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# *Anodic behaviour of lead sulphide in hydrochloric acid*

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The electrochemical extraction of lead directly from lead sulphide has been attempted for some time but with little success. This could probably be due either to the limited solubility of the products or to an incomplete understanding of the fundamental process(es) involved. An attempt is made to understand the dissolution mechanism using synthetic lead sulphide electrodes in hydrochloric acid. The parameters examined are potential, concentration, oxygen, time, temperature, etc. A critical view is given of the anodic behaviour of PbS as a function of these parameters.

## 1. Introduction

It is the general practice at the present time to use pyrometallurgical methods for the extraction of metals from sulphide ores. This process involves a high (and continuously increasing) cost of energy to work at high temperatures especially for low content sulphide ores. Several environmental pollution problems due to the release of sulphur compounds into the open atmosphere are important and still remain unsolved. The environmental problems have resulted in several restraints on these pyrometallurgical procedures, thus encouraging the search for alternate methods of extraction of metals from the sulphides.

Hydrometallurgical isolation of the metals has so far met with only partial success. These methods normally involve a leaching process in an aqueous media in the presence of a redox couple (like $Fe^{2+}/Fe^{3+}$); such leaching processes have long been recognized as electrochemical in nature. It should therefore, be possible to increase the leaching rate further by suitable electrochemical means. As the normal solubility of many sulphides in aqueous media is very low even at high temperatures, electrochemical stimulation should definitely improve the dissolution rate. The additional input of energy required would be offset by the increased production rate of the metal in addition to the production of elemental sulphur directly instead of its oxides (or hydrogen sulphide).

Electrochemical techniques can also help preferential dissolution. If suitable conditions could be established to have a maximum dissolution of the sulphides anodically, the same energy could be utilized to extract the dissolved metal by cathodic deposition.

Based on these principles progress has been made by others [1] in extracting nickel from the nickel–copper sulphide matte. Utilization of such processes for the extraction of nickel and copper from the sulphides is much easier than for lead, as many of the lead salts are either sparingly soluble or insoluble.

Lead chloride is reasonably soluble ($K_{sp} = 1.0 \times 10^{-4}$ at 25° C) in water and slightly more soluble in hydrochloric acid. Thus, in our opinion, a study of the mechanism of leaching of lead sulphide in a chloride medium will pave the way for a better understanding of the dissolution mechanism of lead sulphide. Further, we feel that studies with synthetic lead sulphide (instead of the galena ore as reported by several workers [2–4]) will throw more light on the mechanisms of the processes involved since in the absence of other impurities, supplementary details on the semiconducting behaviour are available which assist a thorough understanding. Hence the preliminary results obtained in the study of the behaviour of lead sulphide electrodes in hydrochloric acid as a function of some key parameters are presented systematically in this paper.

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## 2. Experimental

### 2.1. *Electrode preparation and chemicals*

Many investigators have preferred to use natural galena (with suitable electrical connections) for their electrodes. The main problem is then the development of a high resistance or a crack in the electrode. Skewes [5] tried to have a compact electrode (pressed under pressure) with graphite powder and reports partial success. Only Johnson *et al.* [3] have tried to overcome the difficulties in casting a galena concentrate electrode without voids. With the experience of these workers in mind, we have attempted to cast a PbS electrode from 99.9% PbS synthetic powder (supplied by Ventron corporation). Complete success without any voids could be achieved by cooling the electrode slowly from the bottom by lowering the molten PbS slowly with the help of a motor. Electrodes prepared in this way were given a thin coating of silver print contact cement on one side and soldered with a contact wire. This was then embedded in bakelite powder leaving only one surface of the electrode for the experiments.

The electrodes were polished, in succession, with 240–600 grit emery paper, washed thoroughly with distilled water introduced into the electrolyte and polarized within thirty seconds.

A spectrographic grade graphite electrode (supplied by Union carbide) and a saturated calomel electrode were used as an auxiliary (or counter) and reference electrodes respectively. Analytical reagent grade chemicals and distilled water were used for preparing the solutions.

