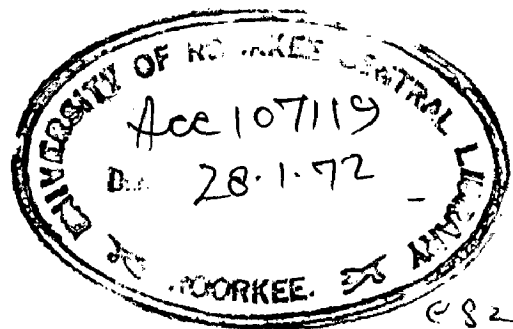


RECOVERY OF COPPER FROM SLAG AND MATTE

A Dissertation
submitted in partial fulfilment
of the requirements for the degree
of
MASTER OF ENGINEERING
in
EXTRACTIVE METALLURGY

BY
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September 1971

C E R T I F I C A T E

Certified that the dissertation entitled "RECOVERY OF COPPER FROM SLAG AND MATTE" which is being submitted by Vinay Kumar Tondal in partial fulfillment for the award of the degree of Master of Engineering (Metallurgical Engineering specialization in Extractive Metallurgy) of the University of Roorkee as a record of the students own work carried out by him under my supervision and guidance. The matter embodied in this dissertation has not been submitted for the award of any other Degree or Diploma.

This further certifies that she has worked for a period of 8 months from January 1971 to August 1971 for preparing the dissertation for Master of Engineering at the University of Roorkee.

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ACKNOWLEDGEMENT

The author wishes to express his extreme sense of gratitude towards his advisor, Mr. Satya Prakash, Lecturer in Metallurgical Engineering Department, University of Roorkee. Without his invaluable guidance, help and above all his sympathetic inspiration it would not have been possible to shape this dissertation.

The author is also indebted to Mr. S.K. Gupta, Lecturer in Metallurgical Engineering Department, University of Roorkee for his profound and timely suggestions during experiments.

Sincere thanks with obligatory sentiments are due to Dr. H.N. Saxena, Professor and Head, Metallurgical Engineering Department, University of Roorkee for his overall guidance and continual encouragement during the course of work.

VINAY K. TEWARI

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ABSTRACT

The concept of direct recovery of Copper from matte by electrolytic refining is one of the revolutionary measures in the development of new and effective extraction techniques. Its achievements must be viewed as a process in itself and as a part of the total process in which cost and performance are equally important measures of effectiveness. It is necessary to find out optimum conditions under which it will be possible to recover Copper with maximum efficiency from the matte.

The direct electrorefining of Copper matte in an aqueous solution of Copper sulphate and sulphuric acid has been studied. The influence of current density, electrode distance, bath composition and temperature on the Cathodic current efficiencies is discussed.

A two tank multielectrode electrolytic cell has been designed and fabricated for the study of above mentioned variables and optimum conditions for maximum recovery of Copper from the matte have been obtained.

An attempt has also been made for the comminution of slag particles and their concentration of the same by froth flotation to recover the copper entrapped in slag in various forms.

Chapter 1

INTRODUCTION

1.1 General Introduction to Copper Extraction :

In the early periods of man's existence it was the stones which were primarily used as weapons and tools for attaining the requirements of livelihood and self protection. After the stone age the era of metals came in with the discovery of metals in native form by primitive hunters around 13,000 B.C. The man discovered that it is possible to utilize some of the properties of metals for making the weapons and implements required for household. There is ample evidence that in India also copper metal has been extracted in a very primitive way from the deposits of copper at an early stage. Egyptians were making copper knives and weapons 8000 years ago and pipes and tubes as early as 2750 B.C. The Roman supply was drawn from Cyprus; became known as Cyprium; was shortened to Cyprum; was corrupted to Cuprum - whence comes our word copper and chemical symbol Cu.

Copper has been used in the industries of the world for so long that inevitably it is regarded as a traditional material. It continues to be used where a greater number of its properties are needed in the product and therefore a satisfactory substitute is not so easy to find.

In 1800 world refined copper consumption⁽¹⁾ was very small and by 1850 it had only risen to some 50,000 tons, but by 1900 had increased to 500,000 tons. Since

that date the total world demand has risen at a rate of about 4.5 percent per annum (Fig. 1.1). Refined copper consumption in 1968 was nearly 6.5m tons, in 1969 7m tons, and in 1970 about 7.3m tons. Copper consumption in Europe in the year 1968 under various heads is as given in table 1.1.

Table 1.1

	1968 Copper consumption (tons)
1. Electric Industry	1350000
2. General Engineering	445000
3. Building Industry	390000
4. Transport Industry	265000

Copper⁽²⁾ is one of the metals in which India is deficient. Because of the severe import restrictions and increased growth of copper consuming industries, it has become an absolute necessity to produce this vital metal from the available deposits and resources in India and intensive efforts are being made to raise the output.

Workable deposits of copper are ~~mainly~~ ^{mainly} located mainly in Bihar and Rajasthan. Exploratory work to discover other copper ore deposits is being intensively pursued by the Geological Survey of India and recently some new deposits have been located in Andhra Pradesh, Uttar Pradesh

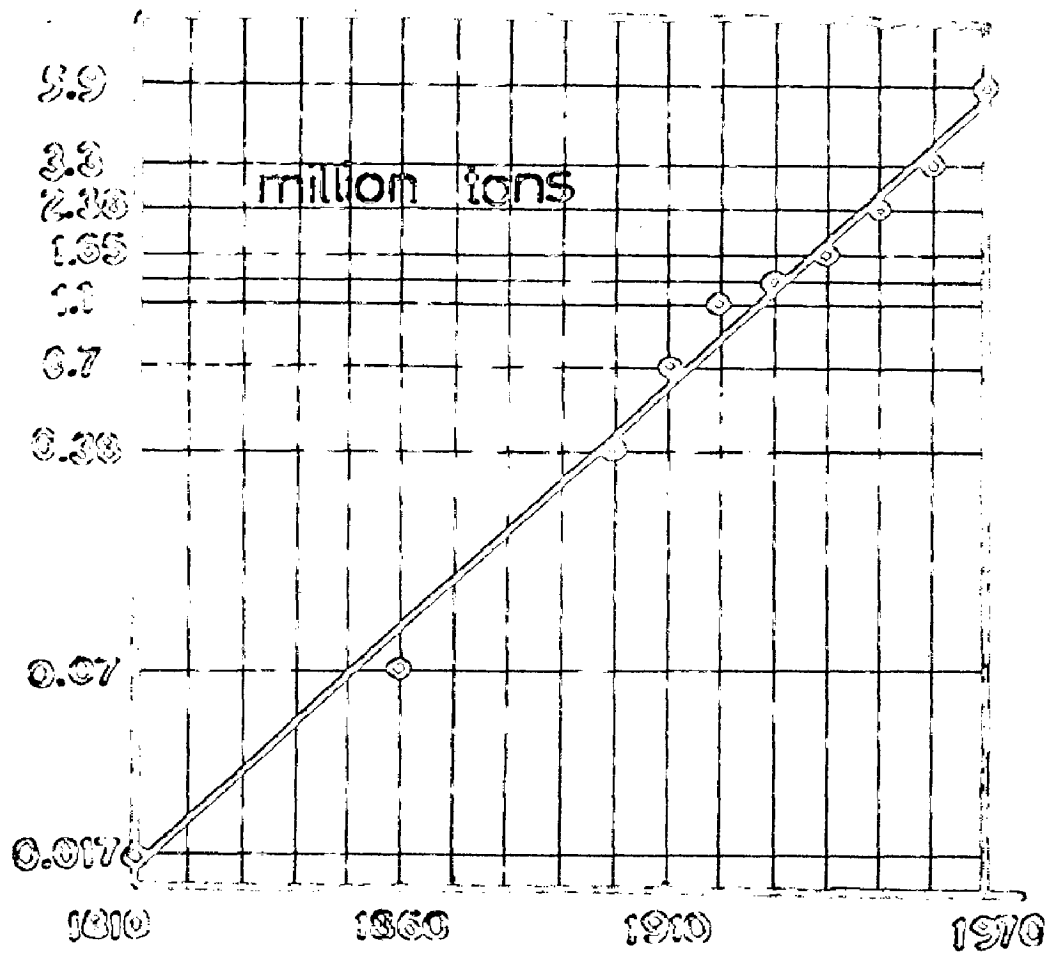


Fig.1.1 World consumption of refined copper yearly average per decade

and Kashmir region. The Bihar deposits are being worked by M/S. Indian Copper Corporation Ltd. and those of Rajasthan to be worked by Hindustan Copper Ltd., a public undertaking.

Keeping in view the increased Copper demand, over present problem of maintenance, competitive costs in producing copper from low grade ores and other resources (old tailings, slags etc.), significant technological improvements have been done.

Expansion and modernization in mining, concentrating, melting and refining are going on all over the world. In most modern methods of copper extraction one, two a more steps have been reduced. The present trends are broadly as follows :-

1. Development and application of autogenous melting process.
2. Switching over to smaller units with higher melting and production capacities.
3. Application of continuous process.

The ore dressing division of the National Metallurgical Laboratory⁽²⁾, right from its inception, is actively engaged on beneficiation studies on various types of low grade copper ores of India. Low grade ores and minerals of complex and diversified nature have been investigated in detail and suitable beneficiation techniques developed.

