ELECTROLYTIC DISSOLUTION OF SPHALERITE CONCENTRATE IN HYDROCHLORIC ACID

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Potentiodynamic studies on Sphalerite compact electrode containing 30% graphite and 10% pitch have been carried out in hydrochloric acid of different concentration. The open circuit voltage varies from 0.240 V to 0.380 V. The dissolution current does not vary with increase of acid concentration upto 1.5 N under various scan rates though "i" dissolution increases with scan rate for a given acid concentration. The cyclic voltammogram indicates that the main oxidative product is sulphur and there is no formation of sulphate as in the case of sulphuric acid medium.
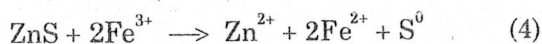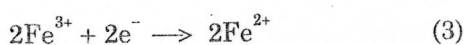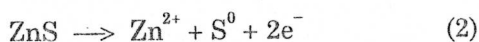
INTRODUCTION

The chemical dissolution of sphalerite has often been described as an electrochemical process [1-2]. The overall reaction is described as

$$ZnS \longrightarrow Zn^{2+} + S^0 + 2e^- \qquad (1)$$
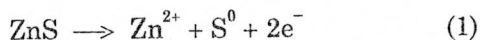
However, sulphate formation is also reported mainly through the direct oxidation of sulphide. The oxidation of sulphur is said to be kinetically hindered. It is known that oxidizing agents increases the yield of zinc in the solution. They raise the potential anodically at the mineral surface and thereby facilitate the dissolution of sphalerite. If the mineral has sufficient conductivity then the oxidizing agent in principle can be exchanged by an externally applied potential.

Most workers describe the leaching process of sphalerite with ferric ions as an electrochemical redox reaction [3-4].

$$ZnS \longrightarrow Zn^{2+} + S^0 + 2e^- \qquad (2)$$

$$2Fe^{3+} + 2e^- \longrightarrow 2Fe^{2+} \qquad (3)$$

$$ZnS + 2Fe^{3+} \longrightarrow Zn^{2+} + 2Fe^{2+} + S^0 \qquad (4)$$

Moreover the dissolution of sulphide minerals are described by two models viz., mixed potential model [5] and the other one based on semi-conducting properties of a mineral [6-7]. The mixed potential concept requires that the mineral is electrically conducting. During leaching the anodic reaction is dissolution of the mineral and the cathodic reaction depends upon the oxidizing agent used. The potential at which the cathodic and anodic reactions are equal is called mixed potential E_m. In the second model, the transfer of electrons from solid to aqueous phase is considered and hence depends upon solid phase also.

In a heterogeneous electrochemical reaction there is a net charge transfer and consequently, the reaction rate is potential dependent. The kinetics of electrochemical reactions involve an activation energy associated with the charge transfer process, because a charge carrier is transported through an interfacial electrical potential gradient [8] which can be controlled externally and hence the electrochemical reaction rate.

Since most of the base metal sulphides viz., sulphides of Cu, Pb and Ni except ZnS are good conductors of electricity, efforts were made as early as 1882 to anodically dissolve these minerals. Commercial process for the electrolytic dissolution of Ni_3S_2 is practised by many companies [9-10]. Efforts were also made to electrowin zinc [11] directly from sphalerite. The

dissolution of sphalerite electrode in sulphuric acid [12] shows that ZnS is oxidized to sulphur and sulphate and the current is dependent on acid concentration.

In this paper attempts are made to improve the conductivity of the ZnS (sphalerite) concentrate by adding inert conducting graphite. The electrochemical studies are carried out with the compacted electrode containing ZnS concentrate and graphite in hydrochloric acid using potentiodynamic method.

EXPERIMENTAL

Unlike in the case of chalcopyrite or galena whose casting technique can be used for the fabrication electrodes, fabrication of suitable stable electrodes with sphalerite is difficult. Moreover, the conductivity of zinc sulphide is very low and has a resistivity of 10^{10} Ohm.cm [13].

