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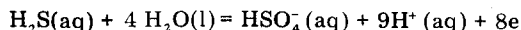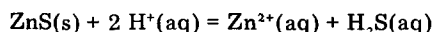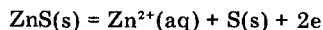
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ABSTRACT

Narasagoudar, R.A., Johnson, J.W. and O'Keefe, T.J., 1982. The anodic dissolution of ZnS electrodes in sulfuric acid solutions. *Hydrometallurgy*, 9: 37—55.

The anodic dissolution of reagent grade ZnS and ZnS concentrate has been studied. The majority of the research was conducted in H_2SO_4 although a limited number of tests were made in HCl and KOH. Polarization studies showed that both Zn^{2+} and S were products in the acidic solutions. ZnS passivated in KOH solutions. The electrodes were fabricated by hand pressing mixtures of ZnS + pitch (5—15%) and sintering at 800°C in a N_2 atmosphere. The open circuit potentials were considered to be mixed potentials resulting from the anodic dissolution of ZnS and the cathodic reduction of S or O_2. Current efficiencies and Zn^{2+}/S ratios were determined at 0.5 and 0.85 V vs. SHE. The results indicated the occurrence of both electrochemical and chemical dissolution steps as well as the further oxidation of H_2S, namely,

$$ZnS(s) = Zn^{2+}(aq) + S(s) + 2e$$

$$ZnS(s) + 2 H^+(aq) = Zn^{2+}(aq) + H_2S(aq)$$

$$H_2S(aq) + 4 H_2O(l) = HSO_4^-(aq) + 9H^+(aq) + 8e$$

The overall dissolution appears to be mass transfer-limited, probably either by the diffusion of Zn^{2+} from the reaction interface, through the reacted layer to the bulk solution, or the dissolution of precipitated $Zn(OH)_2$ in the reacted layer by the diffusion of H^+ into the layer. The concentrate anodes polarized more drastically than the reagent grade ZnS anodes, possibly due to the presence of PbS impurity which would form $PbSO_4$ in the anode pores.

INTRODUCTION

For standard zinc production, the ore concentrate (ca. 54% Zn, 30% S) is roasted to yield a ZnO calcine (ca. 65% Zn, 0.4% S) (Baker et al., 1970), which is then reduced either by electrometallurgical or pyrometallurgical processes. Although most of the SO_2 produced during roasting is recovered by making sulfuric acid, some of it escapes contributing to air pollution. With environmental control guidelines becoming more stringent, the continued use of processes which produce pollutants becomes more expensive. It would therefore be highly desirable to find an alternate process where the pollutant SO_2 is not produced.

Several processes have been studied which allow the recovery of sulfur from the sulfide in the elemental form. One process involves the leaching of the concentrate under an oxygen atmosphere at moderate pressures. Another is the direct electrolytic oxidation of ZnS to zinc ions and elemental S coupled with the electrowinning (reduction) process. A considerable energy saving would also be realized here as the unproductive anodic reaction in the electrowinning of Zn would not be necessary.

The idea of sulfide electrolysis is not new. The anodic dissolution of sulfides of Cu (Oki et al., 1967; Venkatachalam and Mallikarjunan, 1968; Habashi et al., 1968; Habashi, 1971; Zevgolis, 1971; Brennet et al., 1974; Mackinnon, 1976a; Mackinnon, 1976b), Pb (Ito et al., 1961; Sawamoto et al., 1965; Brodie, 1969; Skewes, 1972; Johnson et al., 1978; O'Keefe, 1976a; O'Keefe, 1976b), and Zn (O'Keefe, 1976b; Sawamoto et al., 1965; Kunieda et al., 1971; Oki et al., 1975; Deshmukh et al., 1975) has been studied by various investigators. The successful application of this process to commercial production has been demonstrated by INCO's direct electrolysis of Ni_3S_2 at the Thomson refinery in Canada (Boldt, 1967).

ZnS electrolysis has several major problem areas, one of which is the fabrication of anodes of acceptable electrical conductivity* that have sufficient mechanical strength for handling. This has been dealt with rather extensively in a separate study (O'Keefe, 1976b) and resulted in a successful fabrication method involving the sintering of compressed pellets of ZnS + pitch mixtures. This study reports the results of the anodic dissolution of the ZnS + pitch electrodes.

EXPERIMENTAL

Materials

The materials used in the fabrication of the ZnS anodes were reagent grade ZnS (Pfaltz and Bauer Inc.) and a carboneous pitch binder (Pittsburg and Midway Coal Mining Co.). An X-ray analysis of the ZnS showed that it consisted of both sphalerite (β-ZnS) and wurtzite (α-ZnS).

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*ZnS is a semi-conductor with electrical resistivity = 6×10^9 ohm-cm (Jan et al., 1976).

Anode fabrication

Because of its volatility, ZnS cannot be melted and cast at atmospheric pressure to form a dense material suitable for massive electrodes. To develop a technique for producing electrodes, reagent grade ZnS, with and without binder additions, was compressed in a 1/2 in diameter mold and the resulting compact sintered. Satisfactory compacts (about 1 cm long and porous) were obtained by hand pressing ($\sim$ 35 bar) a mixture of ZnS + pitch (5, 10, and 15%) and sintering at 800 ± 5°C for about 30 min in a N_2 atmosphere (Narasagoudar, 1977). The 10% pitch compacts gave the best stability and were used in most of the studies.

Selected compacts with less than 8 Ω resistance were mounted in transoptic powder to expose one end of the cylinder to the electrolyte. The exposed (front) surface was wet polished (600 grit final) using distilled water and dried in a vacuum desiccator. Electrical connections were made with platinum foil and wire to the back of the compact.

Electrolysis

Steady state and transient studies were conducted in approximately 250 ml of acid sulfate or chloride electrolytes. The cathodes were platinized Pt gauze or an Al rod mounted in transoptic powder. The reference electrode was Hg_2SO_4 (1 M H_2SO_4). All the potentials reported have been converted to the standard hydrogen scale (SHE). The temperature of the electrolysis cell was controlled at 20—65°C using a water bath. In some of the tests, the H_2S produced was collected by passing the effluent gas (N_2 + H_2S) through two traps, each containing 150 ml of slightly acidified 0.5 M $Pb(Ac)_2$. The precipitated PbS was collected and weighed.