Production of copper from sulphide flotation concentrate accounts for about 75 percent of the total production. Also intensive work is going on for the recovery of copper from converter slag. The flotation technique is being adopted for the concentration of desirable oxide mineral of the slag. The standard techniques for this purpose have attained a good measure of engineering proficiency but attempts are still on way to develop better methods.

1.2 Slags in Copper Extraction :

Our knowledge of slag⁽³⁾ and matte, until very recently, was derived almost wholly from a study of the solid products and a general observation of the behaviour of the molten charge in the furnace. The information thus gained has enabled the metallurgists and operators to obtain high melting rates and good recoveries at low cost.

The copper content in slag⁽⁴⁾ depends, to a great extent, on melting conditions which are directly dependent on the operational procedure. Converter slags containing higher copper content are, as a rule, those which are taken directly from the converter with a scoop. The slag samples taken from the overflow hole are of lower copper content. It may be assumed that in a large scale production plant where conditions for slag settling are better, the copper content in the slag would be even lower.

Equilibrium diagram of $\text{SiO}_2 - \text{FeO}$, $\text{SiO}_2 - \text{CaO}$ etc. has been established and has proved helpful even though it is now believed that the compounds which separate on cooling does not necessarily exist as such in the molten state. The classic work of Vogt in which numerous well known minerals were identified in slags has been summarized by Fulton⁽⁵⁾.

Schulmann⁽⁶⁾ has pointed out the importance of applying the laws of physical chemistry and thermodynamics to copper metallurgy and suggests a program of research to this, but only a start has been made. In order to present a complete picture regarding slags necessary scientific facts ~~now~~ are available by more recent theoretical considerations.

Since refinery slags and converter slags are ultimately returned to the reverberatory furnace, the only final loss of copper in slags is that which is carried by the discarded reverberatory slags. There are six possible forms in which the copper may exist in reverberatory slag, viz. as dissolved copper silicate, dissolved copper oxide, matte particles in suspension, dissolved sulphide, dissolved copper ferrite, and dissolved metal. The extent to which the compounds are dissociated in the molten slag is unknown and the available knowledge of the copper content is based entirely on a study of solidified slag. Published

discussions differ, but the most recent studies indicate that although all the above forms are possible, nearly all the copper in the solid slag is as sulphide or ferrite.

A more recent technique, though only on experimental basis, is the concentration of ground slag, its smelting and electrowinning of copper from matte thus obtained by electrolysis. The work performed and discussed in later chapters deals with concentration of ground slag by flotation and electrowinning of copper from matte electrodes by electrolysis.

1.3 Copper Matte in Smelting :

Solid copper matte consists essentially of Cu_2S and FeS , each of which under normal rates of cooling contains small amounts of other sulphides in the solid solution. The equilibrium diagram for this was established by Carpenter and Hayward.

In commercial mattes the copper and Iron sulphides are associated with small amounts of other sulphides and also with ferric oxide and dissolved slag. The ferric oxide, which may at times be considerable in amount, distributes itself according to some and yet undetermined law between the slag and matte. The latter being at the bottom of the furnace under a heavy layer of slag is usually at a relatively low temperature at which the reaction between the sulphide and ferric oxide does not take place.

At times, however, the temperature at the slag-matte interface is sufficiently high to promote the reaction, the violence of which is a direct function of temperature.

Although operating experience through the years has shown that the most desirable slag varies little from plant to plant, this is not true for matte grades, which are found to vary considerably.

1.4 Copper Industry in India and Probable Future Expansion:

Copper industry in India is still in its infancy. Our country faces an acute shortage of the metal with an annual production of only about 10,000 tons against an estimated requirement of 240,000 tons. This huge deficit is met by imports to the tune of 90,000 tons from countries like U.S.A., Canada, Rhodesia and Congo.

Intensive efforts^(7,8) are being made to raise the output to about 50,000 tons by the end of the fourth plan. To this end, Hindustan Copper Limited took over from the National Mineral Development Corporation the following projects :

(i) Khetri Copper Project in Rajasthan - a project in construction stage.

(ii) Bakha Copper Project in Bihar - a project in preliminary stage of development.

(iii) Dariba Copper Project in Rajasthan - a project in exploratory stage.

(v) Balaghat deposit in exploratory stage.

(1) Khotri Copper Project :

The Khotri copper project located in Jhunjhunu district of Rajasthan, is the main project of the company, which is at present in the construction stage. The project comprises two copper deposits, the Madhan Kudhan area (commonly known as Khotri mines) and Kolihan deposits about 7 kms. away, and a process plant comprising a concentrator for beneficiating the ore, a smelter to treat the concentrates and an electrolytic refinery for producing electrolytic grade copper.

In Khotri copper project, it was decided to (i) enlarge scope of the project to produce 31,000 tons of copper, the additional 10,000 tons of copper from the Kolihan, (ii) instal a flash smelter (instead of reverberatory smelting) which would enable recovery of sulphur values of the ore ; and (iii) H_2SO_4 produced from smelter gases to be utilized for the manufacture of a suitable fertilizer.

The Khotri deposits are estimated to contain about 70 million tons of copper ore of 1 percent average copper content. The Kolihan deposits are estimated to have copper ore reserves over 31 million tons of 1.4 percent copper content.

(ii) Bakha Copper project :

Bakha copper project is located in the Singhbhum

district in Bihar. It is estimated to contain about 98 million tons of average 1.01 percent copper ore upto a depth of about 600 meters. In the first phase of its development programme to yield 3,500 tons of copper metal per annum.

(iii) Asisundala lead - copper Project :

The mineral belt of this project located in Guntur district of Andhra Pradesh which is about 22 kms long, contains evidence of ancient work of copper and lead. The estimated results of reserves of copper and lead ore deposits are 18.3 million tons in this area.

(iv) Balachhat copper deposits in Madhya Pradesh :

A very promising ore belt has been discovered in this district whose special feature is said to be the high copper percentage (about 3 percent). In this way it has an edge over Khetri ores because of the low copper content in the latter.

The Indian copper corp. is at present the only firm engaged in smelting copper from the ore mined at their Mosabani mines. The copper produced at Ghatsila was only of fire refined quality till 1965. The existing capacity of 9800 tons is to be expanded to 16,500 tons per year in near future. I. C. C. is now producing at Ghatsila 8400 tons per year of electrolytic copper.

The supply of copper from indigenous production was 7000 tons in 1960. Therefore more than 60,000 tons of

copper was imported from ^Iabroad. In 1964, the import of copper and copper alloys was 65,000 tons and indigenous production was about 9500 tons against an estimated demand of 133,000 tons. The demand of copper for the current year is estimated to be 2,36,000 tons.

1.5 Copper Price Forecast Prediction :

The price⁽⁹⁾ of a widely used metal is ultimately related to the quality of the ore mined. The U.S. producer price for copper cathodes at constant U.S. dollars is inversely proportion to the quality of the ore mined.

A simple relationship⁽¹⁰⁾ permits one to generate the average U.S. producer price of copper in the next year based on knowledge of this year's average quality of ore in the U.S. and this year's GNP deflector.

The relationship is

$$\text{Cu price (Average next year)} = \frac{(\text{Constant}) \times \text{GNP Deflector (this year)}}{\text{ore quality (this year)}}$$

where

GNP Deflector - deflector is that factor which removes inflation from the dollar (1959 = 59 = 100).

Ore quality is as reported by American metal market (Lb copper per lb. of ore).

Copper price in 1950-59 was used to derive the constant, equal to 0.229.

Chapter 2

LITERATURE REVIEW:

2.1 Copper Minerals :

Copper minerals⁽¹¹⁾ are naturally occurring chemical compounds of crystalline structure, among which the native metal is also included.

Copper ores are natural mixtures of copper-bearing minerals and copper free minerals, in which copper is sufficiently abundant and occurs in such a manner that it can be mined and extracted at a profit.

In general⁽¹²⁾ copper ores rarely contain more than 1 or 2 percent copper. Deposits containing less than 0.5 percent copper are not worked at present.

Table (2.1) presents the copper ores most often as :

Table 2.1

Mineral	Chemical Formula	Copper content, percent
Chalcopyrite	$CuFeS_2$	34.6
Bornite	$5Cu_2S \cdot Fe_2S_3$	55.6
Chalcosite	Cu_2S	79.9
Covellite	CuS	68.5
Malachite	$CuCO_3 \cdot Cu(OH)_2$	57.4
Azurite	$2CuCO_3 \cdot Cu(OH)_2$	55.1
Opuntite	Cu_2O	80.0
Tenorite (melonchite)	CuO	79.9

The ores are classified in three groups :
sulphide, oxide and native copper.

The sulphide ores may occur either as massive bodies mainly consisting of copper and Iron sulphides or in small particles of the same disseminated through monzonite igneous rock called "porphyry". The massive ore bodies contain more sulphur and copper. The oxidised ores are mainly of the disseminated type, and the greater part of iron in them is present in the form of oxides, carbonates and silicates.

2.2 Copper Slags :

The slags of copper smelting are similar in composition and properties to the slags of other non-ferrous metals. In all cases they are high in ferrous oxide, in which respect they differ from blast furnace slags which are relatively low in ferrous oxide. This is because before the metal can be extracted from its ore, the iron has to be separated and withdrawn into the slag.