Hence, it becomes necessary to add a conducting inert material like graphite to sphalerite before the fabrication of an electrode.

The zinc sulphide concentrate obtained from M/s Hindustan Zinc Ltd, Udaipur having following composition, Zn = 50.5%, S = 31.61%, Fe = 8.08%, SiO_2 = 4.06%, Pb = 1.74%, Cd = 0.81% has been used in our studies. For the present study, the concentrate is mixed with 30% natural beneficiated graphite and 10% pitch and the mixture is compacted. The details of preparation of compacted electrode are described elsewhere [14]. A platinum wire makes a contact with the electrode. The exposed wire portion and one face of the electrode are masked. The compacted electrodes are fairly stable with a resistivity less than 2 Ohm.cm. The electrodes have an area of 0.7854 sq.centimeter.

For the potentiodynamic studies, a potentio scan (working model POS73), a combined version of potentiostat and scan generator is used. The electrode is first subjected to anodic sweep followed by a cathodic sweep. The output current is recorded in a XY recorder as function of input potential.

Electrodes are gently polished with fine emery sheets of increasing fineness, washed well with distilled water. Cyclic voltammograms are taken only after the electrodes attain equilibrium potential. All potentials referred in the text are with reference to natural calomel electrode.

RESULTS AND DISCUSSION

Studies in hydrochloric acid

Cyclic voltammetric studies have been carried out in hydrochloric acid of concentrations ranging from 0.5 N to 2 N. In this case the open circuit potential varies from 0.24 V to 0.38 V. A typical cyclic voltammogram of sphalerite compact in 1 N HCl at potentials ranging from -0.4 V to 1.5 V at 5 mVs^{-1} scan rates is presented in Fig. 1.

A peak appears in the anodic cycle at a potential of 0.53 V (peak A_1). During the reverse scan, the current does not decrease much upto a potential of 0.6 V and thereafter it starts decreasing sharply making a well defined peak at 0.28 V (peak C_1). Another small peak appears at 0.1 V (peak C_2). In contrast to sulphuric acid [15] a peak has been observed in the range of -0.3 V (peak C_3). such a peak has also been observed in H_2SO_4 during a separate cathodic scan (0 to -0.6 V).

Behaviour of anodic peak A_1

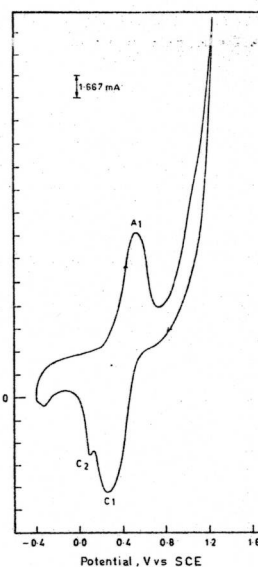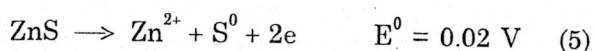This peak may be formed due to the reaction of ZnS oxidation as represented by equation (5).

Fig. 1: Cyclic voltammogram of sphalerite compact electrode in 1 N HCl. Sweep rate 5 mVs^{-1}

$$ZnS \longrightarrow Zn^{2+} + S^0 + 2e \qquad E^0 = 0.02 \text{ V} \qquad (5)$$

Compared to sulphuric acid (Fig. 2) values of peak current obtained in HCl of different concentrations are almost equal to 50% of currents obtained in H_2SO_4 acid of corresponding concentration. Similar behaviour has been observed by Narasagoudar et al. [16]. Table I gives the comparison of peak currents obtained in HCl and H_2SO_4. Though chloride is considered to be a better conducting and corroding system than sulphate, the reason for the low current values, i.e. lesser dissolution rates may be due to the tendency of sulphur produced during oxidation to form covalent bonds. Chloride adsorbs on the surface and can form covalent bonds through an oxidative adsorption more readily than sulphate [17-18].

