

ELECTROLEACHING OF SULPHIDES — A REVIEW

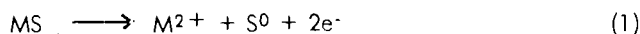
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1. INTRODUCTION

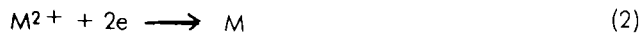
Sulphide minerals constitute a major source of non-ferrous metals like copper, zinc and lead. Conventional processing of these minerals involves pyrometallurgical operations which convert the sulphides directly to metal or oxides. Several environmental pollution problems associated with the release of sulphur compounds into the atmosphere have necessitated a search for alternate methods for the extraction of metals from sulphides. Hydro-metallurgical methods for the extraction of metals have so far met with partial success. One should not fail to realize that hydro-metallurgical treatment of sulphides is not completely free from pollution problems due to sulphur compounds. Many of these routes produce dilute sulphuric acid which must either be neutralised or discarded as gypsum or converted into ammonium sulphate fertilizer. Disposal of acid as gypsum or production and marketing of the ammonium sulphate presents a problem common to both pyro and hydrometallurgy. It is in this context that any hydrometallurgical process which leads to the direct recovery of elemental sulphur is likely to offer a significant advantage. Moreover, the hydrometallurgical processes can be characterised by slow reaction rates and employment of more expensive leaching agents. It should be realised that any leaching process in an aqueous medium involves the presence of a redox couple e.g. Fe^{2+}/Fe^{3+} . The underlying reaction in such leaching processes has long been recognised to be electrochemical in nature. As the normal solubility of many sulphides in aqueous media is very low even at high temperatures, electrochemical stimulation should improve the dissolution rate.

1.1 Basic principles : If suitable conditions could be established to have maximum anodic dissolution of the sulphides with simultaneous cathodic deposition of the metal the result can be considerable energy saving. 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.

Sulphide mineral can be used as an electrode because it is an electronic conductor similar to a metal. In general sulphide minerals have specific conductivities of the order of 10^3 to 10^{-3} $\text{ohm}^{-1} \text{cm}^{-1}$ [1]. As early as 1882 Marchese [2] suggested that this semiconducting property be utilized to decompose sulphides into their compounds by using an electric current. If sulphides are made as anodes in an aqueous electrolyte the metal goes into solution with the release of elemental sulphur.



The cathodic reaction in the process is deposition of metal.



Despite many attempts, commercial exploitation could be effected only in the case of electrolysis of nickel matte by International Nickel Company of Canada in 1951, as also in the cymet process

[3,4] for the electroleaching of chalcopyrite concentrate. In the latter case the aqueous ferric chloride leach of $CuFeS_2$ concentrate was followed by electrochemical dissolution of the resultant slurry.

For production scale operations, the preparation of anodes needs considerable attention. There exists three methods for the preparation of anodes namely (1) melting and casting (2) compacting and sintering and (3) use of slurry electrodes. Metal sulphides can be melted and cast in the form of electrodes strong enough to have sufficient stability under anodic leaching conditions. The method of compacting and sintering is followed in the case of sulphides of higher volatility. Although the operation with slurry electrodes is easier, it is usually associated with lower current efficiencies.

However, if the technical difficulties of the electroleaching process can be solved, it offers a number of advantages (listed below) as a method of treatment of sulphide minerals.

1. Pollution is diminished, as nearly all the sulphur is removed in the elemental form
- 2) It is likely to be competitive due to lower capital cost and energy consumption.
- 3) It is widely applicable to different minerals of various grades.
- 4) The final products are of high purity, being similar to metal obtained by electrowinning.

Many attempts made to electrolyse molten sulphides did not lead to much success because of relatively easy electronic conduction in the melt.

The progress in the field of electrochemical leaching over the last two decades is reviewed in this article.

2. COMMERCIAL PROCESSES

The success of a commercial operation of anodic leaching of sulphides depends on power requirements, electrolyte purification and anode sludge treatment. The ease of mass production of anodes is another factor that has to be given attention.

2.1 Direct electrorefining of matte [5,6]

2.1.1 The International Nickel Co. Ltd. process : The International Nickel Co. of Canada developed the process and erected a pilot plant in 1951 which blossomed into a full scale plant in 1964. In this process, nickel sulphide matte (Ni_3S_2) was melted at 980°C and cast into anodes of dimensions $71.7 \times 123 \times 4.4$ cm. The anodes were allowed to cool in the moulds to 540°C followed by a pre-determined cooling rate. This enabled the preparation of a crack free casting. The analysis of anodes and electrolytes is given in Table I.