### 2.2. *Apparatus*

A Tacussel PRT 20-2 potentiostat, in combination

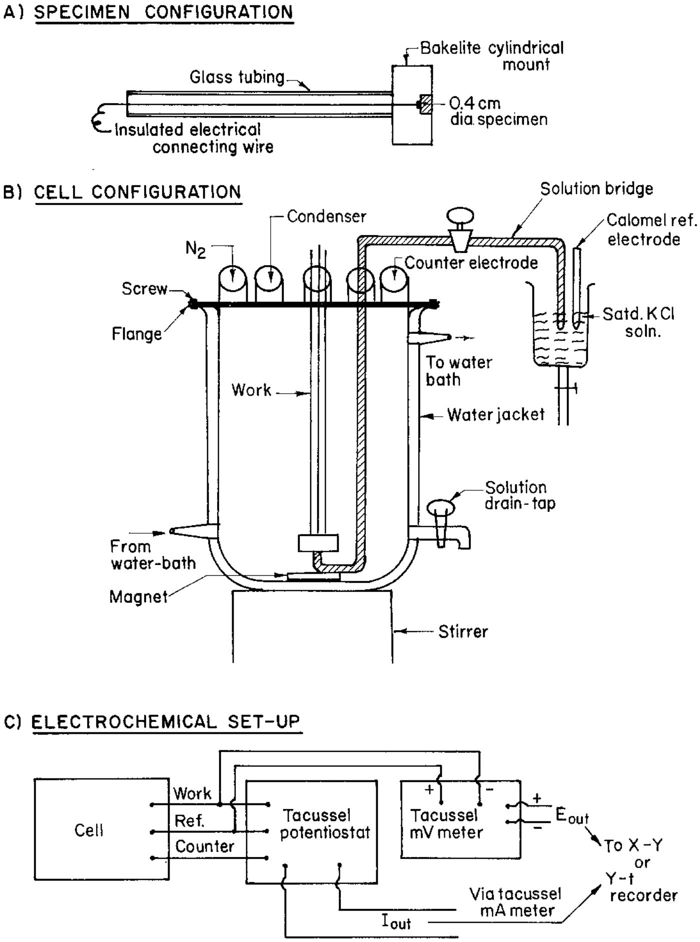

Fig. 1. Experimental arrangement for the electrode, cell and electrochemical measurements.

with a Tacussel servovit function generator was used for the voltammetric studies. A Hewlett-Packard 7000AM $X$–$Y$ recorder and a digital voltmeter were used for the current potential curves and the potential measurements, respectively.

The complete experimental arrangement is shown in Fig. 1.

### 2.3. *Experimental procedures*

Cyclic voltammetric, potential sweep and potentiostatic studies were made. In all these studies, argon gas was passed through the solution for at least one hour before the introduction of the electrode to remove traces of oxygen in the solution. For the studies in an oxygen atmosphere the solution was saturated with oxygen for at least one hour before the electrode was introduced. In both the cases, the inert or oxygen atmosphere was maintained during the experiments. Unless otherwise mentioned the temperature at which the experiments were studied was 25° C maintained by circulating constant temperature water through the outer jacket of the cells.

The experiments were quite reproducible within experimental limits and the results quoted here are from three to four reproducible experiments.

All the potentials mentioned in this paper are with respect to the SCE.

## 3. Results

### 3.1. *Rest potential and dissolution rate of PbS*

The change in the corrosion potential (rest potential or open circuit potential) with time was followed for 100 h at 25° C and 80° C both in the absence and presence of oxygen. It is seen from Fig. 2 that there is no important change in the rest potential even after 100 h with an argon atmosphere. The temperature also seems to have little effect on the corrosion potential.

However, the presence of oxygen appears to have a pronounced effect on the rest potential, making it more noble with time (specially during the first twenty hours) both at 25° C and 80° C. The rest potential of PbS in oxygenated 0.01 M HCl fluctuated at 80° C. The dissolution of lead sulphide under open circuit conditions was far higher in 1.0 M HCl than in the lower concentrations of HCl and in the 1.0 M HCl it increased greatly with temperature both in oxygenated and de-oxygenated HCl. The dissolution rate was low with 0.01 M and 0.1 M HCl (both oxygenated and de-oxygenated) and there was little increase in the dissolution rate with increase in the temperature.