Usually, the copper - smelting slag either goes as a waste or is utilized as a by-product. Yet, it greatly affects the economy of copper smelting, for it carries off valuable metals and also some fuel is consumed in keeping the slag in molten state. The losses increase with increasing metal content of the slag and the quantity of slag produced per unit weight of metal or matte.

The slag yield varies with the charge composition and the quantity of flux added, while the metal content of slag depends on the properties of the slag and the conditions under which a given heat is run.

The metal losses with the slag are customarily classed into three groups :-

(i) Chemical losses due to the fact that the principal reaction of a given melting process fails to proceed to completion, and the oxide of the metal remains partly dissolved in the slag. In the case of copper, it is mainly lost as Cu_2O not completely sulphurised by the iron sulphide. Experience and the calculations show that these losses are negligible.

(ii) Physical losses due to the dissolution of the metal or matte in the slag and the formation of colloidal solutions. The solubility of copper sulphide in slags varies with temperature, the maximum being 0.2 to 0.3 percent.

(iii) Mechanical losses due to the incomplete separation of molten metal or matte from molten slag because of the insignificant difference in their specific gravities, short dwell or the high viscosity of the slag. Usually, this type of loss accounts for the better part of total loss, including that of copper melting.

The slags of copper melting are closest in composition to the slags of nickel, lead and tin melting and carry a total of upto 90 percent of SiO_2 , FeO

and CaO. They also carry upto 15 percent of Al_2O_3 and sometimes as much as 25 percent Fe_3O_4 (Converter slag), as well as oxides of magnesium, barium, sodium and some other metals.

The melting point of a slag is related to its viscosity and composition. As a rule, some increase in the content of FeO, MnO, CaO and BaO reduces the viscosity of slags, while SiO_2 , Al_2O_3 and Fe_3O_4 act often to the opposite. In some cases, materials nearly insoluble in a slag raise its viscosity by forming solid particles suspended in the molten material.

The way in which the main components of reverberatory furnace discard slags are derived directly affects copper losses to the slage. Reverberatory furnace discard slage are mainly derived from two sources - directly from reverberatory furnace operations and indirectly from converter operations. Most work that has been carried out on copper smelting slage has been directed to the study of various factors affecting discard slage as regards copper losses, but these studies have the important disadvantages that they are essentially retrospective.

It is reasoned, and substantiated by experimental work, that the slag formed directly from the solid charge do not contribute significantly to non-sulphide copper losses in slage. It is also reasoned and substantiated

that good slags with low sulphide copper losses can be formed directly if the flux requirements to give the lowest melting point slags with concentrate gangue are calculated in advance.

2.1 Reverberatory furnace slag composition :

Reverberatory furnace slags are complex combination of silicon, calcium, magnesium and aluminium oxides, with ferrous and other iron oxides. Chromic acid becomes frequently a significant component if basic refractories are used. In most cases the major constituents can be regarded as FeO , SiO_2 , CaO , and Al_2O_3 although there are smelters where other metal oxides are also significant.

The slags reflect⁽¹³⁾, in general, the sulphide mineralisation of the concentrate. The more pyritic the concentrate treated, the higher is the iron content in the matte and, consequently, the higher the FeO in the discard slag, conversely, the less pyritic the concentrate, the higher the CaO content of the slag, to make up the deficiency of iron. The slag analysis of GASPE[®] is of interest; this results from the treatment of chalcopyrite concentrate with a silicified limestone gangue which, it has been reported⁽¹⁴⁾, has a low melting point and gives an enviably low copper content in the final slag.

Al_2O_3 is least desirable of the commonly encountered components because of its effect on slag viscosities.

MgO , because of its refractoriness, has long been considered an undesirable component in slags.

The slags with the lowest melting points are generally those with higher FeO content. FeO in the region of common operation decreases the slag melting point, but increases slag density. Excessive CaO increases the slag melting point, but in the area of accepted slag composition it reduces viscosity and density. SiO_2 has the general effect, within normal limits, of raising the melting point and increasing viscosity without increasing slag density.

Much valuable work has been done by Schairer⁽¹⁵⁾ on the $FeO - SiO_2 - CaO - Al_2O_3$ system, but compilation of data for complete coverage of all reverberatory slags, to be of full value should also include MgO , which however would make the study of the overall system extremely complex.

2.2 Copper Content of Reverberatory Furnace Slags :

Ruddlo⁽¹³⁾, Evans⁽¹⁶⁾, Vanyukov et al and others have reviewed the literature on the content of copper in slags. There is difference of opinion on the nature of all the copper present in slags, but there is agreement on the point that some of the copper is present as

sulphide inclusions. They have confirmed the acceptance of the presence of an inseparable copper compound or compounds in reverberatory furnace slags, but there is lack of agreement on the form or forms in which this copper is present. Opinions vary as to whether it is dissolved oxide or sulphide, silicate or ferrite, although Ruddle and Co-workers⁽¹⁷⁾ quoted indications that much of the copper is cuprous oxide in true solution, and that such losses are mainly a function of the oxygen potential of the slag as reflected by its FeO content. Copper losses in reverberatory furnace slags can be attributed to two evident causes - mechanically entrapped sulphide and an inseparable indeterminate non - sulphide phase.

Reverberatory furnace discard slags comprise of variable quantities of mechanically entrapped sulphide copper. Although converter slags carry entrapped matte, and thus contribute to final copper losses, their properties, particularly for constant matte production, suggest that their contribution to sulphide copper losses is likely to be a constant factor. Furthermore, since sulphide copper can be separated from converter slags by settling in the molten state (or by flotation after solidification and grinding), it is reasonable to say that these slags should not be major contributors to final slag sulphide copper losses so long as there is

sufficient residence time in the reverberatory furnace for the sulphides to settle from the denser converter slag. Conversely, non-sulphide copper lost in the discard slag, which appears to be a consistent loss factor, is logically derived from converter operation.

The mineralization of the concentrates is reflected in the proportion of sulphide and non sulphide copper losses. Mineralization giving rise to high grade matte, is associated with more sulphide than non sulphide copper loss in slag, because the copper content of the physically entrapped matte droplets in the slag is high; also, the dissolved non sulphide soluble copper derived from the converters tends to be relatively low, because of the low Iron content of the matte.

2.3 Factors Affecting Copper Losses in Slags :

One feature common to all of the slags is that they are fluid at temperatures low enough to lead to efficient operation. Viscosity, density, volume, interfacial tension, melting point, oxygen potentials as reflected mainly by the FeO content and furnace operating temperatures all affect the copper content of slag. The effect of slag formation temperature, melting point and viscosity can be made less significant by operation at higher temperatures in the furnace although at the expense of fuel efficiencies and costs.

Higgins and Jones⁽¹⁸⁾ evaluated the factors that affect the viscosity of Zambian copper belt slags and assessed quantitatively the influence of the acknowledged major slag components. They developed a "Modified Viscosity ratio" for slags which, at constant temperature, could be related to absolute viscosity (in poise). The formula for modified viscosity ratio (VR) is as

$$VR = \frac{(0.90 \times \% Al^{2O_3}) + (2.83 \times \% Si^{2O_2})}{(0.98 \times \% Fe^{2O_3}) + (0.83 \times \% Mn^{2O_3}) + 0.7 \times (\% Ca^{2O}) + (0.95 \times \% Mg^{2O})}$$

In most slags manganese oxides are generally absent or are present in only small amounts, so the VR will depend largely on the amounts of Alumina or silicon, calcium, magnesium and ferrous oxides in the slag.

In the work by Higgins and Jones, no attempt was made to correlate viscosity ratio or absolute viscosity to actual slag copper loss.

Jones⁽¹⁹⁾ referred to a limiting value for the physical elimination of copper, and this is probably due to the limitations in eliminating non sulphide copper.

2.4 Converter Slag composition and its Effect on Reverberatory Furnace Slag :

Converter slags result from the oxidation of the Iron sulphide of the copper - iron matte and the combination of the resulting oxidized iron with siliceous

flux. The resultant slags are therefore essentially combinations of FeO and SiO₂. Inevitably, there will be other iron oxides present, especially a variable amount of magnetite, the extent of which, above an unavoidable minimum, will depend on the efficiency of the converter operation. Converter slag is usually returned in molten condition to the reverberatory furnace to join slags obtained by direct smelting. In wet charged reverberatory furnace operation converter slags are the main source of iron oxides and oxygen potential in the final discard slags.

2.3 Copper Matte in Smelting :

Copper matte⁽²⁰⁾ has long been regarded as a mixture of simple sulphides Cu₂S and FeS because they are the only ones stable at the high temperatures employed. In the course of time, a noticeable deviation from the composition called for on the basis of this assumption was noted, there being insufficient sulphur to form these two compounds. Investigation of the magnetic properties led to the conclusion that a substantial amount of metallic iron was present. Microscopic examination did not confirm this but indicated rather that considerable magnetite and copper ferrite were present.

Recent investigations of a matte of the following composition seem to bear out the following generalization regarding the composition of this typical copper matte (Table 2.2).

	Percent
Cu	23.27
Fe	41.83
Zn	2.62
S	25.46
O	4.86
SiO ₂	0.68
CaO	0.51

1. The only stable compound formed between cuprous sulphide and ferrous sulphide is $(Cu_2S)_2 FeS$ (this is soluble in Potassium Cyanide).