Table I : Data on INCO process [5]

ANODES		ELECTROLYTE pH. 4	
	%		g/l
Ni	76.0	Ni ²⁺	60
Cu	2.6	SO ₄ ²⁻	100
CO	0.5	NaCl	100
Fe	0.5	H ₃ BO ₃	20
S	20.0		

The anodes corroded smoothly and uniformly. Slimes formed were granular and porous and remained adhering to the anode. The anodes increased in thickness during electrolysis due to the formation of elementary sulphur. The cell voltage increased from 3V to 5V and the cell temperature varied from 55°C to 60°C. The anodes were electrolysed continuously till they were reduced to 10% of the original weight. The anodes were kept in bags. The efficiency of anodic dissolution was 95%. Current density used was 185.8 A/m². The anodic reaction involved can be written as



During electrolysis iron, copper, cobalt, arsenic and lead went into solution while the precious metals were collected in the sulphur slimes. The electrolyte was regenerated from time to time and recycled. A typical analysis of the slimes is given in Table II.

Table II : Analysis of slimes recovered at the nickel sulphide anode [5]

	%
ELEMENTARY S	97.0
SULPHIDE S	0.7
NICKEL	1.25
IRON	0.6
COPPER	0.3
SELENIUM	0.15
PRECIOUS METALS	VARIABLE

Elementary sulphur was recovered from the slimes by melting and filtering. The filtrate was pure sulphur containing 0.15% selenium while the residue analysing 50% sulphur contained all the precious

metals and base metal sulphides. Sulphur was further purified from selenium by distillation while the sulphide residues containing the precious metals were again electrolysed after casting into anodes for concentrating the precious metals in the slime.

2.1.2 Engelhard Industries process : It is similar to INCO's process. However, due to higher copper content of the matte, a slight modification of the process has been effected (Table III).

Table III : Data on Engelhard Industries process [5]

ANODES		ELECTROLYTE TEMPERATURE 50-60°C	
	%		g/l
Ni	46	Ni	50-70
Cu	28		
S	23		
PRECIOUS METALS	0.18	H ₂ SO ₄	80-100

In this process when the matte anodes were electrolysed nickel went into solution, copper was deposited as powder on the cathode which was removed periodically by scraping. The nickel concentration in the electrolyte rose from 120 to 130 g/l while the sulphuric acid concentration fell to 8 from 15 g/l. The nickel sulphate was recovered by crystallization. The slimes were subjected to roasting followed by leaching with sulphuric acid for the recovery of precious metals.

A material balance showed that 43.5 kg of matte yielded 13.6 kg of raw slimes, which after roasting and leaching yielded 0.36 kg residue enriched in precious metals to 20.17%. Copper powder deposited at the cathode (10.9 kg containing 0.075% precious metals) was oxidised and dissolved in sulphuric acid to yield a CuSO₄ solution for electrowinning and 0.13 kg 'copper mud' containing 6% precious metals. These were recovered from the copper by HNO₃ treatment.

3. STUDIES ON BASIC ASPECTS OF ELECTROCHEMICAL OXIDATION OF SULPHIDES

A number of investigations on the anodic behaviour of copper matte and different minerals such as chalcopyrite, Cu₂S, CuS, galena, ZnS etc., have been reported. Such studies are related to mineral processing methods such as flotation apart from extraction of the metal values.

3.1 Cuprous sulphide and copper matte as soluble anode :

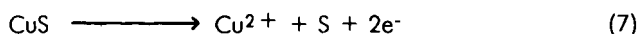
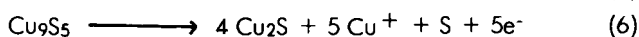
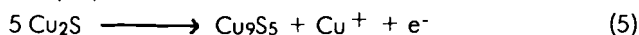
The possibilities of using Cu₂S as a consumable anode have been studied in detail by a number of workers. Loshkarev et al [7] have reported on the anodic dissolution of Cu₂S in CuSO₄-H₂SO₄ electrolytes. They have studied the influence of temperature and current density on the anodic dissolution of copper. At 15°C the anodic current efficiency was found to decrease with increase in current density. However, at high temperatures viz. 55°C and 65°C, increase in current density from 100 to 300 A/m² increased the current efficiency. With increase in temperature the cell

voltage decreased and the anodic current efficiency increased. According to these authors, more than 50% of the sulphur of the anode gets oxidised to SO_2 and SO_3 and passes into solution. About 30% of the anode sulphur is liberated as elemental sulphur leaving 15% as sulphide sulphur. It was also noted that with increase of current density the percentage of oxidised sulphur increased. The anodic dissolution was found to proceed as follows :



Subsequently the discharge of OH^- ions takes place leading to oxygen evolution. This oxygen takes part in oxidizing the copper sulphides and also the elemental sulphur at the anode.

Haboshi et al [8] have also studied the anodic dissolution of Cu_2S and the direct recovery of copper and sulphur from white metal employing a sulphate electrolyte. On the basis of X-ray diffraction analysis of slimes and corroded anode the following mechanism has been proposed.