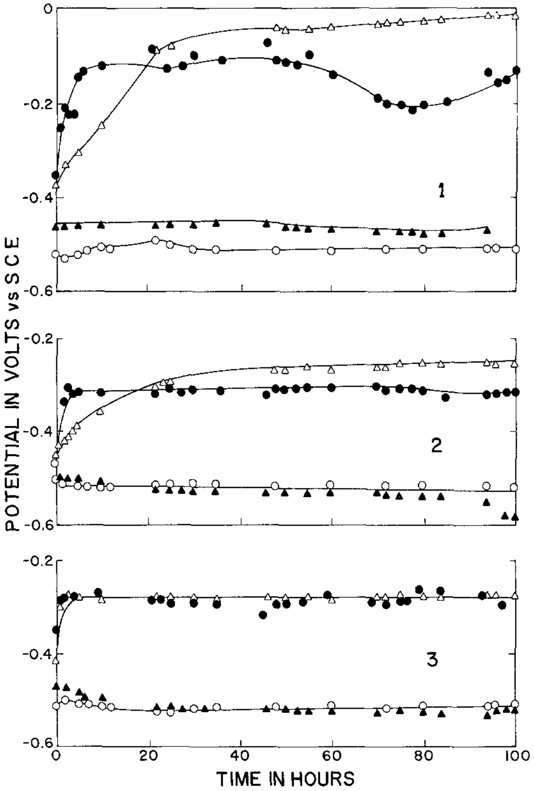

Fig. 2. Rest potential–time curves. 1, 0.01 M HCl; 2, 0.1 M HCl; 3, 1.0 M HCl. ○ Argon 25° C; △ oxygen 25° C; ▲ argon 80° C; ● oxygen 80° C.

### 3.2. *Cyclic voltammetric studies*

Very little is known about the nature of the reactions of PbS in various potential regions. An exploratory study showed two distinct anodic peaks, one near the corrosion potential around − 0.3 V and the other around + 0.5 V as seen in Fig. 3. There appears to be no corresponding reverse peaks on the cathodic cycle. However, there is one small peak on a fast scan and two small peaks on a slow scan at high negative potentials.

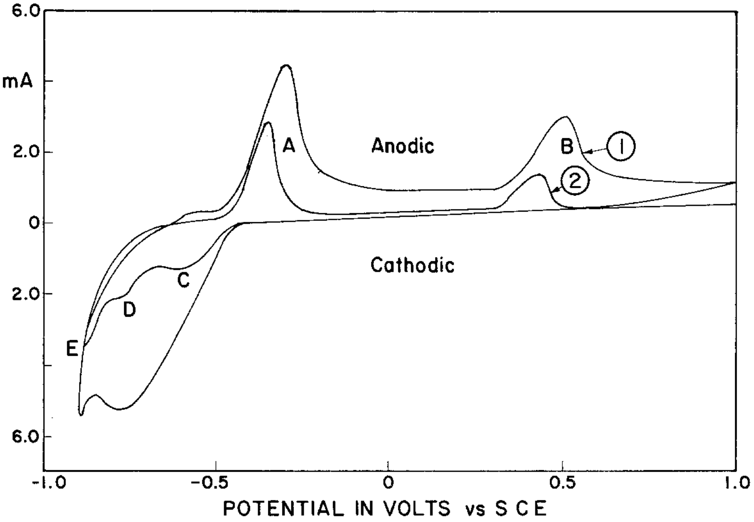

Fig. 3. Cyclic voltammograms at 1000 and 100 mV $min^{-1}$ in 0.1 M HCl. 1, 1000 mV $min^{-1}$; 2, 100 mV $min^{-1}$.

### 3.3. *Anodic behaviour*

*3.3.1. Potential sweep studies.* In a typical anodic polarization curve, from the corrosion potential to more anodic values, the peak around + 0.4 to + 0.5 V is distinct and the peak potential is dependent on the scan rate.

A typical curve at a scan rate of 100 mV $min^{-1}$ is shown in Fig. 4.

Changing the scan rate normally throws more light on the kinetics of an electrode process. The results of studies on the anodic dissolution of PbS at different scan rates shown in Fig. 5, indicate that both the peak potential and peak current change with the rate of scanning. An additional interesting point is that at a scan rate of 1 mV $min^{-1}$ the products accumulated on the electrode surface appear to be different from those at the faster scans. In the faster scans, normally, only lead sulphide and elemental sulphur could be identified by X-ray diffraction methods. But, in the lowest scan rates, there also appeared to be a distinct accumulation of $PbCl_2$ on the surface.

