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Anodic dissolution of galena concentrate in perchloric acid

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A basic study has been made on the anodic dissolution of lead sulphide ore (galena) in perchloric acid. The electrodes used in the research were fabricated by melting and casting the ore in a suitable mould. The phases which were present in sufficient quantities to be detected by X-ray diffraction were PbS and ZnS. Coulombic efficiencies were determined at 40° C at various levels of pH and current density, and were in the range of 90% for most of the tests. Transient studies revealed a non-uniform surface attack and that the dissolution reaction was irreversible, as indicated by the absence of cathodic currents, in the vicinity of the rest potential. Steady-state studies showed the reaction to be activation controlled and that the rate-determining step was a chemical reaction following the first electron transfer.

1. Introduction

One of the main problems facing the non-ferrous metals industry is control of sulphur emissions during extraction and refining. This is particularly true for the smelting of lead ore. Galena (PbS) is the principal starting raw material, and present processing involves an air roast which yields an oxidized lead compound and SO_2. This step is necessary in order to eliminate as much sulphur as possible (usually less than 1% S remains in the roasted sinter), which facilitates the blast furnace reduction to metallic lead [1]. Unfortunately there are copious quantities of sulphur dioxide gas liberated in concentrations between 1% and 7% which must be handled. The methods currently employed to minimize sulphur pollution during roasting are: (1) high stacks and closed loop control; (2) sulphuric acid plants; and (3) both of these [2]. Even when the best available technology is used the results are less than desirable, making it difficult to meet federal or state environmental control guidelines. For these reasons there has been considerable interest in finding new processes for lead extraction designed for maximum pollution abatement and sulphur control.

It is generally felt that the most desirable processes would involve direct reduction of the ore in one stage, which would eliminate the need for roasting with the resultant SO_2 formation. There have been a number of interesting proposals for extracting lead by pyrometallurgy [3, 4] or hydrometallurgy [5, 6] techniques. The use of electrometallurgy also seems to offer some unique possibilities. The International Nickel Co. successfully produces cathode nickel from sulphide anodes, cast directly from converter matte [7]. There have been a number of studies on the direct electrolysis of PbS anodes [8–10] and the results indicate that such a process is quite feasible. However, little research has been conducted on the more basic aspects of PbS anodic dissolution. If electrolytic lead extraction is to become a commercial reality considerably more fundamental work will be needed. The results of some preliminary studies directed with these objectives in mind will be presented.

2. Experimental

The electrolyses were carried out in ordinary three-compartment cells containing approximately 500 ml of electrolyte. The temperature was held constant at 40° C except as noted. Potential measurements were made versus a normal calomel electrode. A salt bridge containing the same solution as the cell was used to prevent contamination by Cl^- from the reference electrode. All potentials have been converted to the normal hydrogen scale (versus SHE) and are so expressed unless stated.

2.1. *Materials*

The lead concentrate powder used to make the anodes was a normal flotation process product and was supplied by St. Joe Minerals Co., Viburnum, Mo. A typical analysis (wt. %) is: 75% Pb, 16·8% S, 4·2% Fe, 1·3% Zn, 0·8% Al_2O_3, 0·45% Cu, 0·4% CaO, 0·3% SiO_2, 0·27% MgO, and 1·3 tr. oz Ag ton^{-1}. The chemicals used to prepare the electrolytes were 'Baker Analysed' reagent grade perchloric acid, Fisher Certified ACS grade NaOH, Pfaltz and Bauer Technical grade $Pb(ClO_4)_2$, and distilled water, Matheson prepurified nitrogen (99·997% minimum) was used to provide an inert atmosphere and for stirring. Electrolytes with pH's greater than 0·25 (0·75 M $HClO_4$) were prepared by titrating 0·75 M $HClO_4$ with concentrated NaOH solution until a desired pH was obtained. This gave solutions of approximate constant ionic strength as well as ClO_4^- concentration. An electrolyte of pH = 2·75 had approximately equivalent amounts of $HClO_4$ and NaOH, i.e., a slightly acidified $NaClO_4$ solution.