Detailed investigations on the consumable anode electrolysis of Cu_2S and copper matte have been carried out by Mallikarjunan et al [9,10]. These investigations were made in sulphate, chloride and their mixtures. The studies on the anodic dissolution of Cu_2S in a sulphate electrolyte showed that at 30°C maximum current efficiency for the dissolution of copper occurs at the lowest current density. With increase in current density the current efficiency is found to decrease. The anodic sludge obtained in sulphate was black in colour. Analysis of the elemental sulphur and sulphide sulphur revealed that over 50% of the sulphur of the anode got oxidised, about 20-30% converted into elemental sulphur and the rest remained as CuS . These authors have also studied the effect of ultrasonic radiation on the anodic dissolution of Cu_2S in a sulphate bath at room temperature. The use of ultrasonic radiation produced significant changes in cell voltage and current efficiencies over a range of current densities.

The passivity developed at the sulphide electrode with the progress of electrolysis in a sulphate electrolyte suggested the use of anode corroding agents such as chloride ions. The chloride ions are said to penetrate through oxide films and make them more porous. The application of a purely chloride bath for the anodic dissolution of Cu_2S has been studied. The anodic sludge obtained with these electrolytes is different from that obtained in a purely sulphate bath and consists of 80% elemental sulphur and 20% CuS . This indicates that practically no oxidation of sulphur of the anode takes place under these conditions. The anodic current efficiency has also been found to be very good.

The possibilities of recovering copper directly from Cu_2S have been discussed so far. However, if the copper matte is blown to white metal in the converter and cast as an anode, a substantial addition of energy and cost would be involved. Instead, if it is possible to recover copper directly from the copper matte, it would be advantageous. With this aim, investigations have been reported [9] with anodes cast from molten synthetic mattes and commercial 40% grade copper matte obtained from Indian Copper Corporation, Ghatsila. Studies in sulphate electrolyte showed that increase in current density led to considerable decrease in current efficiency for the dissolution of copper and a slight increase in the efficiency for iron dissolution. The efficiency for nickel dissolution was not appreciably affected by variation in current density. The total current efficiency for the dissolution of

the metals was found to increase with increase in both temperature. The influence of chloride ion addition to the sulphate bath and the use of a purely chloride bath on the anodic dissolution of copper matte was studied. It was found that the sulphate-chloride bath was preferable from the point of view of the elemental sulphur content of the anodic sludge.

The effect of superimposing A.C. on D.C. is known to prevent passivation of anodes. Such as investigation [11] has indicated a decrease in the anode potential and also the percentage of current utilized for the dissolution of the metals was higher compared to the values obtained with D.C. alone.

The laboratory investigations discussed so far have shown the possibility of consumable anode electrolysis of Cu_2S or copper matte. The practical possibilities should take into account the power requirements, electrolyte purification and anodic sludge treatment. In general the power requirements of such a process using sulphide anode will exceed those for electrorefining with copper anodes. However, the cathodic current efficiency can be improved by using a diaphragm cell wherein the amount of Fe^{3+} ions in the catholyte can be controlled. In fact a diaphragm cell is essential if a chloride containing electrolyte is used. The power requirement must be considered in the light of other byproducts recovered. In view of the large amount of impurities contained in the anode, care should be taken in the purification of the electrolyte.

3.2 Studies on chalcopyrite concentrate as soluble anode :

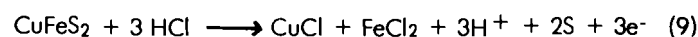
Sawamoto et al [12] used a high current density of 5 A/dm^2 to solubilize CuFeS_2 powder by anodic dissolution and electrodeposit a pure copper powder at the cathode. The temperature of the bath was 60°C and pH was 2.5. The cathode was a copper plate and the electrolyte was CuSO_4 solution. The cathodic current efficiency was 90%. Oki and Ono [13] added graphite powder to the finely-divided CuFeS_2 concentrate to improve the electrical conductivity. They found that the anodic current efficiency for Cu(II) was 80-90% for a graphite concentration in the mixture of $\geq 20\%$.

Kruesi et al [14,15] combined leaching with anodic dissolution to treat CuFeS_2 according to the following scheme :

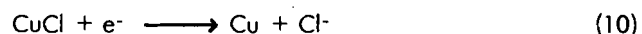
Leaching :



Anodic reaction :



Cathodic reaction :

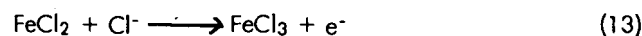


Ferrous chloride was electrolysed in a separate cell to get metallic iron and regenerate the leaching agent as follows :

Cathodic reaction :



Anodic reaction :



The process called the 'cymet process' is being tested on a pilot plant scale in Arizona.

Vasu et al [16,17] studied the anodic dissolution of chalcopyrite concentrate in a slurry electrode as shown in Fig. 1.