*3.3.2. Potentiostatic studies.* To examine the nature of the anodic peak potentiostatic current–time transients were recorded at various potentials before and after the peak potential. Fig. 6 shows the current–time curves recorded for twenty-five hours at + 0.4, + 0.7 and + 1.0 V. It was observed that after each experiment, the electrode surface is found to have a loose deposit which when ana-

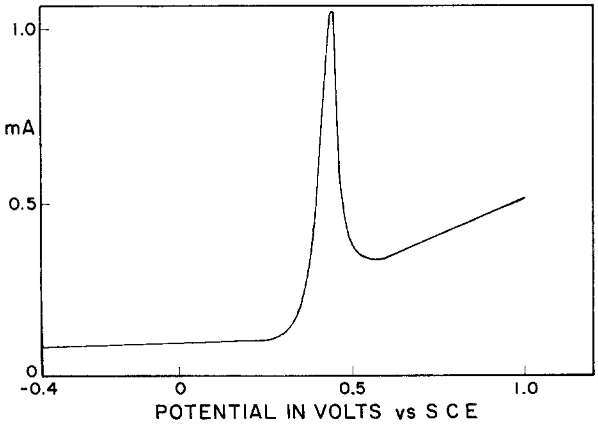

Fig. 4. Anodic polarization curve at 100 mV $min^{-1}$ in 0.1 M HCl.

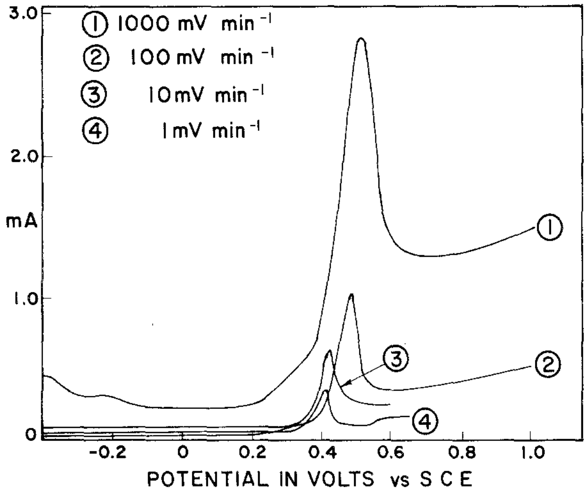

Fig. 5. Anodic polarization curve at different scan rates in 0.1 M HCl.

lyzed showed the presence of elemental sulphur and lead sulphide.

*3.3.3. Concentration of hydrochloric acid.* Anodic dissolution and passivation phenomena are normally influenced by chloride concentration. The effect of chloride concentration on the anodic dissolution of lead sulphide is shown in Fig. 7. The distinct changes in the peak potential and peak current could either be attributed to the pH or the concentration of chloride in the solution.

*3.3.4. Effect of oxygen and temperature.* The dissolution process seems to be affected very little at 25° C by the presence of oxygen as seen in Fig. 8. However, oxygen appears to have a pronounced effect, increasing the rate of dissolution at higher (80° C) temperatures.

*3.3.5. Effect of rotation rate of the electrode.* Rotation of the electrode helps to identify any underlying mass transfer control of the process. A preliminary study showed that the rotation of the PbS electrode probably helps only in removing the accumulated products from the surface thus increasing the current with the speed of rotation. The results are shown in Fig. 9.