2. All copper mattes contain this compound. If the copper content is below 62.7 percent, the matte contains an excess of ferrous sulphide and ferrite or magnetite. Matte containing more than this critical amount of copper has an excess of Cuprous Sulphide.

3. Cooling of matte, depending upon the rate at which it proceeds, causes the precipitation of metallic copper and the formation of higher sulphides, among which is $CuFeS_2$.

4. Mattes may contain upto 10 percent of magnetite. It has not been proved whether this is in dissolved form.

or suspended form, but the latter seems more logical in view of the fact that the average matte is close to the specific gravity of magnetite.

5. Many mattes also contain notable amounts of other metals. Zinc or Nickel, when present in the charge, enters the matte as the sulphide, and lead sulphide is also frequently found.

6. These mattes are excellent solvents for gold, silver and metals of the platinum group. As a matter of fact, so nearly perfect is this action that the only precious metals to escape will be in the undecomposed ore which does not come in contact with the molten matte or in drops of matte which do not liquefy but remain suspended in the slag.

7. All other elements are usually classed as impurities and, although the amounts may be small, they may give considerable trouble in the subsequent refining process. The common ones referred to are arsenic, antimony, nickel etc.

Grade of Copper Matte :

At first glance, it would seem desirable, since matte smelting is a process of concentration, to make matte as high a grade as possible. There are, however, five reasons why matte of the highest grade is not always desirable.

1. The production of a high grade matte in a furnace is always accompanied by a slag of usually high copper content. Slagging out more of the iron will produce more slag; hence more copper will be lost not only because of the greater volume of slag but also because there is less time for lixiviation in the furnace. Furthermore, some of the copper may be oxidized in roasting of ore of low sulphur content. This copper oxide will combine with silica to form a silicate which will be dissolved by the slag.

2. The high grade matte will also necessitate a longer and more expensive roasting operation which will reduce the capacity of the roasting plant and produce more flue dust.

3. The high grade matte occupies less volume than the low grade one and will not be so effective as a collector of gold, silver and other precious metals.

4. It is found that the conversion of high grade matte is much more difficult.

5. Finally, provision must be made to take care of the large amount of hot gases evolved at the top of the furnace.

By reason of the conditions outlined about, copper mattes usually contain 40 to 50 percent copper; a 45 percent copper matte usually gives the most satisfactory results.

The mattes containing more than 70 percent copper are approximately cuprous sulphide in composition, and almost white in color hence the term white metal is generally used. These high grade mattes are also likely to contain stringers of metallic or "nose" copper. They will range in specific gravity from 4.8 to 5.6 as the copper content increases. The percentage of copper in the matte is commonly known as its grade and the amount expressed as a percentage of the total charge as the "mattofall". Analysis of typical copper mattes are given in Table 2.3.

Table 2.3

Analysis of Copper Mattes

	Percent								Ounces per ton		
	Cu	S	Fe	Fe ₃ O ₄	Zn	Pb	Bi	Sb	Ag	Ag	Au
Direct furnace											
I	11.20	25.45	61.65	"	"	0.005	0.001	"	0.02	0.05	0.05
II	54.00	23.36	20.25	"	0.34	0.12	0.004	0.023	0.017	6.0	0.10
Reverberatory furnace	60.76	23.25	11.63	1.13	2.41	0.59	0.042	0.045	0.0	60.4	0.30

2.4 Beneficiation of Copper Slags :

For metallurgical treatments of slags, smaller pieces, sometimes very finely divided (less than 0.1 mm across), are required. For this reason, slags are comminuted, i.e., reduced in size, in breakers, crushers and mills. In this breaking, crushing and grinding equipment will operate efficiently only in the specified range of lump sizes.

Like copper ores, there are two methods for treating copper slags :

- (1) Concentration followed by smelting of concentrates for low grade slags.
- (2) Leaching followed by electrolytic precipitation or precipitation by iron.

The slags can be treated by flotation without much difficulty.

4.1 Crushing and Grinding (21,22) :

Comminution is normally the first step in beneficiation of solid slag. It is usually a single stage process, utilizing in successive steps. The stage starting with crude as mined and comprising of successive reduction steps down to first stage for production of fine particle size is called crushing. The coarsest particle of the crushed product being 1/20 inch or more in size.

Two general type of machines are used for crushing, viz.

1. Reciprocating breakers (Jaw, gyratory, Cono and gyracphoro crushers).

2. Continuous breakers (rolls, single roll crushers).

Primary grinding () may be in one, two or three stage. However, trend is towards one stage grinding circuit. In general, closed circuit multistage grinding is used for harder ores.

4.2 Sizing :

Since the effectiveness of practically all dressing operations is a function of the size of the particles treated, thorough knowledge of the size characteristics of the material handled through adequate sizing technique assumes a place of greatest importance.

There are several methods for sizing mineral particles, the most important of which is screening.

The fundamental function of screening is to pass the undersize particles through the opening and reject the oversize particles. There are two types of screen used; fixed screens (Stationary) and moving screens (Shaking, vibrating type).

4.3 Flotation (21, 22, 23)

Flotation is a process of concentration based on the preferential adhesion to air of some particles from a pulp

and the simultaneous adhesion of other particles to water. It includes the use of enough organic liquid (Oil) to produce a distinct oil phase, in which selective adhesion of some minerals to oil is involved in addition to selective adhesion to air.

The essential known facts are summarized as follows :

(i) Most minerals suitably protected from contamination adhere to water, not to air.

(ii) Paraffin and other hydrocarbons adhere to air in preference to water.

(iii) Some mineral substances adhere to air.

(iv) Minerals (i. e. sulphides) can be made to adhere to air by adding a suitable agent to the pulp.

(v) Most and perhaps all minerals can be made air adherent or water adherent by the use of, or combination of, proper agents.

(vi) Changes in the character of the surfaces of minerals because of oxidation or other processes affect considerably the facility with which they can be made air adherent.

In 1860, William Haynes patented a process for separating oil wetted sulphide minerals from water - wetted gangue minerals by agitation of the dry ground ore with oil and then the mixture with water.

In 1885, H. Bradford patented a method for separating sulphides from gangues by a skin flotation process without the use of oils.

The oil flotation process with its subsequent improvement has meant more to copper industry so far as increased recoveries and reduced costs are concerned. In general, recoveries in concentration have been increased from 65 percent to 90 percent and over, and this in itself has allowed the treatment of very low grade. Ores at a profit than could possibly have been accomplished with the recoveries made by old gravity method of separation.

Direct flotation of slag particles with Xanthates and other organic collectors :

As the slag particles, mainly contain copper in oxide form and in some cases as sulphides, can be directly treated by flotation with Xanthates and other organic collectors. This is due to the fact that there is formation of highly insoluble copper salts by the use of ionizable reagents which possess a substantial non polar portion in their structure. The separation is made more effective through critical adjustment of collectors, PH of solution, and use of modifiers.

Collectors :

Of the flotation agents the most important are the collectors, which are added to cause an adherence.

The general requirement is of non polar surfaces i.e., surfaces in which the atoms are covalently linked and make it water repellent. The only practical way of securing such a surface is by means of organic compounds.

Characteristics of Collectors :

Natural flotability is generally available only in solids in which outer surfaces have non ionic or non - polar character. The boundary must be discontinuous so that there is no transition layer between naturally flatable substances and water. The collector molecule must not be locally reactive but sufficiently active to take the selective mineral away from the water. The localised high activity should also be sufficiently selective with regard to mineral surfaces.

Collectors used in Practice :

(i) Ethyl, Propyl, Butyl and Amyl Xanthates. Particularly the Ethyl and Amyl Xanthates of sodium or potassium.

(ii) Diethyl and Diocetyl Dithiophosphates.

(iii) Oleic and Palmitic acids and their sodium soaps.

Mechanism of Collection :

The mechanism of mineral collection has been the subject of considerable speculation. Present day views are given in the form of two hypotheses, viz. the chemical reaction hypothesis and the adsorption hypothesis.

(1) The "Chemical reaction Hypothesis" stated by Taggart, Taylor, and Knoll : "All dissolved reagents which, in flotation pulps, either by action on the to-be-floated or on the non to-be-floated particles affect their flotability, function by reason of Chemical reactions of well recognized types between the reagent and the particle affected".

(2) The "adsorption hypothesis" as forwarded by work may be stated as "All ions dissolved in the flotation pulp layer adsorb at mineral surfaces. At each mineral surface, the adsorption of each dissolved ion is specific. This specific ion adsorption is also a function of the concentration of the dissolved ion under consideration and that of other dissolved ions. If and when a sufficient proportion of the mineral surface is covered by the effective collector ions, the particles become floatable".

Utilization of Collector Ions :

Collector ions are utilized in three ways :

1. To provide the adsorbed ions or the reacted ions, as the case may be.
2. To eliminate precipitating ions present in the liquor.

3. To provide adequate concentration in the liquor.

Increasing the quantity of collector results in an increase in recovery upto a maximum value. Increasing the quantity of collector is particularly effective in increasing the recovery of very coarse particles.