A diaphragm made of chlorinated polyvinyl chloride was used to separate the anode compartment. A mixture of sulphuric acid and ferric chloride was used as electrolyte. The following reactions

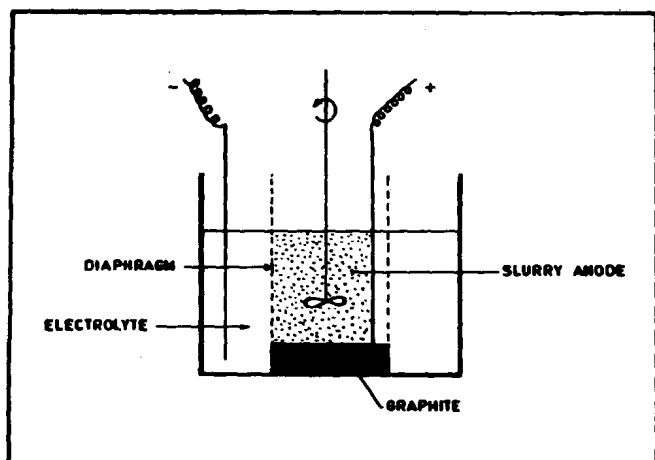
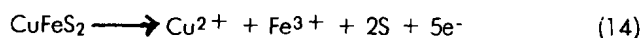


Fig. 1 : Circular cell assembly (slurry electrode) for anodic dissolution [16]

were found to take place :

At the anode :



At the cathode :



Ferric chloride was chosen as an additive to the electrolyte to decrease the resistance of the cell and also due to its leaching action on chalcopyrite. Table IV shows the benefits gained from this method over using sulphuric acid alone.

Table IV : Effect of FeCl_3 in the electrolyte ($200 \text{ g/l} \text{ H}_2\text{SO}_4$ on copper recovery : 30 g CuFeS_2 Anode current density, 3.5 A/dm^2 [16].

$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ g/l	Cu DEPOSITED %	
	FOR 24 Amp.Hr	FOR 48 Amp.Hr
0	6.5	16.4
55	24.4	42.6
110	22.8	44.4
220	20.0	38.5

Also, it was reported that in the absence of ferric ions there was excessive foaming in the anolyte because of oxygen evolution. The presence of too much ferric chloride, however, decreased the recovery of copper at the cathode. H_2SO_4 concentration above 200 g/l did not influence the process, while increasing the pulp

density beyond 1.8 created mechanical difficulties. The problem with this process is two fold :

1. The sulphur formed acts as an insulator between the sulphide particles and therefore the cell voltage increases greatly as the reaction proceeds.
2. Iron in solution will create a disposal problem

The results of chalcopyrite slurry electrode [18] in sulphate bath indicates that increase in temperature increases anodic current efficiency for copper and recovery of elemental sulphur. Increase of H_2SO_4 concentration upto 150 g/l in electrolyte again increased the current efficiency for copper but decreased the sulphur recovery which probably enters the solution as SO_4^{2-} . 20% pulp density gave the best results. Addition of ferric chloride (10 g/l) resulted in an increase of anodic current efficiency for copper by 20% from the 95% in the sulphate bath. Recovery of sulphur also increased. The current efficiency for copper dissolution exceeding 100% should be attributed partly to the coupled chemical dissolution. Mallikarjunan et al [19] observe that the electrochemical dissolution of chalcopyrite concentrate increased with temperature, particle size, acid concentration and stirring in HCl , whereas only temperature influenced the dissolution in H_2SO_4 . The dissolution of copper and iron and elemental sulphur recovery are generally higher in HCl as compared to H_2SO_4 . The anode potentials ($\geq 80^\circ\text{C}$) are active in HCl and reached baser values with the progress of dissolution whereas they become nobler in H_2SO_4 . The addition of Cl^- and Br^- to H_2SO_4 accelerated the leaching of CuFeS_2 . XRD, ESCA and SEM studies of the mineral surface indicated that the morphology changes are only slight in H_2SO_4 , but the surface is severely corroded in HCl . XPS studies indicated the formation of a new phase in anodic leaching whose compositions varied with pulp density, temperature, particle size and acid concentration. This new phase serves as a passivation layer.

Biegler and Horne [20] report that the passivating layer formed on the mineral surface is highly disputable. It has been variously considered to be sulphur or a metal deficient CuFeS_2 like sulphide, or a polysulphide, or a precipitated iron compound. Its effect on oxidation kinetics has been described in terms of physical blockage or solid state diffusion of metal ions, electron transport properties, passive film growth or electrolytic conduction of metal ions. They studied the anodic prewave in depth. The prewave represents the initial stage of leaching process and the product of prewave is regarded as the passivating layer referred to above. The prewave is found with all specimens of chalcopyrites studied. Its characteristic is similar in different acids although polished and rough surfaces gave different prewave shape. The prewave is found in more dilute acid solutions ($\text{pH} \sim 2$) but at higher pH became more obscured by the bulk dissolution current. Surface renewal in nitrogen gives the same result as in air indicating that the prewave is not a consequence of atmospheric oxidation. It is to be noted that a proper understanding of the CuFeS_2 prewave behaviour should allow identification and separation of any impurity effects.