2.2. *Anodes*

Several techniques were tried in efforts to obtain suitable anodes. Pressed and sintered specimens were unsuitable, as they were porous and absorbed electrolyte, which ultimately contacted and interfered with the electrical connections. Melting and solidifying in the same container was unacceptable due to large voids which developed in the resulting mass. A casting method was found that gave acceptable results. It included melting the concentrate in an alundum-coated plumbago crucible (at ~ 1240° C) followed by pouring into a preheated alundum-coated horizontal iron mould, 9 cm long x 4 cm wide x 1·5 cm deep. The melting time was about 30 min. It was desirable to keep this time as short as possible as a small amount of Pb always appeared in the cast sample as a result of the processing. The outer layer of the casting was removed and the remainder cut into rectangular pieces, approximately 1·2 cm x 1·2 cm x 0·8 cm. To form anodes, these pieces were mounted in lucite (1·2 x 1·2 face exposed), flat surfaced by wet grinding on 240–600 grit paper, and finally wheel polished with 1 μm alumina. Before being used for study, the electrodes were ultrasonically cleaned in distilled water and etched for 1–2 min in 0·4 M perchloric acid. The resistance of electrodes prepared in this manner was typically 3–4 Ω.

Microscopic examination of the electrode surfaces showed two phases present. Energy dispersive X-ray analyses of the phases indicated the major phase to be predominantly PbS and the other predominantly ZnS.

2.3. *Rest potentials*

The rest 'open-circuit' potentials of the concentrate electrodes are shown in Table 1. These values were reached 2–3 h after the electrodes were immersed in the electrolyte and were relatively stable. The initial values were usually more negative (~ 100 mV) than these. An odour of H_2S could be detected in the effluent gas from the cell at open-circuit conditions.

Considering the predominant phases present, the most probable reactions occurring on the concentrate electrode are:

2.3.1. *Electrochemical.*

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

$$E = 0{\cdot}357 + 0{\cdot}031 \log a_{Pb^{2+}} \qquad (1a)$$

$$PbS(s) + 2H^+(aq) + 2e = Pb(s) + H_2S(g) \qquad (2)$$

$$E = -0{\cdot}295 - 0{\cdot}031 \log a_{H_2S} - 0{\cdot}062\ pH \qquad (2a)$$

$$Zn^{2+}(aq) + S(s) + 2e = ZnS(s) \qquad (3)$$

$$E = 0{\cdot}276 + 0{\cdot}031 \log a_{Zn^{2+}} \qquad (3a)$$

$$ZnS(s) + 2H^+(aq) + 2e = Zn(s) + H_2S(g) \qquad (4)$$

$$E = -0{\cdot}842 - 0{\cdot}031 \log a_{H_2S} - 0{\cdot}062\ pH. \qquad (4a)$$

2.3.2. *Chemical*

$$PbS(s) + 2H^+(aq) = Pb^{2+}(aq) + H_2S(g) \qquad (5)$$

$$K = 3{\cdot}60 \qquad (5a)$$

$$ZnS(s) + 2H^+(aq) = Zn^{2+}(aq) + H_2S(g) \qquad (6)$$

$$K = 1{\cdot}65. \qquad (6a)$$

Table 1. Comparison of observed rest potentials with thermodynamic values for PbS and ZnS electrodes

Electrolyte	*Ionic strength*	*pH*	*Rest potential* (V) (SHE)	*Reversible potential* (V) SHE			
				Equation 1	*Equation 2*	*Equation 3*	*Equation 4*
$HClO_4$	0·75	0·25	0·170 0·210 0·170 0·107 0·180 0·188	0·171	− 0·124	0·090	− 0·672
$HClO_4 + NaClO_4$	0·75	0·7	0·133 0·185 0·102	0·171	− 0·152	0·090	− 0·699
$HClO_4 + NaClO_4$	0·75	1·2		0·171	− 0·183	0·090	− 0·730
$HClO_4 + NaClO_4$	0·75	3·0	0·168 0·125	0·171	− 0·295	0·090	− 0·842