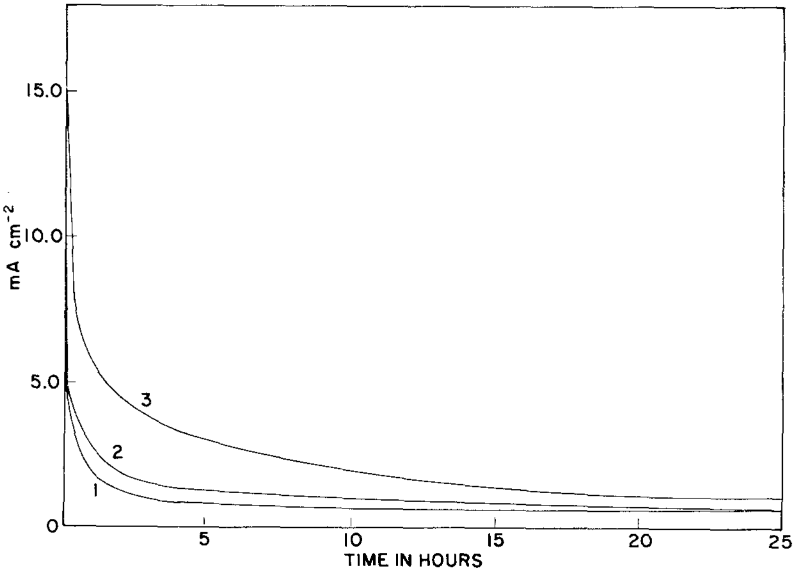

Fig. 6. Current–time curves in 0.1 M HCl at various applied potentials. 1, + 0.4 V; 2, + 0.7 V; 3, + 1.0 V.

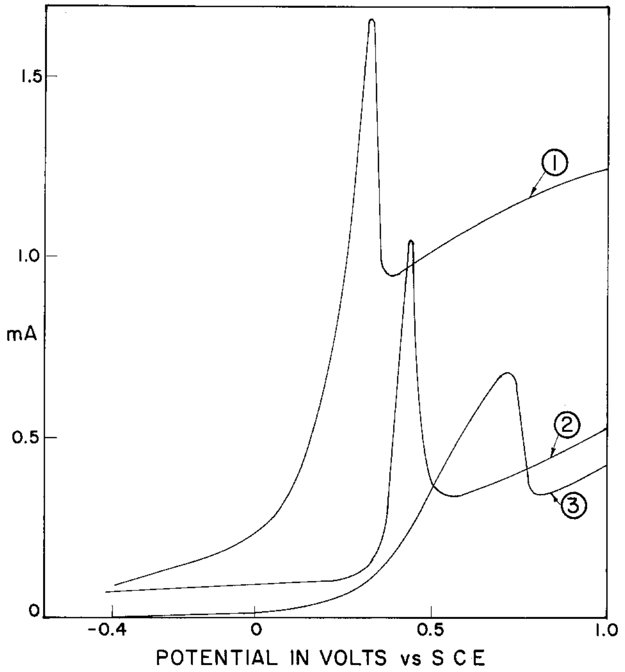

Fig. 7. Anodic polarization curves at different concentrations of HCl at 100 mV min$^{-1}$. 1, 1.0 M; 2, 0.1 M; 3, 0.01 M.

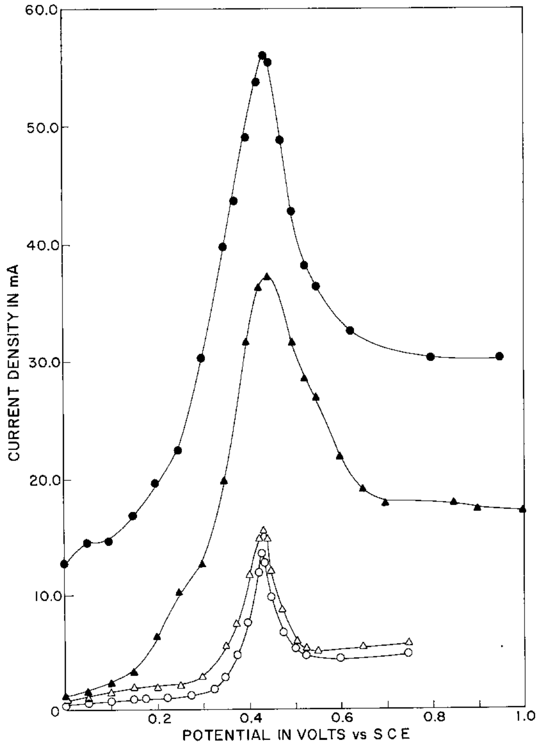

Fig. 8. Effect of oxygen and temperature on the anodic behaviour of PbS in 0.1 M HCl at 1000 mV h$^{-1}$. ○ Nitrogen 25° C; △ oxygen 25° C; ▲ nitrogen 80° C; ● oxygen 80° C.