The electrolyte entrapped in the pores of the anode was recovered by soaking the electrolyzed anode in stirred and heated ($\sim$ 50°C) distilled water. It is hereafter referred to as "anode wash". The cathode deposit was dissolved in acid. The electrolyte, the anode wash, and the dissolved cathode deposit were combined and analyzed for Zn^{2+} by both atomic absorption and EDTA titration. The anode, after recovering the entrapped electrolyte, was dried in a vacuum desiccator, removed from the mount, and pulverized for sulfur analysis. S was determined by CS_2 extraction and/or evaporation at 420°C into a stream of nitrogen. The anodes were subjected to SEM examination and X-ray analysis before and after electrolysis.

The effect of pH and Zn^{2+} concentration was studied using electrolytes containing H_2SO_4 + Na_2SO_4, and H_2SO_4 + $ZnSO_4$, respectively. Quantities were selected to give solutions of constant SO_4^{2-} concentration (1.0 M) (and approximately constant ionic strength).

RESULTS AND DISCUSSION

Open circuit potentials

Open circuit potential measurements were begun when the anode was placed in the electrolysis cell and the N_2 purge initiated. The potential generally became more negative with time, reaching a relatively stable value (the "rest" potential) after about 10 h. The rest potentials increased with increasing pH, from 0.22 V at 0 pH to 0.37, 0.47, and 0.49 V at 0.7, 1.6, and 2.7 pH, respectively. An odor of H_2S (that became less intense with increasing pH) could be detected in the effluent gas from the cell.

The observed rest potentials were considered to be mixed potentials as no single electrochemical reaction for the $Zn-S-H_2O$ system could be found to which they corresponded. A consideration of possible reactions for which thermodynamic data are available led to the following which can account for the observed behavior.

pH = 0

The potentials obtained at pH = 0 and 45°C can be explained as mixed potentials resulting from a self-dissolution or corrsion type reaction as follows. At the anodic sites
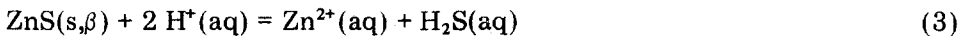
$$ZnS(s,\beta) = Zn^{2+}(aq) + S(s) + 2e \tag{1}$$

$$\begin{aligned} E_{45} &= 0.299 + 0.0315 \log a_{Zn^{2+}} \\ &= 0.110 \text{ V}, (a_{Zn^{2+}} = 10^{-6})* \end{aligned} \tag{1a}$$

and at the cathodic sites

$$S(s) + 2 H^+(aq) + 2e = H_2S(aq) \tag{2}$$

$$\begin{aligned} E_{45} &= 0.141 - 0.0315 \log a_{H_2S} - 0.0631 \text{ pH} \\ &= 0.330 \text{ V}, (a_{H_2S} = 10^{-6}, \text{pH} = 0) \end{aligned} \tag{2a}$$

These combine to give the overall reaction Z

$$ZnS(s,\beta) + 2 H^+(aq) = Zn^{2+}(aq) + H_2S(aq) \tag{3}$$

$$\Delta G^\circ_{45} = + 7.32 \text{ kcal}** \tag{3a}$$

As can be seen from the potentials for reactions (1) and (2), this reaction can proceed spontaneously as written when the activities of Zn^{2+} and H_2S are low.

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*Activities of 10^{-6} were assumed for the species not initially present in solution (Zn^{2+}) or removed by purging (H_2S). This number is often (Verhulst et al., 1972; Criss et al., 1964a; Wagman et al., 1968; Criss et al., 1964b; Barin and Knacke, 1973; Connick and Powell, 1953; Garrels and Christ, 1965; Latimer, 1952; Kellog, 1973; Helgeson, 1967) used so that thermodynamic potentials can be calculated for comparison with observed values.

**1 cal = 4.184 J.

The presence of elemental S on the anode surface to participate in reaction (2) initially can be explained by a slightly different corrosion reaction in the presence of air which involves the anodic component, reaction (1), and the cathodic reaction

$$\tfrac{1}{2} O_2(aq) + 2 H^+(aq) + 2e = H_2O(l) \tag{4}$$

$$E_{25} = 1.271 + 0.0148 \log a_{O_2} - 0.0591 \text{ pH} \tag{4a}$$

Reactions similar to this have been proposed to explain the enhancement of ZnS dissolution by O_2 during leaching operations (Habashi, 1966; Majima and Peters, 1966; Scott and Dyson, 1968; Kunieda et al., 1973). The amount of O_2 initially dissolved in the electrolyte was probably sufficient to allow for the production of enough S by a combination of reactions (1) and (4) so that when the O_2 was removed by purging, local corrosion could continue by a combination of reactions (1) and (2).

pH $\geqslant$ 0.7

A limitation of the local corrosion schemes shown above is in explaining the effect of pH on the rest potential. As noted before, the rest potentials increased with increasing pH. Reaction (1), combined with either (2) or (4), predicts decreasing potentials with increasing pH or at best no change with pH. This is also true for most other feasible schemes where ZnS dissolution is the anodic reaction.

However, it appears that the rest potential at pH $\geqslant$ 0.7 is a mixed potential comprising the oxidation of ZnS by reaction (1) and the reduction of O_2 involving Zn^{2+} and ZnO or H^+ and H_2O.

An experiment was designed to test this hypothesis based on the assumption that the combined N_2 purge and consumption of O_2 by reaction (5) will eventually deplete the electrolyte of O_2 and the rest potential will shift to the value observed at pH = 0. An electrolyte of pH = 1.6 was used. The initial open circuit potential was 0.51 V at the time the anode was placed in the cell and the N_2 purge begun. It decreased to near the rest value of 0.47 V after 10 h. After 43 h, the potential had slowly decreased to 0.42 V, where it suddenly decreased rather sharply to a lower value, then continued to drift lower, reaching 0.27 V after 60 h. At this time, the N_2 purge was replaced with an O_2 purge. The potential rose rapidly to 0.45 V and remained relatively stable, thus indicating the reforming of the ZnO film made possible by the presence of O_2.