Srinivasan et al [21] have studied electroleaching of chalcopyrite by cyclic voltammetric technique. The technique of compacting and sintering was used in the preparation of the electrode. The satisfactory for the preparation of the electrode of 23 mm dia and 9 mm thickness have been reported as :

Electrode composition : CuFeS_2 concentrates + 25% graphite + 5% binder
 Pressure and sintering temperature : 20 tons for 1 min . 250°C for 30 mins .

The preware current was found to increase with H₂SO₄ concentration and chloride addition (Fig. 2).

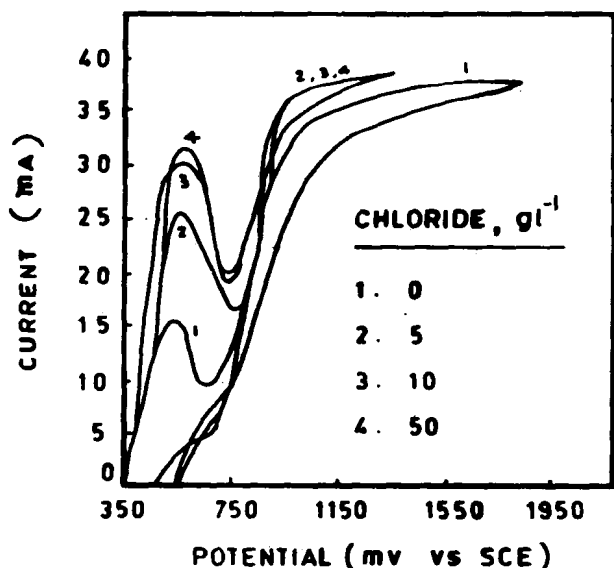
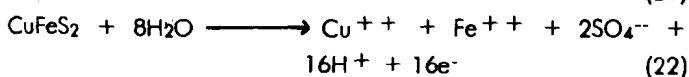
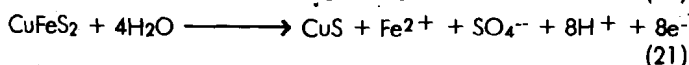
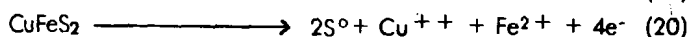
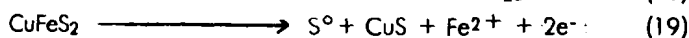
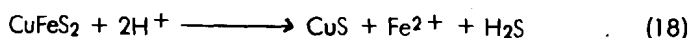


Fig. 2 : Cyclic voltammograms of chalcopyrite electrode with 5% binder and 25% graphite at 10 mV s⁻¹ in 1N H₂SO₄ with Cl⁻ addition [21]

It is to be noted that chloride addition is known to increase anode dissolution by removal of passive films, if any produced.

Peters [1] reporting on the electrochemistry of CuFeS₂, suggests that CuFeS₂ would react by one of the following reaction paths, given in order of increasing thermodynamic potential



At higher potentials (~1.5V vs NHE) the electrode reaction represented by equations (20) and (22) are reported to be predominant. At lower potentials (0.6 - 0.7V) and high temperature (150°C) equation (19) will be operative. Polarisation curves for CuFeS₂ always exhibit a form as shown in Fig. 3.

A limiting current or at least a small current/potential slope is found between 0.7 and 1.0V (SHE) and then a sharp rise in current occurs, that is often linear with potential.

The dependence of the limiting current with scan rate indicates that this process is probably a superficial phenomenon.

At 20°C in 0.1M HCl only 0.01 to 1 coulombs/cm² are consumed in this region, and there is considerable evidence for a dissolution of much more iron (and possibly sulphur) than copper. It is probable that this early reaction is represented by equation (19) or (21) and the current is limited by the rate at which CuS and S⁰ can nucleate and grow. The total coulombs represent only about 0.02 to 2.0 microns of CuFeS₂ decomposition over a uniform

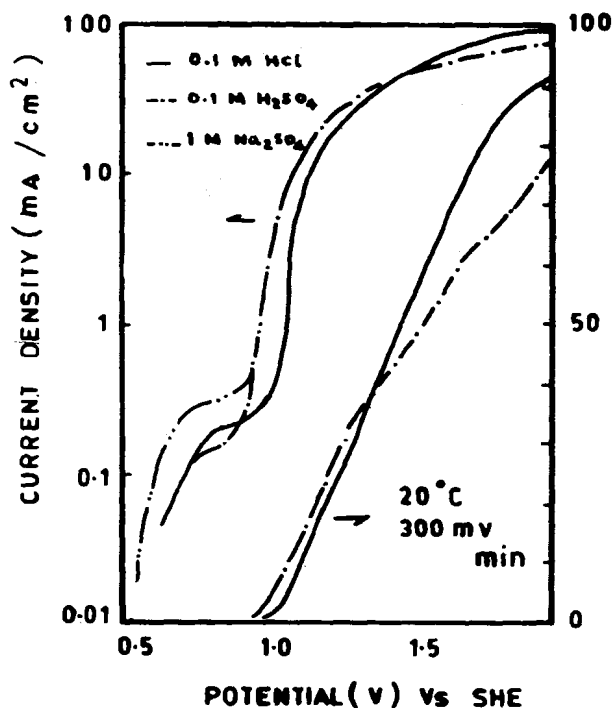


Fig. 3 : Anodic polarization curves for chalcopyrite. Logarithmic and linear scales [1]