## 4. Discussion

It has been reported that the rest potential shifts with time for a minimum of three hours [3]. However, we have observed that the rest potential, in an argon atmosphere, does not vary significantly with time, even after several days. It is not wise at this stage to correlate this directly to some property of the electrode though it could either be due to the instantaneous establishment of equilibrium between the electrode–solution interface or may indicate that the stoichiometry of the lead sulphide electrodes has not changed much during

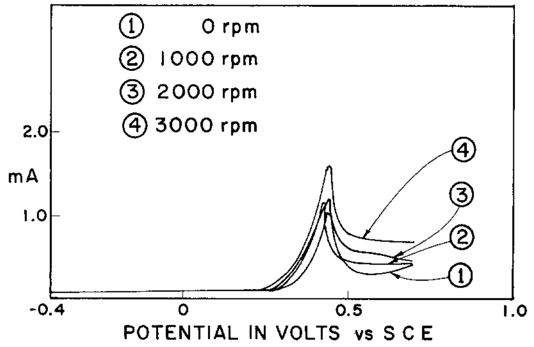

Fig. 9. Effect of rotation of the electrode on the anodic polarization curves in 0.1 M HCl at 100 mV min$^{-1}$.

the process of preparation of the electrode. In an oxygenated solution, however, the rest potential does change with time, during the initial period. Invariably it becomes more noble with time. This slow change could be due to the oxidation of the lead sulphide as suggested by Eadington and Prosser [6]. According to them lead-rich samples, n-type, (as in our case) are oxidized much slower than the sulphur-rich samples.

The extent of dissolution of PbS can be monitored by the dissolved lead in solution. This is around 12–25 ppm after 100 h at 25° C in all concentrations of HCl in the presence and absence of oxygen. The temperature has little influence on the dissolution at lower concentrations of HCl but great influence (up to 300 ppm in 100 h) in the case of 1.0 M HCl both in the presence and absence of oxygen. This may be due to the continuous replenishment of the surface at high concentration of HCl and high temperature.

Fig. 3 showing the cyclic voltammogram suggests that there are two possible anodic reactions. As there are no corresponding reversible cathodic peaks, these anodic reactions are irreversible. The anodic peaks could also be due to the oxidation of products formed at negative potentials but $H_2$ and $H_2S$ may be ruled out because the negative potential limit is insufficient for the formation of $H_2$ and the oxidation of $H_2S$ to S is known to occur at + 0.1 V [7].

PbS dissolves at the cathodic end to generate $H_2S$ and lead which can form $PbCl_2$ at the beginning of the anodic cycle and the peak A (Fig. 3) around − 0.3 to − 0.4 V could be due to this process [13]. The peak B between + 0.4 to + 0.5 V is very likely due to the formation of $PbCl_2$ resulting from the direct dissolution of PbS in the acid.

$$PbS + 2Cl^- \rightleftharpoons PbCl_2 + S^0 + 2e$$

This reaction causes the formation of elemental sulphur, which is difficult to react electrochemically due to its poor conductivity. This explains the absence of a corresponding cathodic peak. The appearance of the small peak C may be due to the irreversibility of $PbCl_2$ (in the anodic cycle) as indicated by the shift in the cathodic peak potential. The origin of the small peak D in the cathodic cycle is difficult to explain at this stage. As mentioned earlier, reduction of S to $H_2S$ may not be possible at this cathodic potential. Speculatively, this could be due to the adsorption of traces of $H_2S$ formed by dissolution of PbS to form Pb and $H_2S$.

$$PbS + 2H^+ + 2e \rightarrow Pb + H_2S$$

or adsorption of atomic hydrogen.

Our main interest in this study is the anodic dissolution of lead sulphide. Fig. 4 shows a typical potentiodynamic anodic dissolution curve polarized from the corrosion potential. This indicates that there is only one peak around + 0.4 V, probably due to the formation of $PbCl_2$ directly from lead sulphide. The thermodynamic calculation for the formation of $PbCl_2$ from PbS as shown below predicts the potential for the reaction.