Steady state polarization studies

Polarization studies for extended time periods were conducted both potentiostatically and galvanostatically. Potentiostatically, the ZnS (sintered ZnS + 10% pitch) electrodes were polarized at 0.50 and 0.85 V in 1.0 *M* H_2SO_4 and 1.0 *M* HCl. The porous nature of the electrodes can be seen in
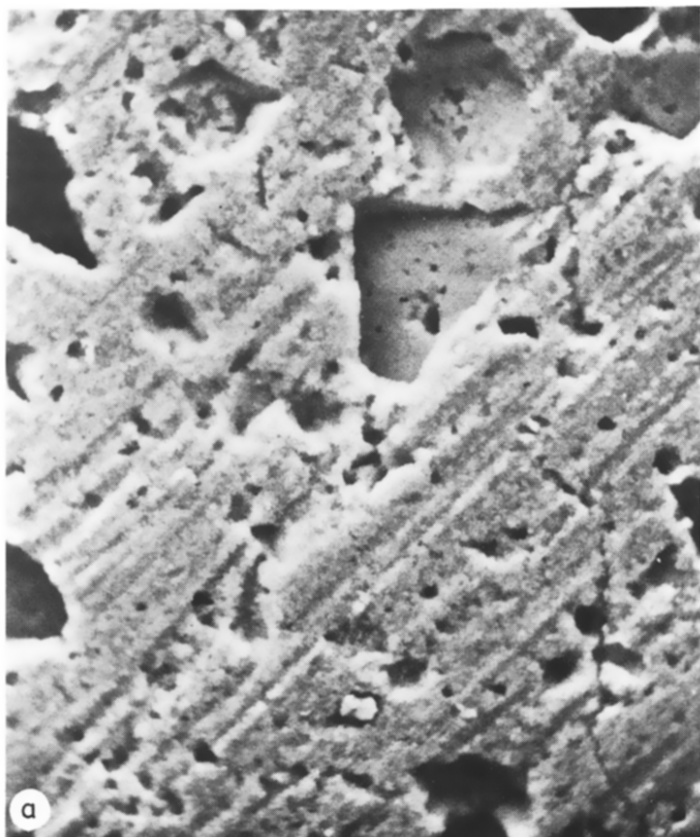
Fig. 1a which shows the polished unreacted surface which has a gray color. As soon as an anodic current is passed, a reaction layer is initiated which is black in color. A cross-section of a reacted anode, Fig. 1b, shows the reacted black layer in front and the original gray layer behind. Some reaction had also occurred in the gray area, though, as elemental S could be extracted from it. X-Ray analyses of the areas showed that the black layer was predominantly S with some unreacted ZnS and vice versa for the gray layer. Most of the S formed was orthorhombic; however, some of it may have been amorphous since the amount of S determined by evaporation in the furnace was greater than that determined by dissolution in CS_2.

The morphology of the electrode surface changed little after polarizing in H_2SO_4; however, it was severely etched when polarized in HCl.

The current—time behavior for ZnS anodes is shown in Fig. 2. for both 0.50 and 0.85 V. During the first one-half hour, there is a rather sharp drop

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*The color difference which is easily discernible by eye does not show up on the SEM photograph.
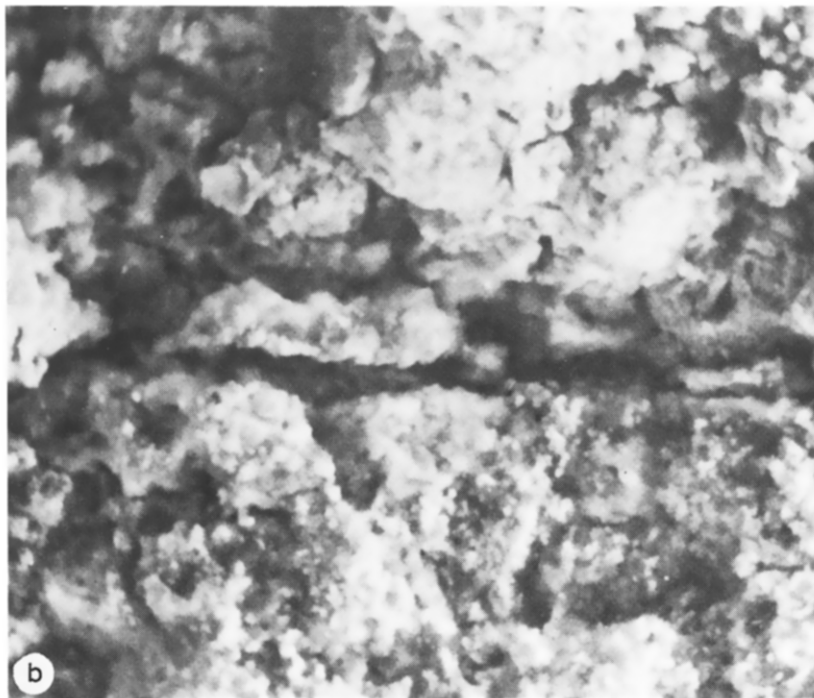
Fig. 1. SEM photographs of ZnS + pitch electrodes. a, polished unreacted surface of a ZnS + 10% pitch electrode (300×); b, cross-section of a ZnS + 15% pitch electrode. Galvanostated in 1.0 M H$_2$SO$_4$ at 10 mA/cm^2 and 45°C for 65 h (100×). (Reacted black layer at the bottom and partially reacted gray layer on the top.).

in current. Afterwards, the current remains relatively steady when the anode is potentiostated at 0.50 V. However, at 0.85 V, the current continues to decrease slowly after the first sharp drop, probably due to a thickening of the reacted layer through which reactants and products must diffuse. At 0.50 V, the current is about the same for both 1.0 M HCl and 1.0 M H$_2$SO$_4$, whereas at 0.85 V, the current for 1.0 M H$_2$SO$_4$ is 2—3 times larger than that for 1.0 M HCl. The tendency of S to form covalent bonds is probably responsible for this behavior. Cl$^-$ adsorbs on most surfaces and can form covalent bonds through an oxidative adsorption more readily than sulfate. This oxidative "chemisorption" of Cl$^-$ on S would block the surface from further reactions such as H$_2$S or HSO$_4^-$ formation and would be favored by an increasing potential. The etching of the ZnS surface is also explained by such a reaction as S—Cl compounds readily hydrolyze, thereby corroding the surface (Cotton and Wilkinson, 1962).