Reversible potentials for reactions 1–4 have been calculated and are also shown in Table 1. (Values of 10^{-6} were assumed for the activities of Pb^{2+}, Zn^{2+}, and H_2S. This number is frequently used in cases where electrode products are diffusing into an electrolyte that initially contained none of the product.) The numerical values of the measured potentials and their variation with pH are such that Reactions 2 and 4 can probably be eliminated as making any significant contributions. The odour of H_2S is probably due to Reactions 5 and 6. The production of Pb^{2+} and/or Zn^{2+} by these reactions might also account for the initial positive drift of the open-circuit potentials. An examination of an electrode etched in $HClO_4$ indicates a selective etching on the PbS-rich phase whereas the ZnS-rich phase remained almost unchanged.

2.4. *Coulombic efficiency*

The faradaic efficiencies for the dissolution of the concentrate electrodes were determined and are shown in Table 2. All calculations for Pb^{2+} and S produced and concentrate consumed as a function of charge passed were based on Reaction 1.* During dissolution at the c.d.'s shown, the electrodes were quite stable dimensionally with very little external evidence of reaction other than a darkening and roughening of the surface. The dissolution occurred at a fairly well-defined interface (or reaction zone) that proceeded uniformly through the electrode leaving behind a 'slime' that consisted of sulphur and a small amount of unreacted concentrate. The slime had to be removed mechanically from the electrode in order to determine its composition. None of it became detached from the electrode during the electrolysis. At higher c.d.'s (> 30 mA cm^{-2}) the electrodes began to swell after the electrolyses had proceeded for a few hours. Portions of the surface sloughed off with some of the sulphur floating to the surface of the electrolyte and the unreacted concentrate settling to the bottom. The coulombic efficiencies in this region dropped from 85% at 30 mA cm^{-2} to 70% at 100 mA cm^{-2}.

The quantity of concentrate reacted was normally determined directly from the weight-loss of the anode. In some instances, it was calculated using the concentration of Pb^{2+} in the electrolyte as determined by atomic adsorption analysis. In order to determine the quantity of sulphur produced, a weight-loss method was also used in which the reacted electrode was crushed then heated to about 400° C in a stream of nitrogen for several hours which removed the sulphur.

2.5. *Transient studies*

Cyclic potential-sweep studies were made with the concentrate electrodes in the previously mentioned electrolytes. A series of measurements was

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* The coulombic efficiencies are increased about 4% if one assumes that the material dissolving is composed of lead, iron, zinc, and copper sulphides as shown in the concentrate composition.

Table 2. Coulombic efficiency for galena concentrate dissolution in perchlorate solutions at 40° C

Electrolyte ionic strength = 0·75	*$Pb(ClO_4)_2$* (M)	*pH*	*i* ($mA\,cm^{-2}$)	*Δt* (h)	*Coulombic Efficiency*† %	*PbS/S*‡	*Utilization*§
$HClO_4$		0·25	0·5	5·0	55*		
			0·5	432·2	89		
			1·0	5·0	81*		
			1·0	155·0	93	1·31	0·74
			3·0	5·0	95*		
			5·0	160·0	93	1·02	0·82
			7·0	5·0	90*		
			10·0	5·0	93*		
			10·0	50·0	89	1·00	0·87
			10·0	70·7	85	0·90	0·90
			15·0	5·0	90*		
			20·0	5·0	88*		
$HClO_4$	0·0128	0·25	5·0	45·4	92		
			10·0	45·0	89	1·01	
$HClO_4 + NaClO_4$	0·0128	0·90	5·0	139·0	92	1·06	
			10·0	68·0	88	1·03	0·88
$HClO_4 + NaClO_4$	0·0128	2·0	5·0	22·5	91		
			10·0	65·4	88	1·02	0·85

* Determined using atomic adsorption analyses. All others used weight-loss.