$$PbCl_2 + S^0 + 2e \rightleftharpoons PbS + 2Cl^-$$

as + 0.520 V versus SCE. $E^0$ value for the above reaction calculated [8] from the free energy values of the reactants and products is 0.4547 V. The activity of the chloride ion is calculated from the $E^0$ values of Ag/AgCl (0.1 N KCl) (as this gives the $f_-$ value instead of the combined $f_\pm$ if it is taken from 0.1 M HCl directly) and found to be 0.077. Thus the peak could be due to the formation of $PbCl_2$. The only problem with this explanation is the limited solubility of $PbCl_2$ ($K_{sp} = 1.0 \times 10^{-4}$ in water) in hydrochloric acid. It has been observed that even after repeated experiments in the same solution there is no visible sign of any precipitation of $PbCl_2$ in the solution. Interestingly enough, the surface products (analysed by X-ray diffraction) do not show the presence of $PbCl_2$ till the scan rate is very slow (1 mV min$^{-1}$). Normally only lead sulphide and elemental sulphur appear on the surface after each experiment as evidenced by X-ray diffraction analysis.

The current–time transients shown in Fig. 6 suggest an active–passive behaviour at the electrode surface. This could either be due to an accumulation of elemental sulphur which reduces the conductivity of the surface or to the formation of a film of insoluble $PbCl_2$. However, the formation of the former or the latter appears to be very porous as there is continued dissolution of the surface indicated by the (residual) low current value even after twenty-five hours of potentiostatic polarization, 0.8–2.0 mA cm$^{-2}$. It has also been observed that when polarized at + 1.0 V there is a lot of deposition of lead on the cathode (thus increasing the solubility of $PbCl_2$ in the solution) stimulating further dissolution of the sulphide. This indicates that continuous anodic dissolution of PbS is possible at + 1.0 V without evolving $O_2$ at the working electrode or $H_2$ at the counter electrode.

Terayama *et al.* [9] have studied the anodic dissolution of lead sulphide in hydrochloric acid media at various pHs and have found a similar active–passive behaviour. However, they report that this passive behaviour is due to amorphous sulphur which gets further oxidized to lead sulphate. They have substantiated their argument on the basis of the potential–pH diagram of Pb–S–$H_2O$. While the formation of amorphous sulphur is reasonable it is too difficult to imagine the oxidation of sulphur to sulphate at these low anodic potentials. Since sulphur is a non-conductor such oxidation is not thermodynamically possible. Moreover, in our opinion the proper potential–pH diagram to be referred to is that of PbS–$H_2O$ [8] and not Pb–S–$H_2O$.

The major cause of the decrease in current beyond the peak may be the formation of non-conductive sulphur. But there is always an additional contribution from the formation of $PbCl_2$ evidenced by the presence of $PbCl_2$ in the surface products formed at slow scan rates. Formation of $PbCl_2$ has also been reported by Mazalov *et al.* [10]. However, on no occasion has sulphate been found amongst the surface products. When polarized at high anodic potentials, say + 1.0 V and higher, traces of sulphate could be found in the solution but not in surface products. This probably suggests the direct oxidation of PbS to $PbSO_4$ rather than sulphur to sulphate. The oxidation of PbS to $PbSO_4$ at these high anodic potentials is thermodynamically feasible either through bisulphate or directly to sulphate.

There is a definite effect of the concentration of chloride on the anodic dissolution of PbS. This could be a combined effect of pH and chloride