Galvanostatic studies conducted on these anodes showed little polarization, if any, at 10 mA/cm^2 in 1.0 M H$_2$SO$_4$. In alkaline solutions, however, the polarization was significant, probably due to Zn(OH)$_2$ precipitation in the pores of the anode.
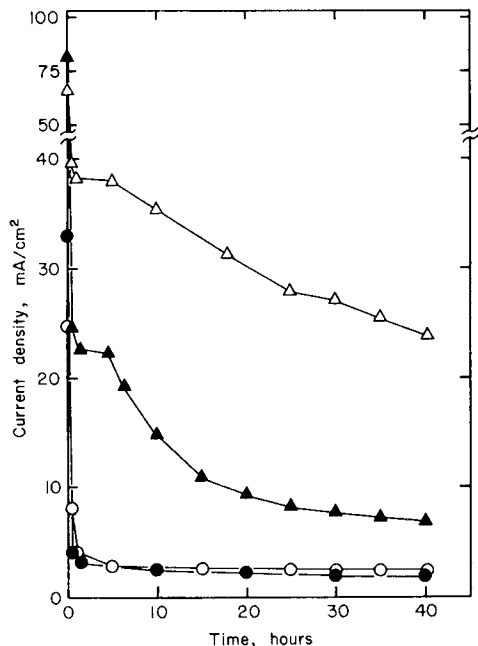
Fig. 2. Variation of current density with time for potentiostatic polarization of ZnS 3 10% pitch electrodes at 45°C. (△, 0.85 V, 1.0 M H$_2$SO$_4$; ▲, 0.85 V, 1.0 M HCl; ○, 0.50 V, 1.0 M H$_2$SO$_4$; and ●, 0.50 V, 1.0 M HCl).

Zinc was deposited on the aluminum cathode during potentionstatic and galvanostatic runs in acidic solutions. A non-dispersive X-ray analysis of the deposit showed only Zn with no impurities.

Apparent current efficiencies for Zn^{2+} production

Apparent current efficiencies were calculated from the quantities of Zn^{2+} produced and charge passed using the reaction

$$ZnS(s) = Zn^{2+}(aq) + S(s) + 2e \qquad (1)$$

The charge passed was measured with a Cu coulometer. The sulfur produced was also determined to check the Zn^{2+}/S ratio. The electrolytes were checked for dissolved impurities by atomic absorption; only Mg^{2+} was detected. Its concentration was so small that it did not affect the efficiency calculations.

The results of product analyses and current efficiency calculations from potentiostatic tests are shown in Table 1. The low current efficiencies (at 0.85 V vs. SHE) indicate that the anodic dissolution of ZnS is not the only reaction occurring. (The molar ratio of Zn^{2+}/S would be 1.0 if only reaction (1) were occurring.) Since this ratio was found to be greater than 1.0, either some of the S from reaction (1) is consumed or Zn^{2+} is produced without

TABLE 1

Products and current efficiencies for the anodic dissolution of ZnS + 10% pitch electrodes in 1.0 M H_2SO_4 at 45°C

Potential (V vs. SHE)	Time (h)	Charge passed (Faradays $\times 10^3$)	Zn^{2+} dissolved (mol $\times 10^3$)	S detected (mol $\times 10^3$)	Current efficiency (%)	Zn^{2+}/S molar ratio
0.85	47.5	47.774	7.152	3.030	29.9	2.36[a]
0.85	40.2	55.247	10.463	6.160	37.9	1.70
0.85	40.2	53.385	8.847	4.697	33.1	1.88[b]
0.85	40.0	21.395	5.339	3.992	49.9	1.34[c]
0.50	47.5	1.625	0.940	1.141	115.8	0.82[a]
0.50	40.2	4.615	2.430	2.930	105.3	0.83
0.50	40.2	4.723	2.475	2.370	105.1	1.04[d]
0.50	40.0	4.062	2.544	2.080	125.1	1.22[c]

[a] Temperature was 25°C.
[b] H_2S collected was 5.3×10^{-5} mol.
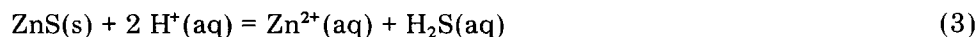[c] Electrolyte was 1.0 M HCl.
[d] H_2S collected was 2.93×10^{-4} mol.

simultaneous S production. For the former case, S could be further oxidized according to the reaction

$$S(s) + 4 H_2O(l) = HSO_4^-(aq) + 7 H^+(aq) + 6e \tag{7}$$
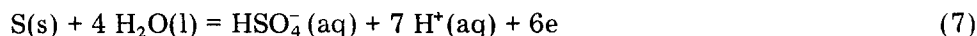
$$E_{45} = 0.323 + 0.0105 \log a_{HSO_4^-} - 0.0736 \text{ pH} \tag{7a}$$

For the latter, Zn^{2+} could be produced without simultaneous production of elemental S by reaction (3), viz.

$$ZnS(s) + 2 H^+(aq) = Zn^{2+}(aq) + H_2S(aq) \tag{3}$$

This reaction also offers an explanation for the odor of H_2S detected in the effluent gas from the electrolysis cell. Since H_2S is unstable at 0.85 V, some of it could further react to yield a stable species such as HSO_4^- according to the reaction

$$H_2S(aq) + 4 H_2O(l) = HSO_4^-(aq) + 9 H^+(aq) + 8e \tag{8}$$
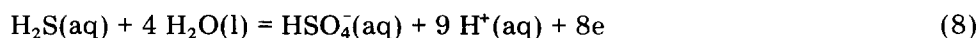
$$E_{45} = 0.277 - 0.0079 \log a_{H_2S} + 0.0079 \log a_{HSO_4^-} - 0.071 \text{ pH} \tag{8a}$$

The oxidation of H_2S and/or S to HSO_4^- at 0.85 V was confirmed by the precipitation of $BaSO_4$ from the 1.0 M HCl electrolyte after electrolysis. A similar test on the electrolyte from a 0.50 V electrolysis gave only a slight turbidity.