This oxidative chemisorption of Cl^- on S would block the surface from further reaction forming S-Cl compounds [19]. Similar behaviour has been observed by Dandapani and Ghali [20] that a passive barrier consisting of sulphur restricts the current flow during the dissolution of PbS in HCl acid and they have also reported that $PbCl_2$ formed is not responsible for the above observation. They have also stated that the dissolution at and after the peak is completely under diffusion control, the passive layer acting as a diffusion barrier.
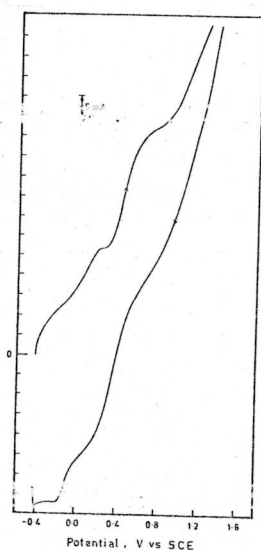
Figs. 3-5 show the effect of acid concentration and scan rate on E_p as well as on I_p in acid concentrations of 0.5 N to 2 N.

These results show that for all the concentrations of the acid there is an increase in the peak current i_p and there is a shift in peak potentials towards anodic direction as the scan rate is increased. Such a behaviour has also been observed in the case of PbS in HCl by Ghali and Dandapani [21]. From Table I it can also be seen that in the case of H_2SO_4, for a given scan rate, there is a regular increase in the peak current as the concentration of the acid increases, whereas it does not vary much in the case of hydrochloric acid upto a concentration of 1.5 N and there is an increase in current as the concentration changes from 1.5 N to 2.0 N. The constancy may be due to the formation of a barrier layer of non-conducting S or S-Cl compound as described earlier. In the case of 2 N HCl the increase in current may be due to the etching of the surface by S-Cl compound [7] or H_2S evolved due to chemical dissolution by the reaction mentioned in eqn. 8 which may disturb the sulphur layer on the surface giving rise to the more anodic current.

Behaviour of cathodic peak C_1

During reverse scanning, a peak appears whose peak potential varies with the concentration of the acid as well as with the scan rate. This may be due to the reactions 6 or 7 (4).
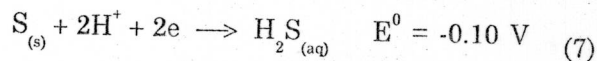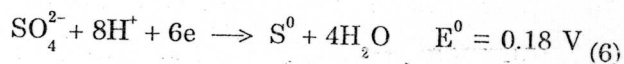
$$SO_4^{2-} + 8H^+ + 6e \longrightarrow S^0 + 4H_2O \qquad E^0 = 0.18 \text{ V} \quad (6)$$

$$S_{(s)} + 2H^+ + 2e \longrightarrow H_2S_{(aq)} \qquad E^0 = -0.10 \text{ V} \quad (7)$$

Fig. 2: Cyclic voltammogram of sphalerite compact electrode in 2 N H_2SO_4. Sweep rate 5 mVs^{-1}

TABLE I: Peak under consideration: Anodic peak A_1
Comparision of peak currents, I_p in H_2SO_4 and HCl acids

Scan rate mVS^{-1}	i_p mA in H_2SO_4			i_p mA in HCl			
	0.5 N	1.0 N	2.0 N	0.5 N	1.0 N	1.5 N	2.0 N
5	17.5	21.5	28.5	8.33	8.33	8.33	13.0
10	22.0	31.0	38.0	11.66	11.00	11.66	19.0
20	26.5	35.0	45.0	16.66	14.50	15.50	26.5
50	28.5	51.0	68.0	24.00	21.50	24.00	42.0
100	33.0	66.0	88.0	35.00	29.00	32.00	57.0
200	48.0	88.0	130.0	45.00	45.00	44.50	66.0

In the case of 0.5 N acids, a definite peak does not appear in the reverse scan when the scan rate crosses 20 mVs^{-1}. This cathodic peak is well defined in 1.5 N and 2.0 N acids (Fig. 3). In 2 N acid (Fig. 4) the peak broadens after a scan rate of 20 mVs^{-1}. The variation of peak potential with concentration of acid and sweep rate is given in Tables II and III gives the values of peak current for different acid concentrations. It can be seen from the table that the peak current first decreases as the concentration of the acid increases from 0.5 to 1.5 N and then it increases with the acid concentration.

