

CHAPTER - I

INTRODUCTION

In recent times, studies on sulphide/solution interface have assumed added value due to interest taken by people in developing solar cells. These sulphide systems have in general given photovoltaic effect over wide range of wavelength of light. But the major trouble has been the degradation (corrosion) susceptibility of these systems due to interfacial reactions. Reports on kinetics studies of these interfacial reactions at sulphide/solution interface are scanty and the details of the reported titles of Russian work in this field are not available. On the other hand, these interfacial reactions have more importance from metallurgical point of view as the metal dissolved from sulphides through such reactions can be won directly on the cathode. After the successful application of such a process by INCO for nickel winning, metallurgists throughout the world could see the possibility of adopting this process for other metals as well. Therefore, the kinetics studies of interfacial reactions at some sulphide electrode surface coupled with a process development of winning metal directly from a sulphide mineral has been chosen as the topic for this thesis.

The problem of dealing with a sulphide system is quite complex in many ways. Firstly, the sulphides are not single component systems like those of metals and at least two components such as metal and sulphur are present. Therefore, from thermodynamics point of view sulphides are to be taken as some sort of alloys. Secondly, metal sulphides are mostly semiconductors, either of p- or n-type. The same sulphide can also exist as both p-type or n-type or a n-type sulphide can change over to p-type due to presence of air or for any other reason. For example, when a n-type galena is broken down to smaller sizes it changes over to p-type. This means studies on sulphides are more complex than those on metals which show metallic conduction. Another complicacy caused by the semiconducting nature of the material is that the normal Butler-Volmer equation applicable to metal systems may lose its significance due to the presence of a space charge layer in the solid side of the interface in addition to the Helmholtz layer in the solution side. This space charge layer may again become negligible when the concentration of charge carriers of the semiconductor is high. These variations may cause anodic and cathodic reactions at the interface to depend on the conduction type and the nature of the semiconductor. Due to these complications the sulphide electrodes have remained virtually unexplored till today.

Although almost no literature is available on electrode kinetics of sulphides, an exhaustive literature is available on

open-circuit potential measurements of the sulphides - both synthetic as well as rock minerals. Investigators like M.Sato, E. Peters, K.E.Wrabetz and coworkers, D.M.Chizhikov and his group have tried to deal with sulphide/solution interface as a reversible interface in terms of Nernst's equilibrium as is observed in some of the metallic systems. M.J.Nicol, T.Biegler and group, on the other hand, through experimentation have proved that the systems attain a steadystate condition as in corroding systems of metals. Contradictions like this on reversibility as a whole as well as on reproducibility for sulphide systems do exist and the behaviour of many systems like covellite and chalcopyrite is not yet clear.

Therefore, in the next chapter a review has been made of the available literature in this line and in chapter- III results have been presented on the studies of electrode kinetics through steadystate anodic and cathodic polarizations for four sulphide systems viz. Cu_2S , precipitated PbS , sintered PbS and CdS , covering both the conduction types with differing carrier concentrations. Based on these experimental results an attempt has been made to arrive at the reaction scheme and mechanism.

In relation to the process development, that followed by INCO at Thompson, Manitoba, consists of casting the nickel matte produced from a conventional pyrometallurgical step into anodes and electrolysing them in an aqueous bath to deposit electrolytic nickel on the cathode. Such aqueous electrolysis using

consumable anode is being followed for years during electrorefining of a number of metals such as copper, nickel, lead etc. These crude metal anodes in electrorefining contain a few other metals as impurities, whereas, the sulphide anode contains other sulphides as major impurities. However, the sulphides are electronic conductors and therefore can be used as electrodes. This process, once successful has a large number of advantages over conventional processes. Therefore, many research investigations have already been conducted and many are still on the way to adopt the process for other sulphides like copper, lead and zinc. In the present study galena has been selected for winning of lead and in the literature review chapter, literature relating to electrowinning of lead from galena is incorporated.

Literature reports the use of baths like chlorides, perchlorates, fluoborate etc., although Australian practice using perchlorate bath with compacted PbS anodes appears to be quite impressive. However, surprisingly no work in acetate bath is reported yet, although this bath may have some advantages over others like its simplicity, cheapness and no action on ceramics. Moreover, it is a solvent for sulphate and a few oxides of lead which may form on the electrode surface during electrolysis. Therefore, an attempt has been made to study the performance of acetate bath for electrowinning of lead using lead concentrate of Zawar, India, which has been presented in chapter IV.