† Ratio of PbS dissolved during experiment to the theoretical amount as calculated from charge passed using Equation 1.

‡ Mole ratio of PbS dissolved to S produced.

§ Ratio of PbS dissolved to PbS dissolved plus PbS in slime.

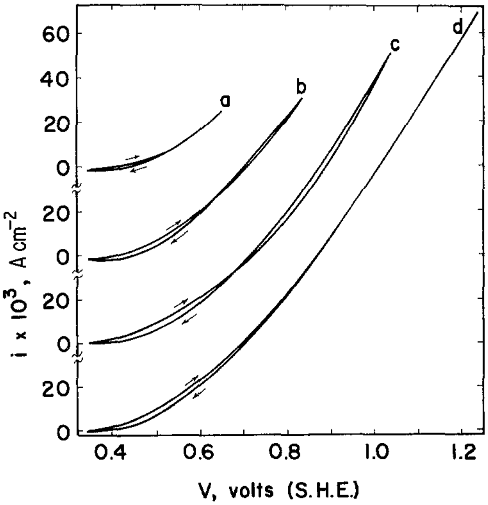

Fig. 1. Voltammogram for the anodic dissolution of PbS Concentrate in 0·75 M $HClO_4$ at 25° C. $\nu = 10\,mV\,s^{-1}$. (Cycles were obtained in sequence a–d).

initiated with a freshly polished electrode on which the rest potential had been established. Generally the cycles were begun by potentiostating the electrode at the rest potential, then increasing the potential at a linear rate until a preset upper limit was reached, and finally decreasing the potential back to the initial value in the same manner.

In 0·75 M $HClO_4$, (pH = 0·25), the first few cycles showed a great deal of hysteresis with the forward-sweep currents (increasing potential) being less than those for the reverse sweep. During this time, the polished electrode surface took on a dark dull appearance. Subsequent cycles showed very little hysteresis or evidence of passivation or rate-limited processes as illustrated in Fig. 1. Appreciable currents commenced at about 0·42 V and increased smoothly with increasing potential up to 1·3 V (the highest tested). A comparison of consecutive repetitive cycles showed acceptable reproducibility at any given point in time. However, repetitive cycles made at the beginning and end of a period of polarization showed that a reacted surface gives larger current densities, all other controlled variables held constant. The increased c.d. is probably due to an increase in the reaction area as a reaction zone is initiated and does not continue indefinitely though as illustrated in Fig. 2 where cycles are shown during which greater amounts of the concentrate are dissolved. This behaviour is consistent with a gradual increase of the thickness of the region behind the reaction zone through which reactants and/or products have to diffuse. Again, none of these curves show current peaks or maxima which would indicate changes affecting the dissolution reaction. At higher potentials, about 1·25 V, numerous small bubbles were formed on and clung tenaciously to the electrode surface. They were not observed either to coalesce or be released from the surface. When the electrode was potentiostated at 1 V, the c.d. decreased continually at a rate of about 20% h^{-1}.

The approximate linearity of the cycles in the upper potential region suggests that the electrode resistance may be an important consideration here. Each ohm of resistance would add 1 mV to the measured potential per mA of current. This becomes appreciable for currents above 100 mA. The initial overall anodic reaction resistance (as measured from the curves) at the higher currents (> 40 mA) is about 3 or 4 Ω (approximately the same as the measured electrode resistance). After extended electrolysis, this increases to about 5 Ω.