The notable differences in the dissolution characteristics at 0.50 and 0.85 V included the larger apparent efficiencies (some in excess of 100%) and the

smaller Zn^{2+}/S ratios (closer to 1.0) for the lower potential. The odor of H_2S in the effluent gas at 0.50 V was stronger than at 0.85 V.

The experimental results suggest that ZnS dissolves at 0.50 V by the simultaneous reactions,

$$ZnS(s) = Zn^{2+}(aq) + S(s) + 2e \qquad (1)$$

$$ZnS(s) + 2\,H^+(aq) = Zn^{2+}(aq) + H_2S(aq) \qquad (3)$$
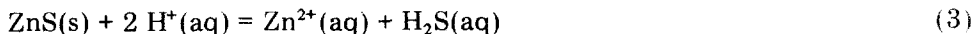
The small amount of HSO_4^- detected indicates that one or both of the products of these reactions (H_2S and S) is being further oxidized, but not nearly to the same extent as at 0.85 V.

Since elemental S (from ZnS dissolution) and carbon (from pitch) are the phases composing the anode slime (besides unreacted ZnS), several experiments were conducted to determine if they were electrochemically active. Electrodes for these tests were prepared from a 0.5 in diameter graphite rod, from pressed and sintered pitch and from pressed and sintered graphite + S. When potentiostated at 0.50 V in 1.0 M H_2SO_4, these anodes yielded currents of only a few microamperes.

To further verify the feasibility of reactions (7) and (8) at higher potentials, tests were conducted in 1.0 M HCl where S (a 50% graphite + 50% S anode) and H_2S (from a H_2S sparge of the anolyte with sintered pitch anode) were subjected to oxidizing conditions (anodes potentiostated at 0.85 V). The currents sustained in both cases were of the order of μA. In the H_2S oxidation test, the current dropped quite rapidly to 1 μA, when the H_2S flow was replaced with N_2. When H_2S was reintroduced, the current increased sharply. A semi-quantitative analysis (Kolthoff and Sanders, 1952) of the electrolytes (including the "anode washes") for SO_4^{2-}, confirmed the oxidation of both S and H_2S.

The data shown in Table 1 allow one to calculate (Narasagoudar, 1977) the amounts of Zn^{2+} produced by the separate reactions, the amounts of H_2S and S produced and oxidized, and the extents of the various reactions assuming that reactions (1), (3), (7), and (8) sufficiently describe the total dissolution process. The results shown in Tables 2 and 3 generally agree with the basic suppositions.

It can be seen from the results of the calculations that consistency between the charge passed during the experiments and the quantities of Zn^{2+} produced is attained only for a unique set of conversions (extents) of the various reactions. In general this set includes: (1) a substantial amount of Zn^{2+} produced by the chemical dissolution reaction, reaction (3); (2) the electro-oxidation of a substantial amount of the H_2S, reaction (8), that is produced by the chemical dissolution; and (3) essentially minimal or no electro-oxidation of the sulfur, reaction (7), produced by the electrochemical dissolution reaction, reaction (1). The primary discrepancy between the experiments and the calculations involved the amount of S. The quantity consistent with the calculations was always considerably less than

TABLE 2

Actual and apparent current efficiencies and the amounts (mol) of Zn^{2+} and S produced by reaction (1) (=A), Zn^{2+} and H_2S Produced by reaction (3) (=B), S oxidized by reaction (7) (=αA), and H_2S oxidized by reaction (8) (=βB) in 1.0 M H_2SO_4

						Current efficiency (%)	
Potential (V vs. SHE)	Temp (°C)	A $\times$ 10^3	B $\times$ 10^3	αA $\times$ 10^3	βB $\times$ 10^3	Actual	Apparent
0.85	25	1.574	5.578	0	5.578	6.6[a]	29.9
0.85	45	4.743	5.720	0	5.720	17.2[a]	37.9
0.85	45	2.857	5.990	0	5.937	10.7	33.1
0.85	45	2.899 (+1.5%)	5.948 (−0.7%)	0	5.948 (+0.2%)	10.9[a] (+1.9%)[b]	33.1
0.85	45	3.553	1.786	0	1.786	33.2[a,c]	49.9
0.50	45	2.126	3.487	0	0.056	90.5	105.1

[a] Assumed that 0 mol of H_2S was collected since the amount involved was small.
[b] The errors in the quantities calculated with the above assumption (a) for run #3 are given in parentheses.
[c] The electrolyte was 1.0 M HCl.

TABLE 3

Extents (%) of the various reactions occurring on the ZnS anode in 1.0 M H_2SO_4

Potential (V vs SHE)	Temp (°C)	Zn^{2+} produced by chemical dissolution reaction (3)	Extent (%) of charge used for		
			Zn^{2+} production by reaction (1)	S oxidation by reaction (7)	H_2S oxidation by reaction (8)
0.85	25	78.0	6.6	0	93.4
0.85	45	54.7	17.2	0	82.8
0.85	45	67.7	10.7	0	89.3
0.85	45	33.5	33.2	0	66.8[a]
0.50	45	14.1	90.5	0	9.5

[a] The electrolyte was 1.09 M HCl.

that found by analysis. A re-examination of the procedure for the sulfur determination (evacuation and flushing with N_2 of the furnace chamber with the sample inside at ca. 25°C and evaporation of the S at 420°C in a stream of N_2) revealed that significant amounts of material were lost by treating an unelectrolyzed pulverized compact. The amounts involved were sufficient to account for the discrepancy.