Increasing the quantity of collector to exorbitant levels may result in decreased flotation. The possible causes for this effect are related to the formation of complex ions, or to the adsorption of an additional layer of collector ions oriented with the polar group towards the water.

The process by which collection is increased is generally termed as activation, and that by which it is decreased is termed as Depression.

Effect of pH on Flotation :

Control of pH is important in two ways :- Firstly the concentration of soluble salts can be reduced to the point where the tendency for surfaces to become alike is kept within bounds. Secondly, a double salt that consumes the collector may be "locked up" as a precipitate, in this form it consumes less collector.

Froths and Frothing agents :

Froth flotation is conducted in three main steps :

1. Selective Chemical modification of the surface of specific mineral particles to affect flotability or non flotability.

2. Contact between air bubbles and mineral particles and rejection of nonfloatable minerals.

3. Separation of floatable minerals from non floatable minerals.

The requirements of a suitable froth in flotation are that it should have buoyancy to bear the mineral particles to the surface of the pulp. It must be stable enough to exist until bubbles with their main loads can pass over the lip of the flotation machine and it should not be so stiff that it will be difficult to break it up after removing from the cell. Finally it should be fluid enough to flow over the lip of the cell without clogging it.

2.5 Recent Developments in Copper Extraction :

The sustained demand for copper together with increase in price, has had the natural effect of spurring interest in uncovering new deposits and reexamination of known low grade deposits, old tailings, constant improvements in efficiency of ore concentration.

In batch wise process there is a temperature fluctuation in the various furnaces. In continuous process this variation is decreased and this will lead to saving cost refractory. Attempts have been made to develop better methods and present trends are broadly based as follows :

1. Development and application of autogenous melting process.

2. Switching over to smaller units with high smelting and production capacities.
3. Application of continuous process.

(1) Development In Smelting :

(A) Flash Smelting :

One of the most interesting developments in recent years is the autogenous smelting⁽²⁴⁾ of copper sulphide concentrates. The process has now been in operation for some years at the Harjavatta smelter of the Outokumpo Co. the largest copper producers in Finland and also at the copper smelter of International Nickel Co. of Calcutta.

The process consists of introduction via a burner of dry concentrate and flux to a furnace smelting chamber, preheated air or oxygen required for combustion being injected along with the concentrates. The mixture flashes as it enters the furnace. The iron and sulphur burning to oxides ($2FeS + 3O_2 = 2FeO + 2SO_2$) as combustion is supported by the oxygen. Matte and slag collected on the furnace hearth and are tapped off and treated in the conventional manner. Grade of matte is controlled by regulating the amount of air or oxygen supplied for combustion.

Although the process eliminates the need for external fuel it is essential that the air required

for combustion is preheated (500°C) to maintain heat balance. Slag contains about 0.3 to 1 percent of copper.

Disadvantages :

1. Large amount of slag^{is} formed so more loss of copper in slag.
2. More magnetite formation which causes working difficulties in a converting process.

Advantages :

1. Fuel economy
2. Easier control
3. High grade matte production
4. Low capital cost of plant
5. Recovery of S as H_2SO_4

(B) Electric Smelting (24)

Where the cost of power is low electric smelting has many advantages. The furnace employed is of the resistance type either circular in shape or of the ordinary reverberatory outline. Electricity introduced to the charge is with the electrodes of the sodorberg pattern made of carbon upto 50 inches in diameter placed either in a line or in the form of a triangle according to the shape of the furnace. As the electrodes are consumed, they are lowered into the molten bath. Power consumption ranges from 370 to 530 k wh/ton of charge fed to the furnace or 4,500 to 5,500 k wh/ton of Cu_2S . Capacity of furnace is 500 tons/day.

Advantages :

1. Low power consumption
2. High thermal efficiency
3. Steady operation
4. Long life of reverberatory roof and lining.
5. Small volume of gases rich in SO_2 gas.

(ii) Direct production of copper from sulphide copper concentrates :

In order to overcome the disadvantages of the conventional method of converter copper, production consisting of agglomeration, concentration, roasting, melting and converting, Schmidt et al developed direct production of converter copper from sulphide concentrates by continuous treatment in smelting furnace. In this process copper bearing material is charged into the smelting furnace where it is melted to produce slag and matte. The matte is oxidized by oxygen enriched air which is blown from the top and introduced by means of blowers to produce converter copper and slag. The oxygen content in the blast is dictated by the thermal balance of the equipment or by the requirements for SO_2 concentration in combustion products. The equipment is preheated before starting operation. The pressure of the blast ranges from 4 to 6 atmospheres. The O_2 in the blast is 42 percent, production capacity of the set up 6 tons of copper concentrate / 24 hours. Slag contains about 0.2 percent Cu higher than in the slag of conventional process.

Disadvantages:

Great amount of flue dust loss from charge.

Advantages:

1. Avoids three steps in conventional process.
2. Low capital cost.
3. Small plant gives a large out put.
4. Possibility of automation.

(iii) Continuous production of Copper from concentrates:

Continuous conversion of copper matte^(25,26).

In pilot plant study copper matte was produced in melting furnace which was connected to continuous converter through a connecting channel. Molten matte was supplied through an opening in the rear wall of the converter. Air was blown into the melt under a pressure of 6 atmospheres through blowers. The following facts act a major role in this process.

1. Blowing the matte in conversion stage results in Iron oxide together with the quartz present from slag and copper is produced in the last.

2. Converter slag, white matte and converter copper form a system of three liquid phase which are mutually miscible only to a limited extent.

Converter slag (1200°C)	Sp. wt.	3.2 to 3.629/cc
White matte (60% Cu)	Sp. wt.	5.2 9/cc
Copper	Sp. wt.	7.59 9/cc

3. During conversion stage, converter copper is formed only when the matte consists mostly of Cu_2S .

Advantages :

1. The process is continuous so shut down times are eliminated, heat losses minimized and thermal shocks practically eliminated.

2. Refractory life is more because the zone of highest temperature in the equipment is in the centre of the melt.

3. Feeding of material into the pot can be done continuously.

4. Slag formed have comparatively low copper content.

5. Dust losses are less and waste gas is high in SO_2 content which can be used for H_2SO_4 manufacture.

(iv) Smelting Directly in Copper Converter :

Pilot plant studies⁽²⁷⁾ have been done for smelting copper concentrates directly in a Polanco - catch converter. The converter melting cycle was started with approximately 10 tons of molten state matte about 40 to 50 percent Cu which was obtained from blast furnace, reverberatory furnace or electric melting furnace. The concentrate and flux are charged through a retractable chute, rather than feeding large quantities of flux separately at widely spaced intervals. Oxygen

enriched blast was blown at 4 to 5 Kg. per Sq cm at a airblow of 70 cubic m per minute and oxygen flow of 20 cubic m per minute. The O_2 concentration in the enriched blast was 33.5 percent.

Two steps in converting :

1. Matte enrichment process (or smelting)

The grade of matte gradually decreases during the charging of copper concentrates into the converter, but the grade again increases during the subsequent charging of silica flux.

2. Blowing of Matte :

Further smelting of concentrates is no longer possible as white matte stage has been reached. The white matte charge is blown to blister copper.

Advantages :

1. Simple flow-sheet for treating copper concentrate.
2. Fuel and flux economy.
3. Production of Blister copper from concentrate in one simple step.
4. Economic recovery of "S" as H_2SO_4 from high grade CO_2 gas.
5. Low capital cost.

(v) Direct Production of Copper by HDSO Process (20) ;

Incentive to develop continuous processes :

- (a) The steeply rising cost of the larger batch

- (b) The high cost of large cranes, railway systems, ladles, ladle repair shops etc. necessary for batch handling of liquid products.
- (c) The desire to economize in size requirements, foundations and buildings.
- (d) The necessity to reduce heat losses and to utilize maximum economy in fuel and electric power consumption.
- (e) The more sophisticated and reliable instrumentation and generally simpler control in continuous processes.
- (f) The greater amenability to automation and consequent reduction in man power requirement.

In Corcora process all the steps are performed in a single furnace. This process has now gone through the pilot plant stage in which furnaces have been operated continuously for upto six weeks in nine campaigns. Plans are now completed for entry into semi-commercial evaluation phase. As shown in Fig. 2.1, the furnace is divided into three zones.

1. A melting zone with functions similar to reverberatory or blast furnace.

2. A converting zone with functions similar to conventional converter but operating continuously and with a horizontal as well as vertical composition gradient maintained.