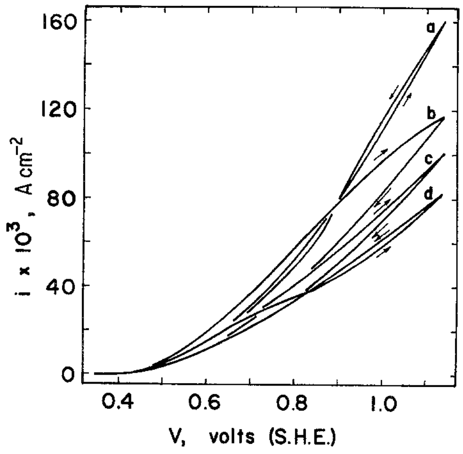

Fig. 2. Effect of polarization time on the voltammogram for the anodic dissolution of PbS concentrate in 0·75 M $HClO_4$ at 25° C. (a) taken at the beginning of a polarization period, (b–d) taken consecutively at the end of the polarization period. $\nu = 10\,mV\,s^{-1}$ for (a) and (d), $1\,mV\,s^{-1}$ for (b) and (c).

When the electrode was polarized cathodically from the rest potential, cathodic currents became appreciable at potentials below about 0·18 V. Gas evolution could be seen at potentials below zero and an odour of H_2S detected. When the cycles were initiated at potentials below about − 0·12 V (instead of the rest potential), an anodic peak at ~ 0·23 V and increased anodic currents between 0·30 and 0·80 V were observed (Fig. 3). The curves resumed their former shape when the initial potential for the cycle was changed back to the 'rest' value.

The incorporation of Pb^{2+} (0·01 M) in the electrolyte caused a significant change in the voltammogram (Fig. 4). Considerable hysteresis was always present at the lower potentials. In the initial cycles and before the electrode had been extensively reacted, a small cathodic peak was observed at about 0·43 V during the reverse sweep. After the electrode had been polarized above 0·8 V, an anodic peak appeared in the forward sweep at 0·50–0·54 V and after several sweeps in this range, the cathodic peak disappeared. The current during the forward sweep was considerably less than that in 0·75 M $HClO_4$ (without Pb^{2+} added) but was approximately the same for the reverse sweep.

In an electrolyte of pH = 0·9 (and with Na^+ present), the behaviour of the concentrate elec-

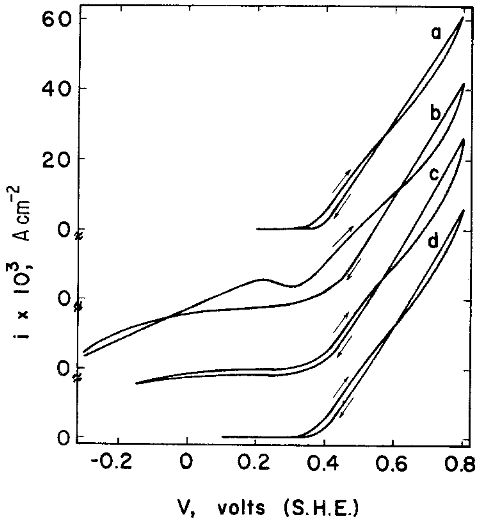

Fig. 3. Effect of lowering the initial potential on the voltammogram for the anodic dissolution of PbS concentrate in 0·75 M $HClO_4$ at 25° C. $\nu = 10\,mV\,s^{-1}$. (Cycles were obtained in sequence a–d).

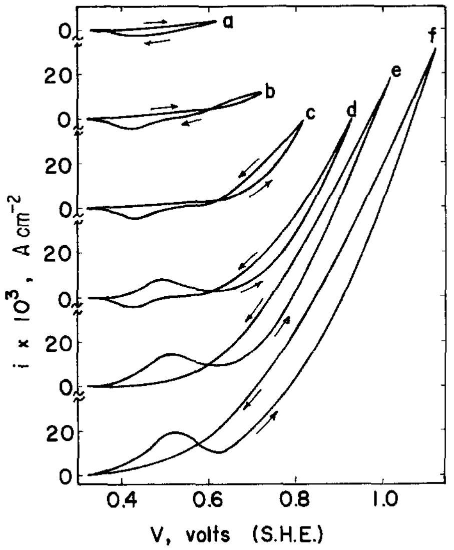

Fig. 4. Effect of Pb^{2+} (0·01 M) addition on the voltammogram for the anodic dissolution of PbS concentrate in 0·75 M $HClO_4$ at 25° C. $\nu = 10\,mV\,s^{-1}$. (Cycles were obtained in sequence a–f).