Several intersting trends can be seen from the extents of the reactions in Table 3. First is the effect of potential on the fraction of the H_2S oxidized. It increases from 9.5% at 0.50 V to 80—90% at 0.85 V in 1.0 M H_2SO_4. The

fraction oxidized in 1.0 M HCl at 0.85 V is significantly less (66.8%). A comparison with Table 2 shows that more H_2S was produced at the higher potential (also greater proportion of chemical dissolution) but the greater extent of oxidation was responsible for the lesser amount being collected (Table 1). The higher chemical dissolution rate probably results from a LeChatelier type shift associated with the fast removal of the H_2S. The relative proportion of Zn^{2+} produced from the chemical dissolution also changes with potential, from 14.1% at 0.50 V to ~60% at 0.85 V.

The actual current efficiencies, based on the charge passed for producing Zn^{2+} by reaction (1) alone, are consistently lower than the apparent values (Table 2). This is primarily due to neglecting Zn^{2+} contributions from reaction (3). From Table 3 it can also be seen that at 0.85 V, only 10—17% of the charge passed is used for the anodic dissolution of ZnS, the rest being used for H_2S oxidation. However, this increases to about 90% for ZnS dissolution at 0.50 V. The Zn^{2+} contribution from reaction (3) increases when the rate of H_2S oxidation is high.

In any commercial process using the anodic dissolution of ZnS it would be desirable to minimize the H_2S released as well as reduce the charge used for its oxidation. Table 3 indicates this is most effectively accomplished by lowering the potential, but this would also lower the total dissolution rate. In this regard, Oki and Kammel (1975) have been successful in decreasing H_2S evolution by using redox couples of Fe and Mn. It can also be seen that H_2S production is lower in HCl than in H_2SO_4. This is probably explained by a preferential adsorption of Cl^- on the ZnS surface which is well known for its interference with other electrode reactions that involve adsorption of reactants.

Temperature effect

The effect of temperature on the dissolution rate is shown in Fig. 3. The Arrhenius plot yields an apparent activation energy of 4.4 kcal at 0.85 V. Such a low value normally indicates mass transfer limitations. This might be expected considering that reactants and products must diffuse through a considerable thickness of "reacted" layer that contains C, S, unreacted ZnS, etc.

pH effect

Figure 4 shows the effect of pH on the rate of dissolution at 45°C and 0.85 V. The decreasing rate with increasing pH suggests that H^+ is a reactant in either the rate determining step (r.d.s.) or some equilibrium step prior to the r.d.s. Of the surface reactions, reactions (1), (3), (7), and (8), only reaction (3), the chemical dissolution of ZnS, has H^+ as reactants. However, the increased H_2S production with decreasing pH should give a higher oxidation rate (electrochemical) of H_2S, i.e., a larger current. Also, any passivation
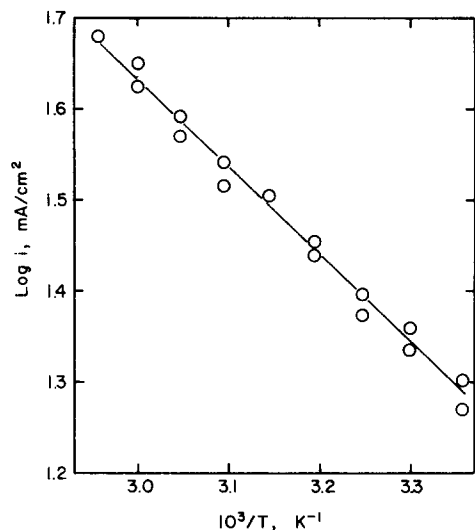
Fig. 3. Effect of temperature on the anodic dissolution of ZnS + 10% pitch electrode in 1.0 M H$_2$SO$_4$ at 0.85 V (SHE).
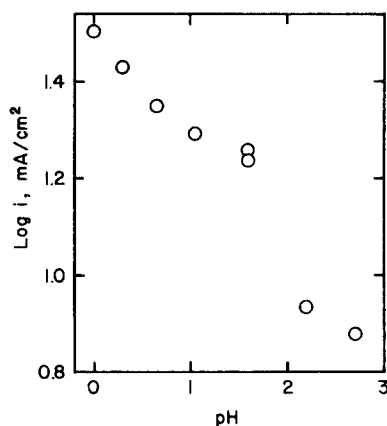
Fig. 4. Effect of pH on the anodic dissolution of ZnS + 10% pitch electrode in SO$_4^{2-}$ solutions at 0.85 V (SHE) and 45°C.

due to zinc oxide or hydroxide precipitation in the pores of the reacted layer would be reduced as the pH is decreased, thus leading to increased currents.

Effect of Zn^{2+} and atmosphere

The currents obtained with increasing Zn^{2+} additions decreased only slightly. This behavior would be consistent with a mass transfer limited process where a high concentration of Zn^{2+} exists at the reaction interface due to reactions (1) and (3) and are carried into the bulk solution primarily by charge transport. However, the mass transfer limitation is probably imposed by the diffusion of H$^+$ as discussed later.

Nitrogen, oxygen, and hydrogen sulfide were used for purging the electrolyte as well as sparging the anode surface during the electrolyses. There was no change in the rate of dissolution with N$_2$ or O$_2$ purging or sparging. Kunieda et al. (1971) and Oki and Kammel (1975) have proposed an electrochemical (reciprocal galvanic) model for the dissolution of ZnS in contact with graphite or CuS, by slurry electrolysis in which oxygen reduction was the cathodic reaction. At the anodic sites (ZnS particle)

$$ZnS(s) = Zn^{2+}(aq) + S(s) + 2e \qquad (1)$$

At the cathodic sites

$$\tfrac{1}{2} O_2(aq) + 2 H^+(aq) + 2e = H_2O(l) \qquad (4)$$

This suggests that the presence or absence of oxygen has a significant effect on the rate of dissolution. However, with a bulk electrode sample such as used in this study, no effect was observed when either N_2 or O_2 sparging was used.