surface. At the lower end of the range, the process could represent depletion of iron from the CuFeS₂ surface layers, which might have been altered by the preparation procedure.

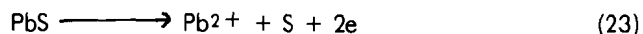
At higher potentials the current increases to substantial levels. The overvoltages are very high and there is usually a linear relation between current and potential. In sulphate media, CuFeS₂ seems to preferentially corrode deeply in the grain boundaries while the surface appeared passive.

3.3 Studies on anodic leaching of galena : Sawamoto et al [22] have studied the anodic dissolution of galena containing 40-70% of graphite in fluoborate and perchlorate media. The anodic dissolution of PbS and galena concentrates in HCl - NaCl electrolytes has been investigated by Dixit et al [29] and anodic current efficiencies of over 95% in an electrolyte consisting of 0.3M HCl and 250 g/l NaCl have been obtained. There are several reports which reveal the possibility of electrowinning of lead directly from galena anodes and they stress the following points : (1) Necessity of graphite addition for improving its conductivity (2) the oxidised species formed at the anode range from elemental sulphur to sulphate and oxides depending on the pH of the bath, the electrode potential and current density (3) a temperature slightly above ambient is required for good current efficiency (4) good current efficiency can be obtained at low current density.

From a commercial view point two aspects need attention. As already pointed out the anode must be easy and economical to fabricate and should be able to stand the electrolytic operation; secondly the electrolytic bath should be such as to dissolve most of the metallic content of the anode and permit selective deposition on the cathode. Most of the reports deal with either compacted anodes or slurry anodes. Because of the high volatility of PbS, the method of melting and casting has been discarded. Although the slurry anodes would appear simpler and more economical from an operational point of view, current efficiency seems to be a major problem which is as yet unsolved. Australian workers [23-

27] have reported the compaction character of galena concentrate in detail and two methods of anode preparation either by hot or cold pressing at low temperature and low pressure followed by heat treatment look quite promising.

As far as the electrolytic bath is concerned, the literature reports the use of chlorides, fluoborate and perchlorates. Skewes [23] has made extensive studies on winning lead from lead concentrate anode in a perchlorate bath. He observed that the reaction



at the anode should be predominant at potentials below 0.9V (SHE) and obtained a current efficiency of 85% for the reaction by electrolysis at a temperature of 333°K, current density being 150 A/m². Japanese workers [22,28] have reported the use of fluoborate bath. Dixit et al [29] have studied the same in acidic chloride bath. Paramaguru et al [30] advocate the employment of an acetate bath consisting of ammonium acetate, acetic acid and lead acetate. It has been pointed out that the bath has the following advantages: (1) simplicity (2) cheapness (3) no action on materials made of ceramics (4) it is a solvent for several of the oxidation species of lead including PbSO₄ which may be formed with PbS electrode. The effects of graphite content in the compact, bath composition, time of electrolysis, temperature of the bath, current density and compaction pressure were studied on a laboratory scale to optimise the operating conditions. A compacted electrode containing 6.25% graphite resulted in a current efficiency of 70% for the dissolution of lead sulphide in a bath of ammonium acetate (0.5M), acetic acid (0.35M) and lead acetate (0.1M) when electrolysed at 333°K with a current density of 110.5 A/m².

Effective electrowinning of lead directly from its sulphides requires a fundamental understanding of its electro-dissolution process. Studies made on the anodic dissolution of PbS in HCl have shown that there are obstructions to the electro-dissolution process. Detailed surface examination (SEM, XRD etc) indicates crystalline sulphur, PbCl₂ and PbSO₄ are responsible for the observed phenomena. Use of perchlorate medium has been advocated as a feasible proposition. The industrial application of this highly oxidising medium is not attractive due to the accompanied formation of the insoluble oxides of lead. Studies [31] have been made on the effect of media such as fluoboric, fluosilicic, sulphuric, hydrochloric acids etc. Fluoboric and fluosilicic acids have not been favoured due to the fact that PbS develops passivation in the earlier stages of the studies. Very little anodic dissolution is reported in H₂SO₄ due to the very low solubility of the product PbSO₄ ($k_{sp} 1.06 \times 10^{-8}$ at 25°C). Sulphamic acid is attractive as a medium due to the high solubility of the dissolution products, lead sulphamate and the high dissolution rate (of PbS) observed. However, it creates problems due to slow hydrolysis of the acid at room temperature (to ammonium bisulphate and then to ammonium sulphate especially at high anodic potentials). This makes sulphuric acid less productive industrially. HCl on the other hand is more viable due to the reasonable solubility of PbCl₂ formed ($k_{sp} 1.0 \times 10^{-4}$ at 25°C in water and a bit higher in HCl) and the associated low overvoltage of the chloride medium. Voltammetric behaviour of PbS in HCl has been extensively studied by Ghali and Dandapani [32]. The typical voltammogram for PbS in HCl as shown in Fig. 4 indicates two possible anodic reactions.