3. A slag - matte separation zone.

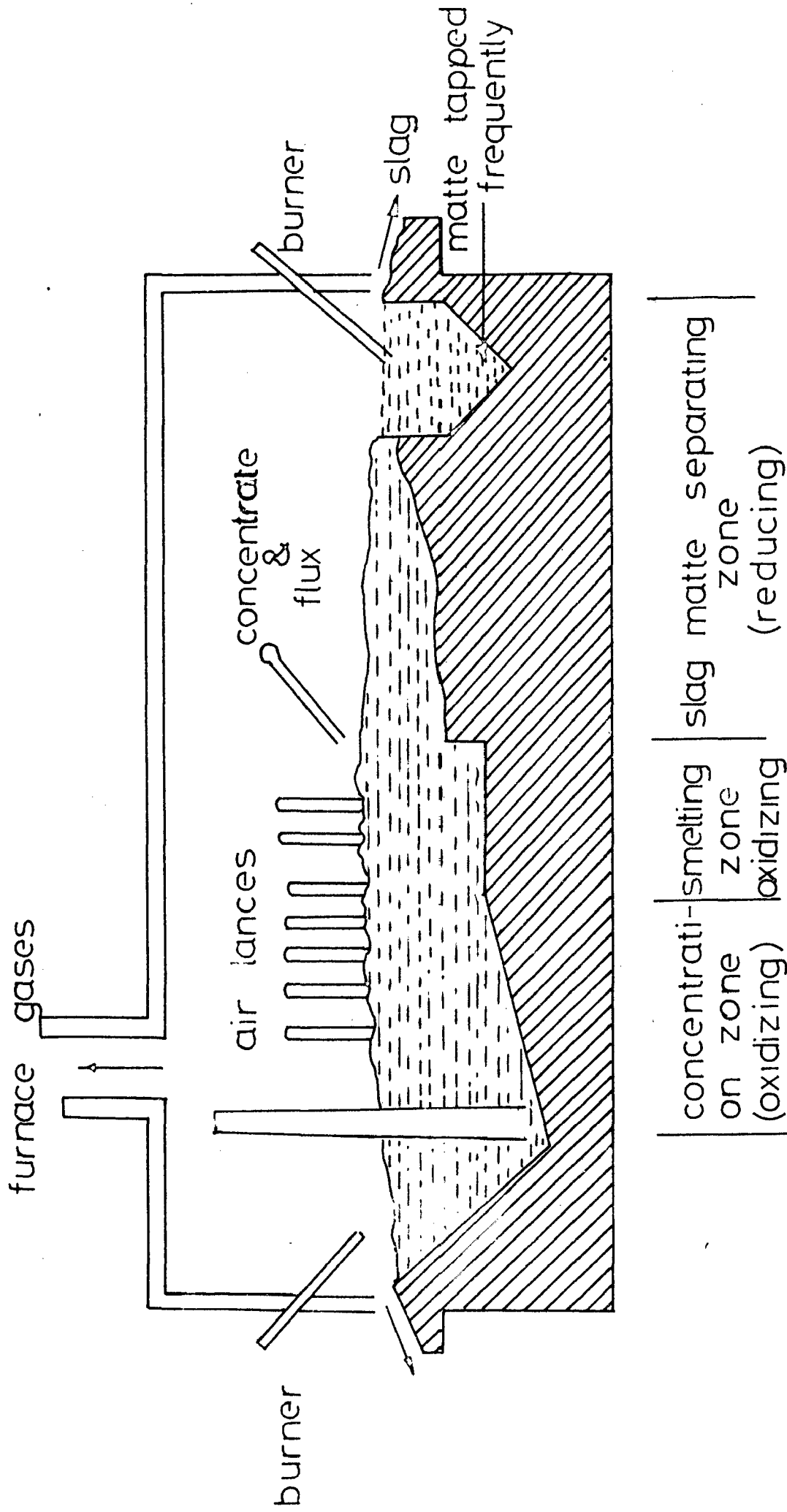


FIG.2.1 VERTICAL SECTION OF WORCRA SMELTING CONVERTER

In addition there is an auxiliary chamber at the end of the converting branch and into which metallic copper with about 1 percent sulphur flows through a better passage from the copper roll. If desired, further refining with respect to sulphur and some other elements can be effected in this chamber before the metal flows on to be cast into anodes and other shapes.

In the pilot plant trials copper in slag values below 0.4 percent have been achieved and it is confidently expected that with larger furnace and greater experience with reducing treatment more attractive figures for copper losses will be achieved.

Advantages :

1. Reduction in site requirements, foundation and buildings for the smelter.
2. The elimination of the necessity for roasting or sintering ahead of melting.
3. The elimination of handling of slags.
4. Reduction in fuel consumption.
5. Reduction in man power requirements as a result of lesser operations.
6. Increased use of automation.
7. A slight lowering of copper losses in slags and dust.
8. Less capital cost and possibility of computer control.

(v2) Mathematical Model for a Copper Converter Control (29) :

Aim of mathematical model is to :

- (1) yield a dynamic record of reaction ratio
- (ii) have a knowledge of converter contents
- (iii) predict end points

Individual converter operations are controlled by

- (1) quality and quantity of input materials
 - (2) air flow rates
 - (3) depth of blowing
 - (4) bath temperature
 - (5) flux addition rates
 - (6) skimming quality
- and (7) crane service.

These variables are interrelated as bath temperature is related to the oxidation reaction rates which are related to airflow rates, depth of blowing etc.

The steps involved in Mathematical Modelling are as follows :

- (A) Review of fundamental operations.
 - (B) Analysis of required information.
 - (C) Development of process measurement inputs.
 - (D) Development of mathematical equations.
 - (E) Model construction.
 - (F) Computer programme model
- and (G) Computer simulation of actual operations.

It is necessary to have continuous measurements of various variables in the converter so as to develop a scheduling information and automatic controls over flux addition rates, depth of blowing and air flow rates. Thermodynamic approach was found to be more suitable in developing the mathematical model.

(A) Review of fundamental operations :

First step was to consider the fundamental relations involved in the converter i.e. slag phase reactions, finish phase reactions, oxidation reaction of FeS before Cu_2S oxidation and gross material balance.

(B) Analysis of required information :

Analysis was made as follows to get information required of all the parameters throughout a charge cycle.

- (a) Quality and analysis of each material input to a converter.
- (b) A continuous measurement of converting rates based on gas and temperature balance.
- (c) Quality and analysis of each material output from a converter.
- (d) Operating temperature.

(C) Development of process measurement inputs :

Crane weighing devices were used for material inputs and outputs and flow meter for airflow rates. Material analysis was done with X-ray techniques or chemical methods.

Bath temperature and stack gas temperature were measured with the help of radiation pyrometer or thermocouple.

(D) Development of mathematical Equations :

The input data was converted into usable form by putting it in form of equations.

(E) Model construction :

The equations are arranged in sequence corresponding to operations that occur in a charge cycle. Process control information was calculated for each 10 minutes throughout a charge cycle.

(F) Computer programme model :

The computer programme was prepared and written in Fortran language to process punch cards input data, i.e., for offline computer applications.

(G) Computer simulation of actual operations :

All necessary instruments and measurement devices are installed on the converter. Computer process data is collected for 10 converter charge cycles. Coded information was placed on punch cards. Computer programme of the model was stored in computer memory and charge cycle decks were prepared. Necessary model revisions were made and tested by reprocessing the 10 batches of input data.

It is seen the revised mathematical model represents the actual converter operations.

2.5.1 Direct Electrorefining of Cuprous Sulphide and Copper matte :

A number of investigations⁽³⁰⁾ have been undertaken with regard to the metal sulphide electrodes in aqueous solution. Krabatz, in collaboration with Hoddack and Horbet, carried out an investigation of metal sulphide electrodes in aqueous solution. According to these workers, the electrochemical behaviour of heavy metal sulphide electrodes in aqueous solution is influenced by the non-stoichiometric excess sulphur in these materials.

Lozhkarov and Vogisov found that with increasing temperature the voltage of cell decreased and the yield increased in the anodic dissolution of Cu_2S in $CuSO_4$ electrolyte. According to Chizhakov and coworkers, experiments in the anodic solubility of sulphide alloys and mattes have confirmed the possibility of dissolving and separating the valuable components.

Wear and Ward⁽³¹⁾ used molten Cu_2S both as cathode and anode in a cell having molten $BaCl_2$ as the electrolyte, and produced pure copper at the cathode and pure sulphur at the anode, current efficiencies being over 90 percent. The use of copper matte as a cathode, however, was found to result in a regulus of 80 percent Fe and 20 percent Cu.

Recently interest has been shown in the application of Ultrasonic in electroplating from a electrolytic bath.

The method involves mounting an ultrasonic vibrator in the tank of an electrolytic bath to irradiate the electrodes - thereby increasing the rate of metal deposition and improving the coating properties (hardness, flexibility and density). Muller and Huss found that copper had a fine grain structure and greater tensile strength when deposited on a vibrating cathode from a sulphate solution; and Holl⁽³²⁾ reported increases in current efficiency and a decrease in deposition potential when Ni was deposited in an ultrasonic field. The effects of ultrasonic vibrations with various frequencies in the electrodeposition of Cu and Zn from cyanide and sulphate electrolytes have been studied by Koshen and Schlaun; and the anodic dissolution of Cu in an ultrasonic field has also been studied by Kochergin and coworkers.

Cell arrangements for direct electrorefining :

Venkatachalam and Mallikarjuna⁽³¹⁾ have done studies on this line with ultrasonic irradiation using both cylindrical and rectangular anodes. Experiments with copper matte as anode were carried out on a large scale. The ultrasonic power supply (Dawa Instruments Ltd.) with an output of 500 W and a frequency of 40 kc/sec was used (shown in Fig. 2.3).