In the case of sulphuric acid, it has been observed that the i_p increases uniformly with the acid concentration. In this case, the decrease in current may be due to the adsorption of chloride ions on the electrode surface which can reduce the amount of sulphur oxidation [10] and subsequently the reaction involving SO_4^- ions (eqn. 8).

$$S^0 + 4H_2O \longrightarrow SO_4^{2-} + 8H^+ + 6e \quad E^0 = 0.12 \text{ V} \quad (8)$$
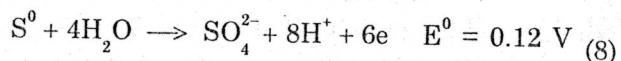
In the case of 2 N acid the chemically produced H_2S may help to expose the fresh areas on the surface so that the reaction 5,8,6/7 may proceed without much hindrance. The oxidation of H_2S can be seen at potentials ranging from -0.04 V to -0.08 V in the form of peak, which is not seen in lower acid concentrations.

Behaviour of cathodic peaks C_2 and C_3

The second cathodic peak C_2 appears around 0.06 V to 0.10 V in 1-2 N HCl. This peak when compared to the peak obtained in sulphuric acid is small in size and peak current is also less. Moreover, the peak does not appear after a scan rate of 20 mVS^{-1}. The reduction in the peak current may be due to the fact that the amount
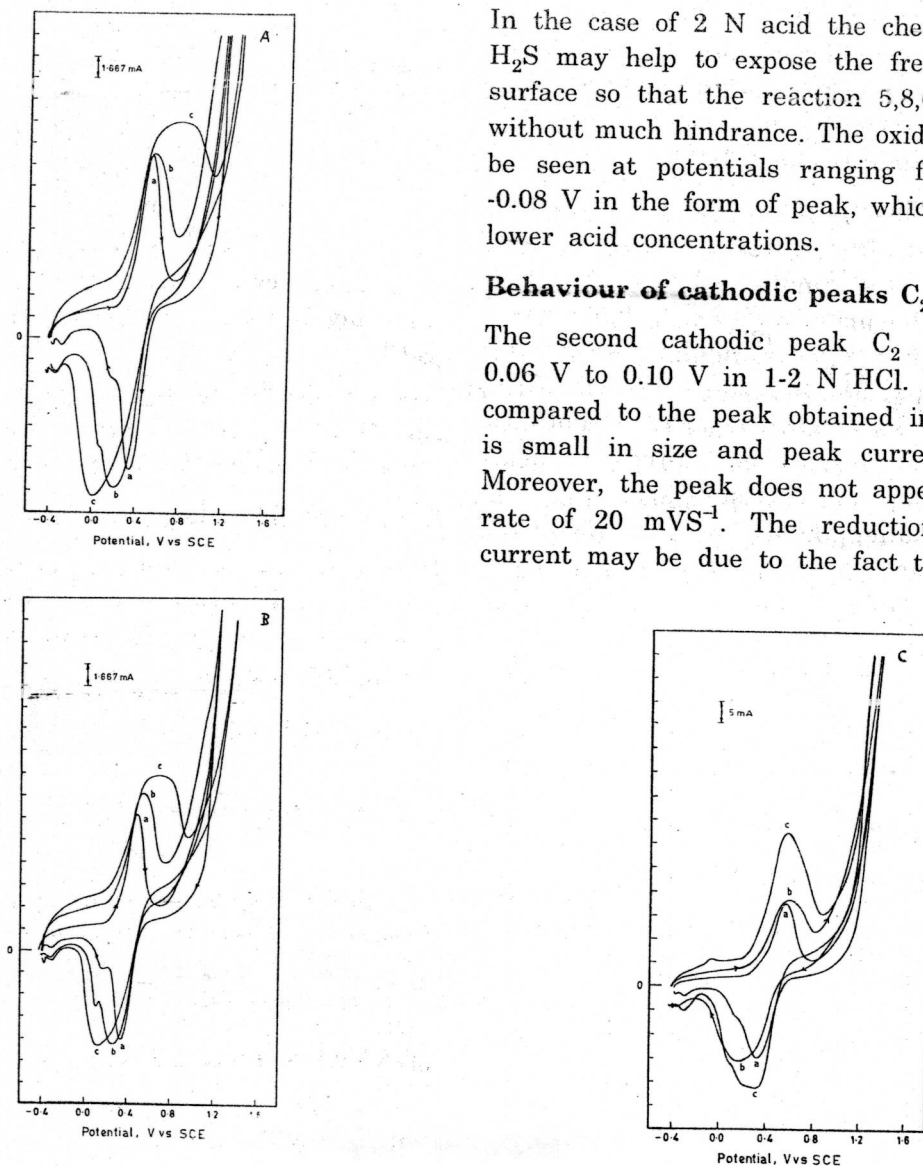