The introduction of H_2S into the cell caused pronounced decreases in the current. When the concentration of H_2S in the cell was reduced by purging with N_2, the current increased. This behavior, which was observed at various thicknesses of the reacted film (various times during an extended electrolysis), is explained by the deposition of ZnS in the electrode pores and/or on the electrode surface by the reverse of reaction (3). Such a non-conducting material (ZnS not in contact with C) would reduce the rate of the electrochemical reaction. The equilibrium relationship for this reaction is

$$\frac{a_{Zn^{2+}}\, a_{H_2S}}{a^2_{H^+}} = 9.30 \times 10^{-6} \text{ at } 45^\circ C$$

Thus at pH = 0, when the product of the activities of Zn^{2+} and H_2S exceeds 9.30×10^{-6} ZnS precipitation is favored. This could easily occur when $\bar{p}_{H_2S} = 1$ atm (during purging). When H_2S purging is ceased, the deposited ZnS begins to dissolve by reaction (3) and the current increases.

Transient polarization studies

Cyclic potential sweep studies were made on ZnS electrodes in the previously mentioned electrolytes. Freshly polished as well as slime-covered (reacted) surfaces were used. After the rest potential had been established as described previously, the cycles were begun by potentiostating the anode at the rest potential, and then increasing the potential at a selected linear rate until a preset upper limit was reached. After the upper limit was reached, the potential was returned to the rest potential at the same rate.

Figure 5 shows cyclic voltammograms of a slime-covered ZnS electrode in 1.0 M H_2SO_4 at 45°C. The characteristics of the voltammograms depend on the initial state of the electrode surface. If the electrode is allowed to equilibrate with the electrolyte and establish the normal rest potential, 0.24 V, the inital current is anodic, increasing very rapidly for the first 150 mV above the rest potential, then more slowly to a maximum value at the highest potential (first cycle). The latter increases are those that might be expected from the effect of potential on the diffusion of charged species. (The initial rapid current increases are probably associated with an activation controlled process.) During the reverse sweep of the voltammogram, the current decreases slowly to the vicinity of 0.6 V, where it begins decreasing rapidly and changes polarity before reaching the starting potential. Fairly substantial cathodic currents are observed at the end of the cycle when the starting potential had been reached. (The potential at which the current changes polarity will hereafter be called "cross-over potential.") Repetitive cycles, taken before the electrode is re-equilibrated with the electrolyte,
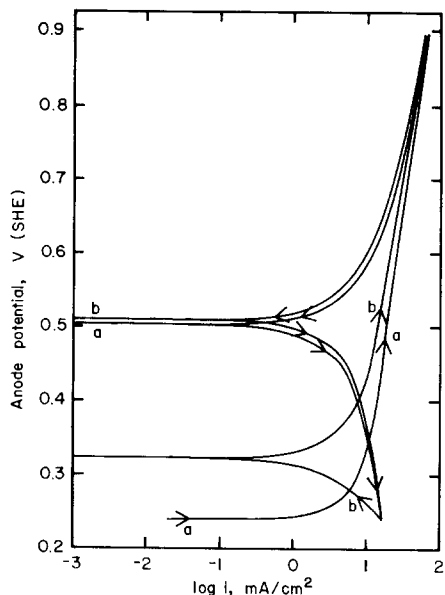
Fig. 5. Effect of state of the anode and sweep rate on the voltammogram for the anodic dissolution of ZnS + 10% pitch electrode in 1.0 M H_2SO_4 at 45°C. a, 1st cycle after equilibration, 10 mV/s; b, 2nd cycle, 10 mV/s.

begin with a cathodic current which decreases rapidly and changes polarity at varying potentials between the initial rest potential and ca. 0.35 V (as shown by the second cycle). The subsequent cycles also always exhibit an inflection point in the ascending portion of the curve in the region of 0.50—0.55 V.

The equilibration of the electrode with the electrolyte apparently involves the reaction (cathodic) of products formed during the ascending potential portion of the curve and the diffusion of these products away from the electrode. If sufficient time is allowed for this equilibration, either by allowing time to elapse between cycles or potentiostating the electrode at the rest potential, the initial current will again be anodic. Otherwise it will be cathodic. Varying the sweep rate is decreased, the cross-over potential decreases.

In the second cycle the initial current is cathodic and decreases with increasing potential. This cathodic current is the net current that results from both anodic and cathodic processes on the surface. When sufficient reaction products (from the earlier cycle) are present, the cathodic current will be greater than that from the usual anodic dissolution and a net cathodic current results. This current decreases with increasing potential for several reasons: (1) the reactants (reaction products from the earlier cycle) are being consumed, (2) the over-potential for the cathodic reaction is being decreased by the increase in the applied potential, and (3) the over-potential for the anodic reaction is being increased by the same potential change. The summa-

tion of these two currents gives smaller and smaller cathodic currents with increasing potential until the polarity is changed. Thus, the potential at which the polarity change occurs depends on the amount of the reaction products formed as well as the nature of the reaction.

Simultaneously with the ZnS oxidation, reaction (1), some of the H_2S produced by the chemical reaction (3) is also being oxidized, reaction (8), since its stability decreases as the potential increases. As the potential increases above 0.35 V, S on the electrode surface can be oxidized to HSO_4^-. This and/or the increased rate of H_2S oxidation may be the cause of the inflection point at about 0.54 V, although in the case of S oxidation, the amounts involved would have to be very small. Between this and the most positive potential of the test, reactions (1), (3), (8), and possibly (7) are all occurring simultaneously during both the forward and the return portions of the cycle. During the return sweep the current begins to decrease rapidly at about 0.60 V. It is proposed that this is associated in part with the commencing of the following cathodic reaction, involving $Zn(OH)_2$ and/or ZnO, for example.

$$Zn(OH)_2(s,\epsilon) + 2\ H^+(aq) + S(s) + 2e = ZnS(s) + 2\ H_2O(l) \tag{9}$$
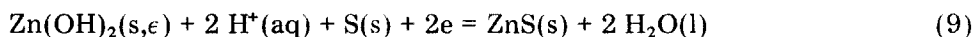
$$E_{45} = 0.621 - 0.631\ pH \tag{9a}$$

As the potential is decreased further, the rate of the cathodic reaction eventually approaches the rate of the anodic reactions and the total current approaches zero. It is at this point that the peak appears (current changes polarity) in the voltammogram. With further potential decreases, the cathodic current increases giving larger net cathodic currents. During the reverse sweep, if the potential is held constant at any point between the cross-over potential and the rest potential, the cathodic current decreases, changes polarity again, and becomes anodic. However, if the potential is held constant above the cross-over potential but below 0.621 the anodic current increases. This occurs because the cathodic portion of the net current decreases as the $Zn(OH)_2$ is consumed and the net current increases in the anodic direction.