As there are no corresponding cathodic peaks these anodic reactions are irreversible. PbS dissolves at the cathodic end to generate H₂S and lead, which can form PbCl₂ at the beginning of the anodic cycle and the peak around -0.3 to -0.4V could be due to this process. The peak between +0.4 and +0.5V is very

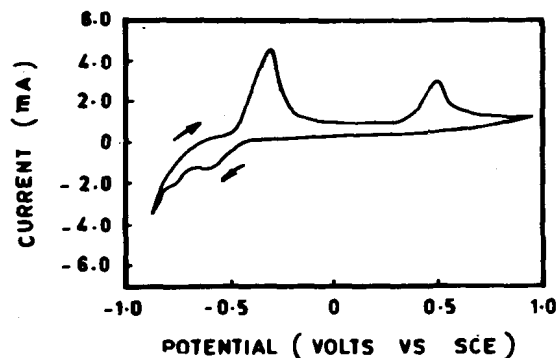
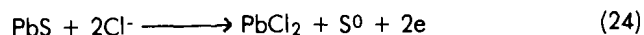


Fig. 4 : Cyclic voltammogram of lead sulphide in 0.1M HCl at 1000 mV min⁻¹ [32].

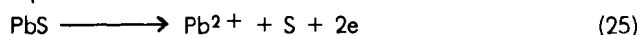
likely due to the formation of PbCl₂ resulting from the direct dissolution of PbS in the acid.



The effect of temperature and oxygenation on the dissolution of PbS in HCl medium has also been studied by Ghali et al [33]. Oxygen seems to inhibit the dissolution both at room temperature and higher temperature in 1.0M HCl, though temperature alone in the absence of oxygen increases the dissolution rate. In 0.1M HCl, oxygen accelerates the dissolution as a result of its depolarising nature, whereas in 1.0M HCl it plays a major role in the oxidation process producing elemental sulphur, PbSO₄ and possibly lead oxides.

The electro-oxidation of galena in neutral or alkaline media [34] is more complex than in acid solutions. The formation of bulk products of galena oxidation in acid media appears to be simple. Lead sulphide dissolves with the formation of elemental sulphur. Some PbSO₄ is formed when the electrode is polarised above 1.0V. In HCl medium the anodic film is reported to contain always some unreacted PbS + S. Moreover, at high anode potentials, the formation of higher valence lead species is quite possible and as seen in the voltammogram (Fig. 5) for acid solutions, the reduction peak for Pb⁴⁺ to Pb²⁺ is not so sharp unlike in the case of electrolytes of higher pH.

Only a cathodic wave is observed. The initial potential region of the anodic scan involves a prepeak or prewave formation which has been well established in voltammetric behaviour of sulphides. Elemental sulphur and Pb²⁺ are the only species formed in the potential region of the prepeak in acid solutions. It appears that the prepeak is associated with the reaction



occurring at certain active sites at surface and these sites are soon covered with a layer of sulphur reducing this activity. The voltammetric behaviour in alkaline media indicates the passivating tendency of the galena electrode. Formation of species like PbO may be the possible reason for passivation. High pH can promote the oxidation of sulphur to higher oxidation state such as S₂O₃²⁻ as predicted by Eh-pH diagram of PbS-H₂O system. The reduction peak for Pb⁴⁺ to Pb²⁺ is more marked in electrolytes of higher pH indicating the tendency for PbO₂ formation, at higher anodic potentials, a fact that has to be considered while attempting the recovery of lead through electroleaching of galena.