Venkatachalam and Mallikarjuna found that the efficiency of the dissolution of the metal was greatest at the lowest current density. The voltage of the bath

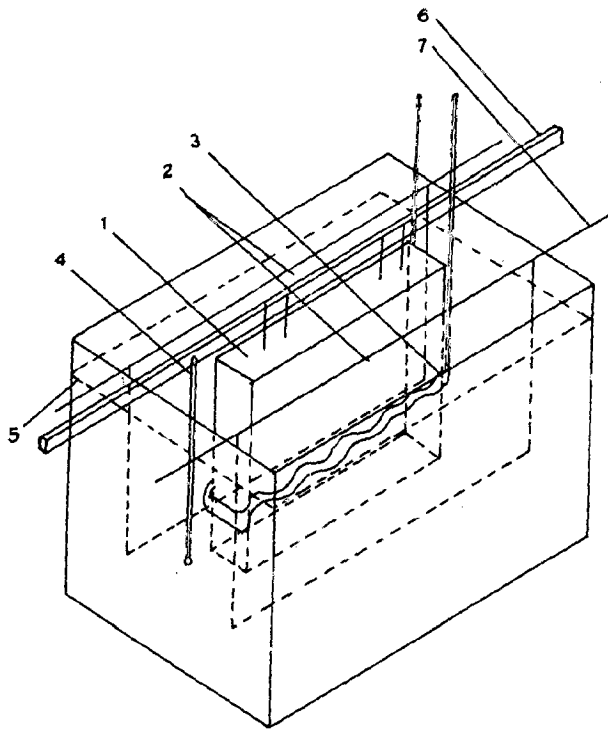


Fig 22 schematic diagram of electrolysis cell. 1 copper matte anode: 2 copper cathodes: 4 thermometer: 5 electrolyte level: 6 support for anode: 7 cathode support.

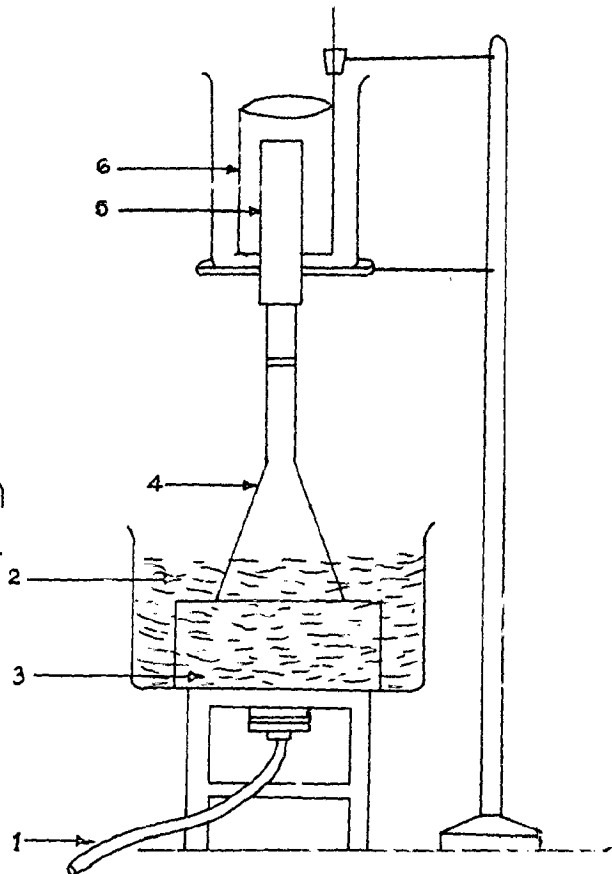


Fig 23 schematic diagram of ultrasonic system
 1 cable to ultrasonic generator: 2 water bath:
 3 ultrasonic transducer
 4 stainless steel cone:
 5 Cu_2S anode: 6 copper cathode.

also increased with the progress of electrolysis. They also found that the H_2SO_4 concentration did not affect the cathodic current efficiency but the cathodic current efficiency increased with the concentration of copper in electrolytic bath and attained approximately constant values thereafter. The set up used by them is as shown in Fig. 2.2.

Electrochemistry of the process :

As reported by Chikhilov and Co-workers Cu_2S is an electronic conductor in both the solid and molten state.

$Cu(II)$ sulphide is a semiconductor showing an exceptionally high electronic conductivity as compared to Cu metal.

$Cu(II)$ sulphide⁽³³⁾ is converted to $Cu(I)$ sulphide at elevated temperatures in the presence of air, and at lower temperature in a H_2 atmosphere.

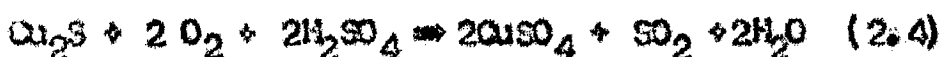
↑
Ionization of copper is the first step in the process of anodic dissolution.



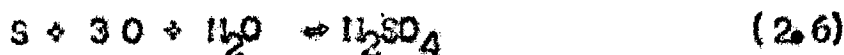
For a short time, it will be 100 percent anodic efficiency for the dissolution at the lowest current density. As the film of CuS formed, the anode potential rises with the discharge of OH^- ions leading to oxygen evolution.



Copper dissolution takes place by the chemical oxidation of CuS and Cu₂S by the oxygen evolved as



The sulphur at the anode can be oxidized by the oxygen as



Hence the amount of sludge is maximum at the lowest current density which is associated with the least oxidation.

The FeS of the anode can dissolve both chemically and electrochemically as



The S²⁻ ions can interact with Cu²⁺ ions in solution as well as oxidized at the anode as



The Fe²⁺ ion can be oxidized to the Fe³⁺ ion by the equation given below



Electrochemical oxidation of Fe^{2+} at the anode takes place as $\text{Fe}^{2+} - e \Rightarrow \text{Fe}^{3+}$ (2.12)

The effect of ferric ion is essentially chemical to dissolve the copper at the cathode and thus it acts as a harmful impurity



The loss in cathodic current efficiency can be attributed to the reduction of Fe^{3+} ions to Fe^{2+} ions at the cathode, but no correlation has been made yet.

2.5.2. Electrode Potential and anodic Polarization of sulphides (34)

The equilibrium potentials of Cuprous sulphide and copper - Iron matrices have been measured in solutions containing copper ions. The $\text{Cu}_2\text{S}/\text{Cu}^{2+}$ couple is +0.160V more positive than the $\text{Cu}^+/\text{Cu}^{2+}$ couple. It has been suggested that the non stoichiometric Cuprous sulphide behaves more nobly on account of the excess S.

Many attempts have been made to recover metals and by products like S in elemental form directly from sulphide ores. The various processes developed in an attempt to achieve this have been reviewed by Habashi. As good electronic conductors, the sulphides present no difficulties to their use as anodes.

Electrochemical preparation of Metal sulphides :

Wrabetz in collaboration with Noddack and Herbst carried out an investigation of metal sulphide electrodes in aqueous solutions. They found the electrochemical properties of heavy metal sulphides in aqueous solutions to be influenced by the presence of non-stoichiometric excess sulphur in these materials. The sulphide electrodes differ from a normal electrode system in that only a minute Faradaic current can flow without a complete exhaustion of the available excess sulphur and a corresponding alteration in the composition of the electrode surface.

It was observed that many metal sulphide electrodes in contact with solution containing the corresponding cations establish a reversible potential. Similar to the electromotive series in case of metals, the metal sulphides were also found to have their own emf series. The reversible potentials established by the metal sulphides in contact with solutions containing the corresponding cations have, however, been found to be more noble than those established by the respective parent metals. Moreover, many of the metal sulphides in solutions containing the different concentration of the cations showed the electrode potential to be governed by the solute activity in accordance with the Nernst relationship.

The equilibrium potentials established by the metal electrodes in different solutions of various concentration have been studied for sulphate electrolyte (100 g/L

H_2SO_4 and 1 M $CuSO_4 \cdot 5H_2O$) and chloride electrolyte (100 g/L NaCl and 1 M $CuCl_2 \cdot 2H_2O$).

It has been reported that equilibrium potential with $CuSO_4$ is greater than equilibrium potential with 100 g/L H_2SO_4 and also equilibrium potential with $CuCl_2$ is greater than equilibrium potential with 100 g/L NaCl.

2.6 Effect of Various Variables on Copper Extraction From Matte :

(1) Current density :

The influence of current density is substantial, the maximum current efficiency⁽³⁰⁾ is obtained at the lowest current density. At any particular temperature the total current utilized for the dissolution of matte anode is found to decrease with increasing current density. In short, the efficiency of copper dissolution decreases considerably with increasing current density.

But the current density can not be decreased indefinitely for the output of products will be very small and the capacity of the plant will be lowered. Thus the current density should be kept at an optimum value, and not raised too high as

(a) To avoid simultaneous discharge of H^+ ions which causes the deposit to be spongy, dissolution of deposit and facilitate the hydrolysis of cuprous sulphate.

(b) To avoid the reduction reaction $Cu^{2+} + e \rightarrow Cu^+$ which lowers current density.

(2) Applied Voltage :

The voltage of the bath increases with the progress of electrolysis; if the rate of attainment of the higher voltage is faster, the greater is the current density. The decrease in the cell voltage observed after some time may be due to the loosening of the anodic film.

In electrorefining the energy absorbed in liberating the copper at the cathode is counter balanced by the energy generated in dissolving copper at the anode; i.e. equilibrium potential of the anode and cathode are practically same ($E_a = E_c = 0$). Thus the voltage necessary for the electrorefining is the sum of the voltage to overcome the resistance of electrolyte, electrodes, slime clinging to the anode and also the contact resistances.