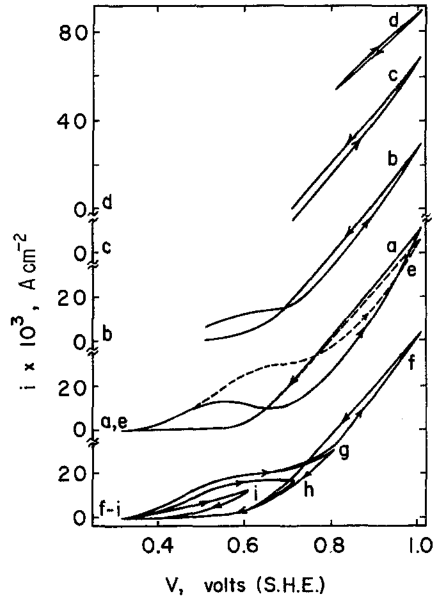

Fig. 5. Effect of changing the upper and lower potential limits on the voltammogram for the anodic dissolution of PbS concentrate in $NaClO_4$ + $HClO_4$ (pH = 0·9) at 25° C. $\nu = 10\,mV\,s^{-1}$. (Cycles were obtained in sequence a–i.)

trode was similar to that in 0·75 M $HClO_4$ + 0·01 M $Pb(ClO_4)_2$. The small cathodic peak was again observed in the initial cycles. Upon repeated cycling to higher potentials, an anodic peak also appeared at 0·50–0·54 V. The effects of increasing the upper and lower potential limits are shown in Fig. 5. The reaction resistances from the linear portions of the curves are typically 3–4 Ω.

Cyclic voltammograms for 0·75 M $NaClO_4$ were similar to those shown in Fig. 1. No current peaks were noted when cycles were begun at the rest potential. When the cycles were begun at − 0·28 V, an anodic peak developed at 0·5–0·6 V (Fig. 6). It disappeared upon subsequent cycling from the rest potential. The linear portions of the curves correspond to reaction resistances of about 3–4 Ω.

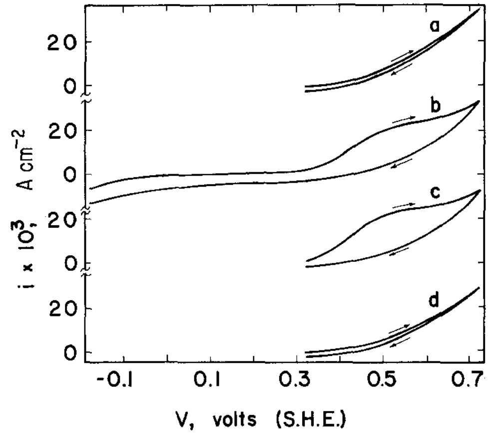

Fig. 6. Effect of lowering the initial potential on the voltammogram for the anodic dissolution of PbS concentrate in 0·75 M $NaClO_4$ at 25° C. $\nu = 10\,mV\,s^{-1}$. (Cycles taken in the sequence a–d.)

