements that are known to significantly influence carrier densities are present in natural galena such as that investigated in the present work. Sato [27] and Peters [28] have shown that galena, and similar binary sulfides, can display a continuous range of rest potentials determined by the sulfide stoichiometry. Such characteristics were depicted by Kobayashi and Kametani [29] on an Eh–pH diagram for the Pb–S–H_2O system in which variations in stoichiometry were represented in terms of charge carrier concentrations.

Richardson *et al.* [30] applied the rotating ring-disc electrode (RRDE) technique to demonstrate that lead and sulfur are removed from galena on potential scans within the region of stability of the mineral. It was concluded that sulfur is removed cathodically at potentials below 0.15 V in pH 4.6 solution by the process:

$$(1+x)\mathrm{PbS} + 2x\mathrm{H}^+ + 2x\mathrm{e}^- \longrightarrow \mathrm{Pb}_{1+x}\mathrm{S} + x\mathrm{H}_2\mathrm{S} \tag{6}$$

and lead atoms removed at potentials above this value by

$$\mathrm{PbS} + 2x\mathrm{H}^+ \longrightarrow \mathrm{Pb}_{1-x}\mathrm{S} + x\mathrm{Pb}^{2+} \qquad (7)$$

Reaction 6 will be the precursor to the formation of lead metal (Reaction 4) and Reaction 7 would occur prior to the formation of an oxidized phase. The thermodynamically favoured product of galena oxidation is sulfate and this species is formed on the extended exposure of galena to air [7]. However, oxidation of sulfur and sulfides to sulfate is slow and requires significant overpotentials to occur in the time scale of flotation [31]. As a result, elemental sulfur exhibits a region of metastability at potentials positive to the lead sulfide domain.

The rest potential of the galena electrode in pH 4.6, 8.0 and 9.2 solutions was found to be −0.01, −0.12 and −0.18 V, respectively. The value at pH 4.6 is significantly less than that at which zero current was observed in the RRDE studies that employed galena sourced from Kansas [30]. This indicates that the Broken Hill galena used in the present work has a higher metal content, and hence is more n-type than the Kansas mineral.

As the potential of the galena electrode is increased, either electrochemically or through exposure to an oxidizing environment, removal of excess lead atoms becomes favoured, followed by the creation of lead vacancies. This will result in a change of the galena from n- to p-type. That such a process would take place under conditions relevant to flotation was recognized by Tolun and Kitchener in 1964 [32]. Eventually, the potential will reach a value at which the formation of elemental sulfur is favoured, together with lead ions or a lead oxide species depending on pH. As pointed out in Section 1, XPS studies [4, 7, 9] have indicated that a metastable metal-deficient sulfide surface layer with stoichiometry outside the stable range for the bulk mineral is formed prior to separation of an elemental sulfur phase.

The metastable metal-deficient lead sulfide phase formed by oxidation of galena will overlie a stable metal-deficient phase which, in turn, overlies the bulk phase. As long as a significant oxidizing potential is maintained, the rate of removal of lead atoms from the surface will equal or exceed the rate of diffusion from the bulk. When the oxidizing conditions are terminated, the surface region can relax to the condition corresponding to the potential finally attained. Since this will be above the initial rest potential, there will always be a driving force for lead atoms to move to the surface.

Kobayashi and Kametani [29] estimated the time for the stoichiometry of lead sulfide to equilibrate with respect to the partial pressure of sulfur at 373 K by extrapolation of the data reported for elevated temperatures by Bloem [33]. Since the partial pressure of sulfur is related to potential [29], this is equivalent to the time to reach equilibrium at a set potential. Using the approach of Kobayashi and Kametani, a layer of galena 100 nm thick would be expected to equilibrate in about 1 h at 298 K. This estimated diffusion rate for lead in galena is much less than that for copper in binary copper sulfides; films of the latter species 1–5 mm thick were found [34] to equilibrate in a few minutes. The estimate does indicate, however, that the diffusivity of lead atoms in galena is sufficient to explain the relaxation of the composition of the surface layer observed in the present study.

In addition to being mobile in binary copper sulfides, copper is known to have a significantly greater diffusion coefficient in galena than that of lead [26]. Such high mobility accounts for the concentration of this minor element at the surface of galena during oxidation in acetic acid solution. By contrast, accumulation of copper has not been observed near the surface of galena as a consequence of the oxidation of the mineral in air. This may be because oxidation is less extensive in air than in acetic acid solution, in which medium the oxidized lead species are soluble, or because by the time electron spectra are determined typically, lead atoms have had sufficient time to attain an essentially uniform distribution within the initially lead-depleted sulfide lattice. It should be noted that investigations [30] on pure, synthetic lead sulfide have suggested a more rapid oxidation rate in air under ambient conditions than that for natural specimens of galena. In this particular case, spectra were determined quite soon after insertion into the spectrometer, thereby affording less time for possible lead atom redistribution. Nevertheless, it is clear that oxidation of the pure material can occur at least as rapidly as the natural mineral, so that the presence of minor elements such as copper is not the cause of either the incongruent oxidation or the relaxation of the oxidized surface layer observed for the galena under investigation in the present work.

4. Conclusions

(i) Electron spectroscopic investigations of the surface oxidation of galena on exposure to air confirm the absence of significantly altered sulfur environments.

(ii) Voltammetric studies of the oxidation of galena in air or in aqueous solutions in equilibrium with air show that a metal-deficient sulfide layer is formed at the mineral surface.

(iii) The composition of the metal-deficient layer relaxes slowly back towards that of the bulk mineral when the oxidizing conditions are removed.

(iv) This relaxation accounts for the absence of evidence of altered sulfur environments in electron spectra from galena after limited oxidation.

(v) The important surface species in effecting self-induced flotation of galena is a metal-deficient sulfide in which the composition at the interface with the solution is significantly enriched in sulfur atoms.

(vi) Correlation of the potential dependence of self-induced flotation, and of the extent of metal-deficiency at an oxidized galena surface, indicates that the equivalent of about one half a monolayer of excess sulfur is required for significant flotation to be effected.

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