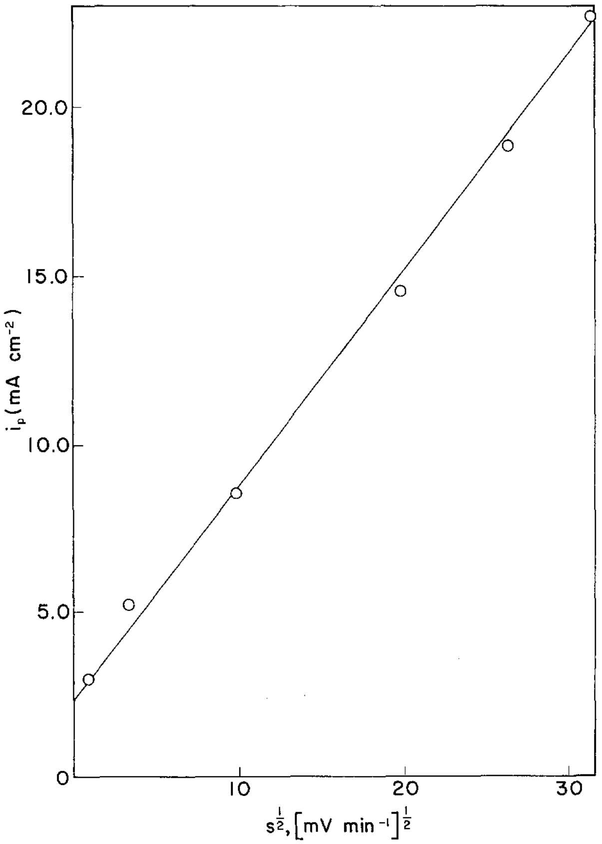

Fig. 10. Linear plot of the peak current versus square root of the scan rate for PbS in 0.1 M HCl.

concentration. Though we are not much interested in low concentrations of HCl (0.01 M) the peak shift is of the same order as the change in pH. The dissolution increases with the decrease in pH which agrees with the potential–pH diagram.

The temperature has a tremendous effect in increasing the dissolution rate (4 to 5 times) both in the presence and absence of oxygen. This could be due to activation of the surface processes by an increase in the operating temperature.

Normally, it is expected that the rotation of the electrode should have a significant effect on the rate of the dissolution, if the whole process is controlled by the diffusion of the reactants and products from the solution to the electrode and the electrode to solution, i.e. the whole process is partly or fully mass transfer controlled. The preliminary results shown in Fig. 9 indicate that mass transfer has very little control on the dissolution process.

The results discussed above suggest that the anodic peak obtained in this case is mainly due to the active–passive behaviour of the PbS electrode by the formation of a film of $PbCl_2$. This is further established by the potential sweep curves obtained at various scan rates (Fig. 5). A similar behaviour was observed by Froment *et al.* [11] in their studies on the corrosion of iron. The nature of the formation and behaviour of $PbCl_2$ at the peak potential could be substantiated from a plot of the peak current against the square root of the scan rate (Fig. 10). The linearity of this plot [12] and the non-linearity of the plot of the peak potential against the logarithm of the scan rate [12] (Fig. 11) confirm that the process is completely irreversible. Though these plots are normally applicable to cyclic voltammetry it seems justified to use this type of analysis for our studies since the peak potential obtained in the cyclic voltammetric studies (shown by △ in Fig. 11) and the potential sweep curves are more or less the same.

In summary, the results presented above show that the anodic dissolution of lead sulphide is possible forming directly lead chloride and amorphous sulphur with some possibility of oxidation of lead sulphide to lead sulphate at high anodic potentials. The nature of the reation shows that the process is commercially viable for continuous operation. The effects of temperature, pH, etc., show that the process is activation controlled. The small effect obtained by rotation of the electrode probably indicates that the mass transfer problems are very much limited in this case.

## Acknowledgements

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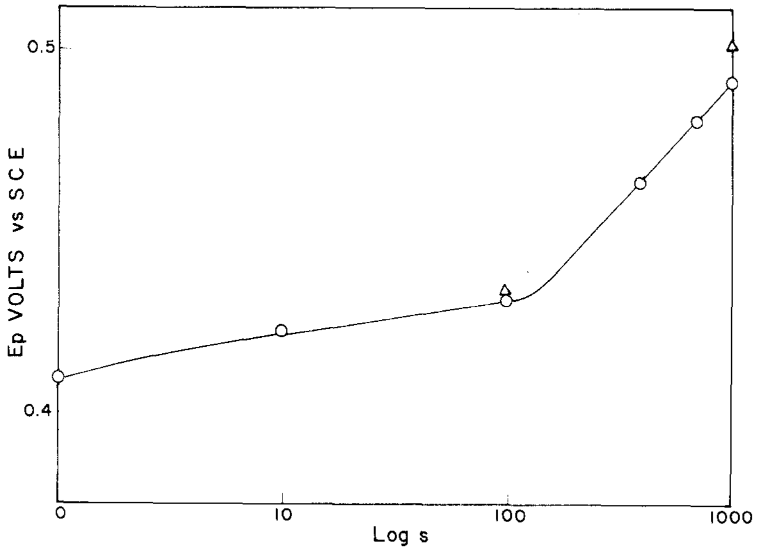

Fig. 11. Plot of the peak potential against logarithm of scan rate for lead sulphide in 0.1 M HCl. △ see text.

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