2.6. *Steady-state studies*

Steady-state polarization relationships were obtained potentiostatically for the previously mentioned electrolytes and are illustrated in Fig. 7. Limiting c.d.'s of about $10^{-2}\,A\,cm^{-2}$ were obtained at 0·55–0·60 V, independent of pH. Once in this potential region, the current continually decreased with time. Further increases in potential gave higher initial currents which steadily decayed with time (see Fig. 8). All the polarization curves had linear Tafel regions at low c.d.'s, from about 5×10^{-5} to $2 \times 10^{-3}\,A\,cm^{-2}$. These are sufficiently low so that the resistance of the anode (< 5 Ω) does not significantly affect the

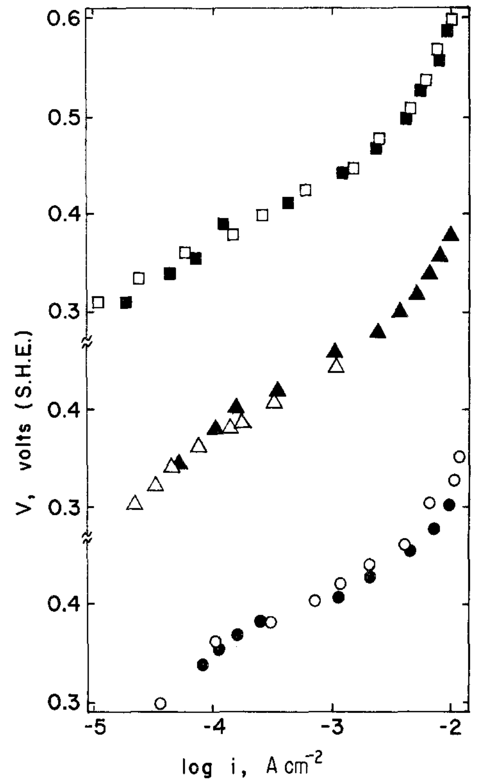

Fig. 7. Polarization curves for the anodic dissolution of PbS concentrate. (○, ●—0·75 M $HClO_4$; △, ▲—0·65 M $NaClO_4$ + 0·1 M $HClO_4$; □, ■—0·75 M $NaClO_4$.)

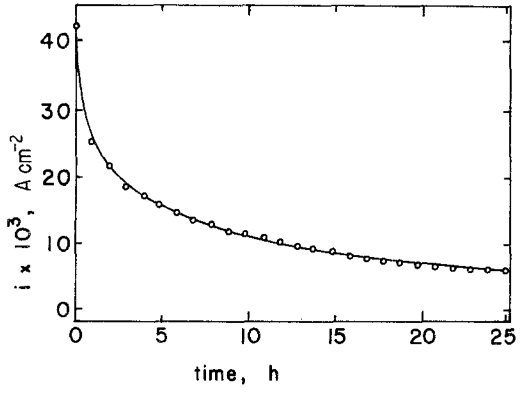

Fig. 8. Variation of current with time for the anodic dissolution of PbS concentrate at high (1·48 V) potentials in 0·75 M $NaClO_4$.

observed potentials or Tafel slopes. The majority of the Tafel slopes were 60–80 mV, independent of pH and Pb^{2+} concentration. A few curves (4 out of a total of 35) had slopes of 90–120 mV. No reason could be found for this anomaly.

Fig. 9 shows current density for varying pH at constant potential. The pH effect ($\partial \log i/\partial$ pH) is very small, possibly slightly negative. The effect of temperature on the rate is shown in Fig. 10. The plots yield apparent activation energies of 10·2 and 12·6 kcal at 0·42 and 0·38 V, respectively. The effect of potential on the activation energy, $\partial E'_a/\partial V = 60\,\text{kcal V}^{-1}$, is much higher than that predicted by the Tafel slope. This indicates temperature effects other than simply those on the activation process.

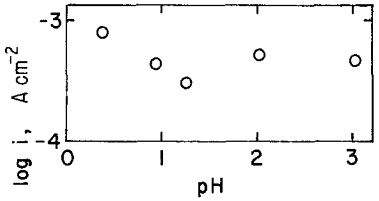

Fig. 9. Effect of pH on the anodic dissolution of PbS concentrate in ClO_4^- solutions at 0·40 V.