Fig. 3: Effect of acid concentration on voltammogram of sphalerite compact electrode
(A) a = 1.5, b = 1.0 c = 0.5 N HCl at 5 mVS^{-1}
(B) a = 1.5, b = 1.0 c = 0.5 N HCl at 10 mVS^{-1}
(C) a = 1.5, b = 1.0 c = 2.0 N HCl at 20 mVS^{-1}

of sulphur available for reduction may be less as some of it may form a strong coordinate bond with chloride ions which may require sometime to release the sulphur free and hence no peak at higher scan rates (6).

The exact reason for the formation of peak C_3 is not clear. It may be due to the reactions mentioned in equation (9,10).
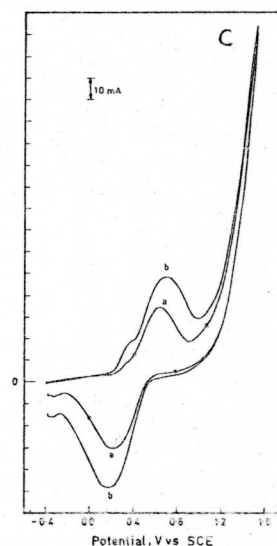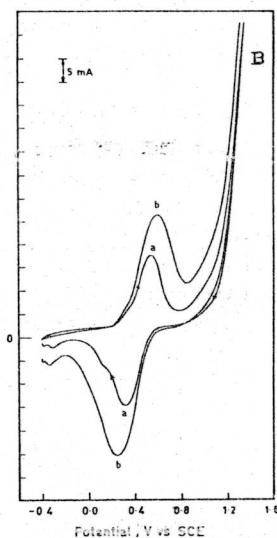
$$ZnO + 2H^+ + 2e \longrightarrow Zn + H_2O \quad E^0 = -0.68 \text{ V} \quad (9)$$

$$Zn(OH)_2 + 2H^+ + 2e \longrightarrow Zn + 2H_2O \quad (10)$$

TABLE II: Peak under consideration: Cathodic peak C_1
Variation of peak potential, E_p with scan rate in 0.5, 1.0, 1.5 and 2.0 N HCl

Scan rate mVS^{-1}	E_p, V in HCl			
	0.5 N	1.0 N	1.5 N	2.0 N
5	0.120	0.280	0.340	0.360
10	0	0.200	0.360	0.360
20	-0.160	0.170	0.330	0.300
50	—	0.080	0.330	0.200
100	—	0.050	0.230	0.090
200	—	0	0.200	0.100

$Zn(OH)_2$ of reaction (equation 10) may be formed by the hydrolysis of Zn^{2+} ion in the hydrogen ion deficient zone of the compact by the reaction.

$$Zn^{2+} + 2H_2O \longrightarrow Zn(OH)_2 + 2H^+ \quad (11)$$

Again this is not well defined beyond a scan rate of 20 mVS^{-1} except in 1.5 N acid.