A recent trend in studies on hydrometallurgical processing of galena concentrate is to leach them in chloride media. The fused

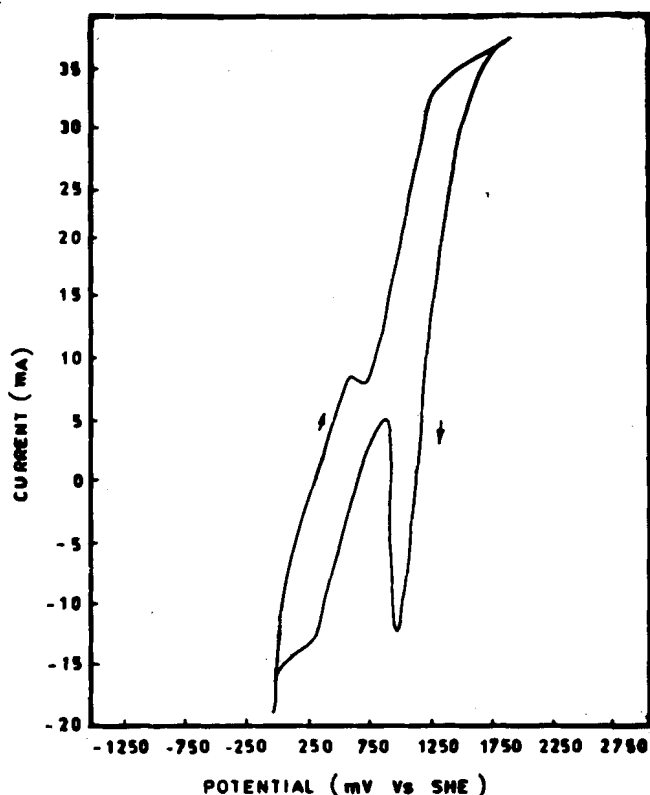
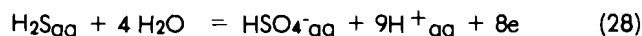
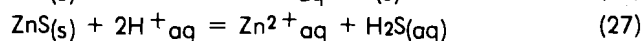
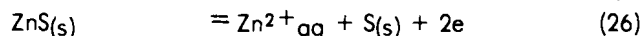


Fig. 5 : Cyclic voltammogram of galena electrode in acetate buffer of pH 4.64 at 5 mV s^{-1} with positive potential limit of 1750 mV [34]

salt route has no clear commercial or economic advantages due to the loss of energy and efficiency. Mackinnon [35] has summarised different trials that had been carried out to obtain satisfactory lead deposits in compact form from aqueous chloride media and concluded that in most cases deposits obtained are characteristically non-compact and powdery even at low current densities. Glycine [36] has a certain activity in dissolving PbCl_2 and its addition to acidic aqueous solutions containing chloride was found to prevent passivation of lead chloride during the electrodisolution of galena. Also it was found that an adherent deposit can be produced at 20 mA cm^{-2} c.d. and a temperature of 45°C from an electrolyte containing 0.11 M PbCl_2 , $2 \text{ M NH}_2\text{CH}_2\text{COOH}$ and 5 M HCl on lead and copper substrates both in stirred and unstirred conditions. The addition of organic compounds as phenol and ethyl alcohol and an ampholyte as gelatin in certain quantities showed a remarkable progress in the efforts to produce a dense and fine crystalline deposit.

3.4 Anodic leaching of zinc sulphide : In comparison with the volume of literature on the electrochemical processing of copper and lead sulphides, reports of studies on zinc sulphide are meagre. The use of an anode consisting of 30% ZnS and 70% graphite powder in acidified ZnSO_4 solution has been reported for the recovery of zinc [37]. The basic aspects of ZnS anodic leaching has been investigated by O'Keefe et al [38]. The electrodes were fabricated by hand pressing (pressure $\sim 35 \text{ bar}$) a mixture of ZnS + pitch (5-15%) and sintering at 800°C for 30 minutes in nitrogen atmosphere. The compacts were found to have a resistance of $< 8 \Omega$. The open circuit potential was considered to be mixed in nature, resulting from the anodic dissolution of ZnS and the cathodic reduction of sulphur or oxygen. The results indicated the occurrence of both electrochemical and chemical

dissolution steps as well as the further oxidation of H_2S namely



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

ZnS electrolysis has several problem areas one of which is the fabrication of anodes of acceptable electrical conductivity (ZnS is a semiconductor $6 \times 10^9 \text{ ohm cm}$) that have sufficient mechanical strength for handling. Because of its volatility ZnS cannot be melted and cast at atmospheric pressure to form a dense material suitable for massive electrodes.

4. CONCLUSION

Direct electrochemical processing of sulphide minerals has to overcome the problem of preparation of the electrodes by pressing and sintering. The difficulties encountered are high resistivity, high bath voltage and high cost of making compacts. However, if the technical difficulties of the electroleaching process can be solved, it seems to offer a number of advantages like minimisation of pollution and lower capital cost. Among the metal sulphides, galena seems to offer the maximum chances of success due to the higher electrochemical equivalence of lead and minimum interference by impurities. The application of the technique appears rather limited in the case of chalcopyrite as it calls for cell complexities due to iron intake. For zinc sulphide, the possibility is still remote as zinc deposition is very sensitive to impurities and the conductivity is relatively poor. In production scale processes, the problems encountered in the preparation of electrodes may persuade one to think of slurry electrodes where the operation is simpler.

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