The $Zn(OH)_2$ of reaction (9) can form in the reacted zone (slime) by the hydrolysis reaction

$$Zn^{2+}(aq) + 2\ H_2O(l) = Zn(OH)_2(s,\epsilon) + 2\ H^+(aq) \tag{10}$$
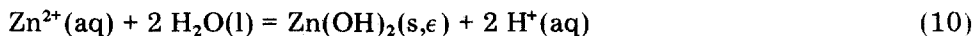
$$\Delta G_{45}^{\circ} = +14.81\ kcal \tag{10a}$$

When ZnS is dissolving, the concentration of Zn^{2+} in the slime is increased substantially above that in the bulk electrolyte. Simultaneously hydrogen ions are moved out of the slime by charge transport since they initially are the principal charge carriers. Under these local conditions of high Zn^{2+} concentration and high pH, $Zn(OH)_2$ can readily precipitate. It would appear that if the $Zn(OH)_2$ were to keep accumulating in the pores, the current should decrease eventually. However, this does not happen since the cessa-

tion of current at any point allows H⁺ to diffuse back into the region and dissolve the $Zn(OH)_2$. Precipitated $Zn(OH)_2$ is known to form a porous layer that is not protective to Zn.

Zinc hydroxide formation can occur both by the precipitation reaction (10) and by ZnS oxidation, reaction (9), in the anodic direction, above 0.621 V. Although the results are not conclusive, the latter is probably occurring only slightly, if at all. If $Zn(OH)_2$ were forming by the oxidtion of ZnS, it would probably be in the nature of a film which would be more passivating than the precipitated $Zn(OH)_2$, thereby reducing the current. Also from Fig. 6 it can be seen that the cross-over potentials during the reverse sweep are about the same for the cycles whose upper limits are 0.55 V and 0.90 V. For the upper limit of 0.55 V, $Zn(OH)_2$ would not be formed anodically as it is cathodically reduced below 0.621 V. However, since conditions are favorable for its precipitation, its presence is explained in this manner thus making it available to participate in the cathodic reaction.
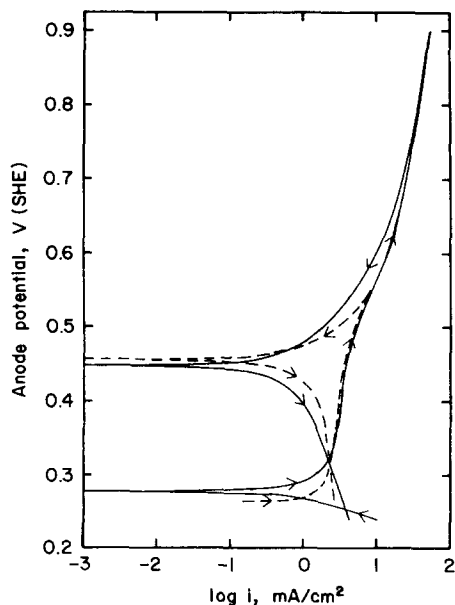

Fig. 6. Voltammogram for the anodic dissolution of ZnS + 10% pitch electrode in 1.0 M H_2SO_4 at 45°C and 1 mV/s sweep rate with different upper limits of potential. ——, 0.9 V; ---, 0.55 V.

As mentioned above, the cross-over potential during the reverse sweep decreases with the decreasing sweep rate. This occurs because the slower the sweep rate, the greater is the time available for the dissolution of $Zn(OH)_2$ by the reverse of reaction (10). Consequently smaller amounts of $Zn(OH)_2$ are available for reaction (9), which shifts the cross-over potential to lower values. The effect of temperature and pH on the cross-over potential is also

similar. As the temperature increases, the solubility of $Zn(OH)_2$ increases causing the cross-over potential to decrease as was observed. With increasing pH, $Zn(OH)_2$ becomes less soluble causing the cross-over potential to increase as was also observed at various sweep rates.

The effects of Zn^{2+} additions on the voltammograms were insignificant although there may have been a slight downward trend in current with increasing Zn^{2+} concentration. This is in keeping with the Zn^{2+} concentration in the slime controlled mainly by the current rather than Zn^{2+} concentration in the bulk electrolyte. The voltammograms showed no change at all with N_2/O_2 purging/sparging over the tested potential range (0.40—1.00 V) in 1.0 M H_2SO_4 at 25°C. Voltammograms taken on freshly polished and reacted surfaces show that the slime layer does reduce the current, thus offering some additional resistance to the reaction. In general, the effects of T, pH, Zn^{2+}, and gases as atmosphere on the voltammograms appear to be consistent with the observed behavior in 1.0 M H_2SO_4 at 0.85 V and 45°C under steady state conditions.

CONCLUSIONS

In sulfuric acid ZnS dissolves both chemically and electrochemically. The products undergo further change depending on the process parameters such as potential, pH, temperature, etc. The chemical dissolution could be decreased by increasing the electrolyte pH; however, this would yield lower rates. Another alternative would be to use a different electrolyte, such as HCl, where the direct electrochemical dissolution is favored. Redox couples could be used (Oki and Kammel, 1975) to yield a more desirable form of the reaction products (e.g., oxidation of H_2S). A higher pitch content could be used to improve the electrodes and yield higher rates. The electrode porosity could be increased to decrease the passivation. Another possible area where additional research may be desirable is to determine the effects of other constituents in the anode which might serve as catalyzers.

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