CONCLUSION

Cyclic voltammetric studies with compacted sphalerite electrode in HCl medium show that the main reaction is the oxidation of zinc sulphide and there is no much variation in dissolution rate upto 1.5 N. Moreover, dissolution current is less than in sulphuric acid of comparable concentration. The
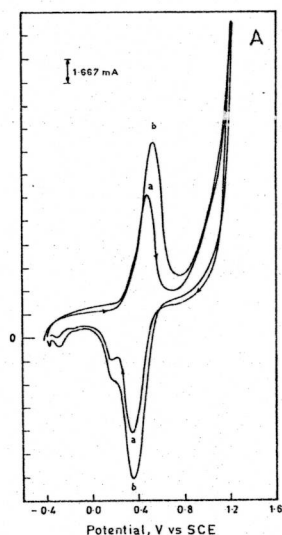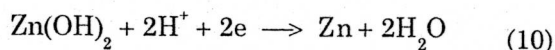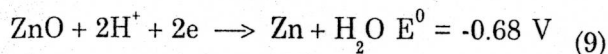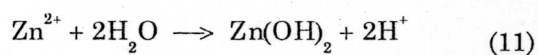

Fig. 4: Effect of scan rate on voltammogram of sphalerite compact electrode in 1.5 N HCl
(A) a = 5, b = 10   (B) a = 20, b = 50   (C) a = 100 b = 200 mVS^{-1}

reduction in the current is attributed to the covalent bonding of "S" released with chloride ion.

The appearance of cathodic peak depends upon acid concentration and scan rate and is mainly due to sulphur reduction to H_2S.

TABLE III: Peak under consideration: Cathodic peak C_1 Variation of peak current, i_p with scan rate in 0.5, 1.0, 1.5 and 2.0 N HCl

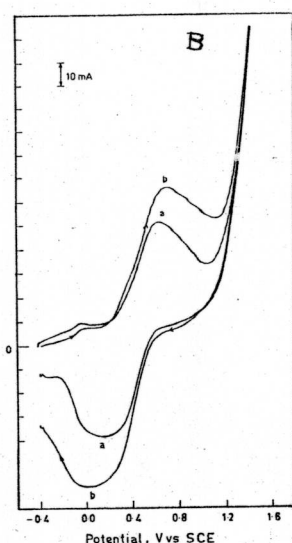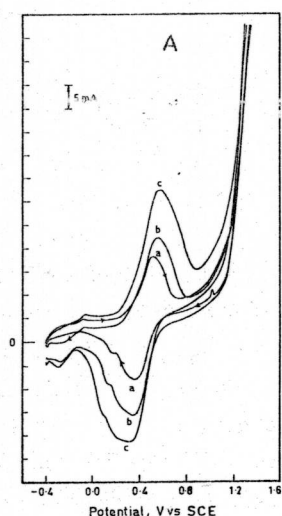| Scan rate mVs^{-1}	i_p, mA in HCl			
	0.5 N	1.0 N	1.5 N	2.0 N
5	11.33	10.50	8.83	13.50
10	16.33	14.00	12.50	19.00
20	21.60	18.00	17.00	26.50
50	—	27.00	26.50	45.00
100	—	35.00	34.00	63.00
200	—	52.00	49.00	76.00

Fig. 5: Effect of scan rate on voltammogram of sphalerite compact electrode in 2.0 N HCl
(A) a = 5, b = 10, c = 20
(B) a = 50, b = 100 mVs^{-1}

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