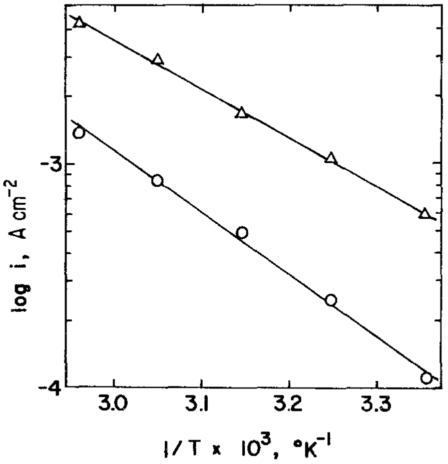

Fig. 10. Effect of temperature on the anodic dissolution of PbS concentrate in 0·75 M $HClO_4$ (0, 0·38 V; △, 0·42 V.)

3. Discussion

The initial difficulty encountered in the electrochemical dissolution of galena concentrate was the fabrication of suitable electrodes from the powder. The casting process described above was found to give electrodes of sufficient conductivity that were physically stable to action by the perchlorate electrolyte. (A lack of careful control in the fabrication of the electrodes from the concentrate causes very unreproducible behaviour). The electrodes were slowly attacked (chemically) at open-circuit conditions by the electrolyte as evidenced by the odour of evolved H_2S. This reaction apparently ceases when the anodic dissolution begins as the H_2S odour does not persist past this time.

The anodic dissolution occurs with very high efficiencies for the production of divalent lead ions and elemental sulphur despite a rather complicated and sometimes unpredictable polarization behaviour. The intrinsic resistance of the material is obviously a factor to be reckoned with in the polarization behaviour when c.d.'s exceed 10^{-1} A cm^{-2}. Film formation (oxide formation as contrasted to sulphur accumulation) also occurs in this region. This was revealed by ESCA analysis which showed partially oxidized sulphur to be present on an electrode surface that had reacted at high potential. Only sulphur was present when the potential remained in the linear Tafel region.

The transient measurements revealed several items of behaviour of the concentrate electrodes. First the non-uniform nature of the surface attack was indicated both by a hysteresis in which the current during the reverse portion of a cycle exceeded that of the forward portion and by the currents of subsequent cycles exceeding those of prior cycles. The absence of cathodic currents in the vicinity of the rest potential indicated the concentrate dissolution to be irreversible. The polarization of the electrodes up to $\sim 0{\cdot}2$ A cm^{-2} (at $\sim 1{\cdot}2$ V) indicates no passivating film to be formed in the normal range of operating potentials for anodic dissolution. The appearance of the peak at 0·50–0·54 V during the forward sweep at $\text{pH} = 0{\cdot}25$ with Pb^{2+} additions and at $\text{pH} = 0{\cdot}90$ would seem to be associated with the formation of some reactive substance at open-circuit conditions.

The steady-state polarization studies indicate a reaction that is activation controlled and a reaction sequence whose rate-determining step is a chemical reaction following the first electron transfer (60–80 mV Tafel slope $\simeq 2{\cdot}3RT/F$). Since there is also no pH effect, then H^+ or OH^- are not involved as reactants or products prior to or as reactants in the r.d.s. One sequence that meets these requirements is:

$$PbS(s) = PbS^+(s) + e \qquad (7)$$

$$PbS^+(s) + H_2O(aq) \xrightarrow{\text{rds}} PbOH(s) + S(s) + H^+(aq) \qquad (8)$$

$$PbOH(s) + H_2O(aq) \rightarrow Pb(OH)_2(s) + H^+(aq) + e \qquad (9)$$

$$Pb(OH)_2(s) \rightarrow Pb^{2+}(aq) + 2OH^-(aq). \qquad (10)$$

The latter part of this sequence would be the same as previously proposed for the dissolution of Pb in aqueous solutions [11]. The slow step suggested for Pb dissolution was Equation 10. As this latter reaction was considerably faster than the observed PbS dissolution, no problem is presented with the reaction shown in Equation 8 as the r.d.s. for the PbS sequence.

Acknowledgements

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