(3) Composition of Electrolyte :

The composition of electrolyte and operating conditions are so adjusted so as to attain minimum deposition of impurities with high current and energy efficiency.

In many baths additions of acids are made to lower the resistance of the electrolyte. The potential drop through the electrolyte itself is lowered for the same current density. It is not possible to change the conductivity of solution without making changes in some other properties such as the metal ion concentration.

The addition of H_2SO_4 to $CuSO_4$ solution increases the conductivity, but the common ion effect decreases the Cu^{++} ion concentration. The advantages of acidifying copper sulphate solution are as follows :

- (i) It increases the conductance of the bath.
- (ii) It inhibits the hydrolysis of Cuprous sulphate.
- (iii) It dissolves part of the copper separated in the bulk of the bath.

The electrolyte should not have too high a concentration of $CuSO_4$ otherwise it will increase the resistance of the bath and consequently the current efficiency will be lowered. Similarly the concentration of the bath should not fall below a certain value otherwise it will start depositing along with Cu^{++} ions. Very low metal concentration yield powdery deposits even at low current density. Small amounts of gelatins and gums are generally added to the bath to improve the physical characteristics of deposits.

(4) Temperature :

Temperature affects the recovery of copper from matte in the following ways :

- (i) It increases the conductance of the bath.
- (ii) It diminishes the polarization of electrodes, hence hydrogen over voltage and precipitation of oxides is decreased.
- (iii) It increases the chemical solubility of the anode.

(iv) It increases the chemical dissolution of deposited metal at cathode.

(v) It diminishes the cell voltage.

The net overall effect is to increase the current efficiency ; at any particular current density the current efficiency increases with increasing temperature.

Chapter 3

FORMULATION OF THE PROBLEM:

It has been already established that the step of converting can be bypassed by direct electrorefining of copper from matte. The main advantages being reduction in steps of the process, economy in electric power if cheaply available, reduction in manpower, less capital cost and saving in time. In this process there are many variables the effect of all these, in the present work, have been studied so as to obtain the best conditions for maximum recovery of copper from matte. The variables studied are as follows :

- (i) Current density
- (ii) Electrode distance
- (iii) Bath composition
 - (a) Changing CuSO_4 concentration of both
 - (b) Changing H_2SO_4 concentration of both
 - (c) Only H_2SO_4 in bath.

Electrorefining was done with separate matte electrodes cast from matte obtained from I.C.C., Chatolla. The study of the feasibility of this process which is, though, at present confined to pilot plant and laboratory stages, promises far reaching consequences.

It has been reported in literature that the melting stage as well as converting stage invariably contain some

amount of copper either in oxide, sulphide or silicate form. This copper content can be as high as a 3 percent in case of conventional products. Lately many new technological developments have taken place in the production of copper involving less loss of copper in slag so slag can act as a source of copper. The recovery of copper from slag is only possible after comminution and flotation concentration. The slag from Chhotalla plant was obtained and it was subjected to beneficiation and an attempt was made to get the concentrate after flotation.

Chapter 4

EXPERIMENTAL WORK :

In the present work an attempt was made to study the recovery of copper from slag s and mattes obtained from I.C.C., Ghatsila. Slag was firstly ground and sized and then it was subjected to flotation for concentration. Matte was cast in the form of electrodes and copper was deposited on pure copper cathode in electrolytic bath and effect of various variables was studied by finding cathodic current efficiency.

4.1 Materials Used :

4.1.1 Copper slag:

The copper slag of the following average analysis was used for experimental work.

Table 4.1

Constituent	Percent
Copper	3.1
Sulphur	2.7
Iron	41.6
Silicon	24.5

4.1.2 Flotation reagents :

(a) Xanthate :

Potassium Ethyl Xanthate in the form of solution (100 g/L) was used as collector for the flotation of ground slag.

(b) Pine oil :

Pine oil was used as a frothing agent.

(c) Sodium Hydroxide :

This was used (strength being 1/10) for the purpose of pH control.

4.1.3 Copper Matte (Uno an modo) :

The matte was obtained from I. C. C., Ghatalia having the following composition.

Table 422

Constituents	Percent
Cu	42.1
Fe	27.6
S	24.9

4.1.4 Electrolyte :

Chemically pure copper sulphate crystals and sulphuric acid (specific gravity 1.84) were used to prepare electrolyte.

4.1.5 Cell :

Cell was made from 0.5 cm thick perspex sheet as shown in Figure. Chloroform and "Dobesivo" adhesive were used for joining purpose.

4.1.6 Pure copper sheets of 2 mm thickness were used as cathode for matte refining. Anodes were sand cast from I.C.I., Chatsia.

IV 2 Method :

4.2.1 Crushing :

The slag was in the lumpy form and for further treatment it had to be crushed. It was crushed in Denver Laboratory specification bearing roll crusher. The slag was crushed to a size of minus 10 mesh.

4.2.2 Grinding :

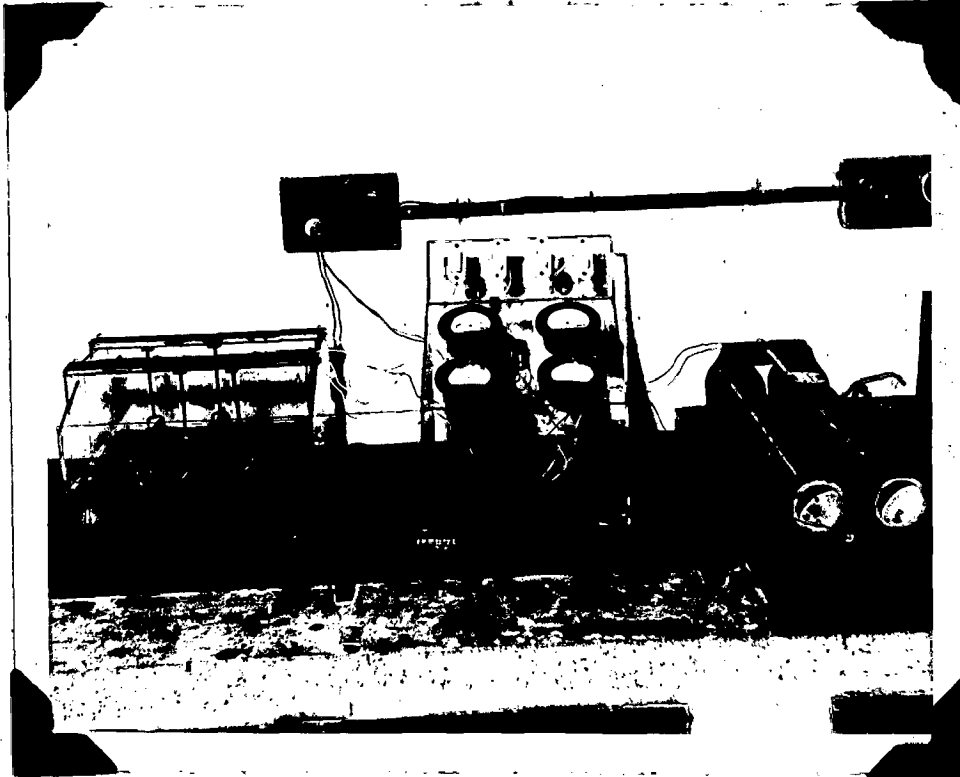
After crushing, the slag was charged into the ball mill where it was subjected to dry grinding by means of steel balls of different diameters for 2 hours.

4.2.3 Screening :

The ground slag was separated in sizes ranging from mesh no 5 to 350 with the help of a sieve shaker. For flotation purpose the slag of mesh sizes, ranging from 170 to 300 was taken.

4.2.4 Flotation :

After grinding, the concentration was done in a Denver Laboratory flotation machine. Ground slag of



PHOTOGRAPH OF THE
EXPERIMENTAL SET UP

170^g/300^g particle also was taken in a steel tank to fill it up to the given mark. The optimum conditions for flotation of the ground slag were taken from previous work done in this department. 1.C.C. of Potassium Ethyl Xanthate was added in the tank and it was conditioned for 3 minutes with no air flow. After this 1.C.C. of pine oil was added in the tank and air was let into the inflowing pulp for 3 minutes. NaOH was added to pulp for maintaining pH value of approximately 9.2. The froth collected at the top of the tank was ~~with~~ removed as concentrate. The copper content of slag concentrate was determined by spectroscopic analysis with EDTA (Ethyleno Diamine Tetra Acetic acid). 0.05% Cu²⁺ solution was prepared by dissolving 1.25 gm of copper (filings) after washing with petroleum ether in 5 ml of concentrated HNO₃. This was dissolved to 1 litre. It was standardised with EDTA using Fast Sulphon Black as indicator. Thus EDTA was standardised. Buffer of pH 2.2 was prepared by adding 1 M HCl to 300 ml of 1 M sodium Acetate.

2 gm. of slag concentrate was dissolved in HNO₃ and it was diluted to 1 litre. Filtration was done by taking 10 ml of this solution of copper concentrate plus 20 ml buffer plus 100 ml H₂O. The wave length was set at 745 nm. Absorbance was recorded after every addition of 0.5 ml of EDTA and it was stopped when absorbance became constant. A plot is drawn between absorbance and volume of EDTA. From the volume of EDTA used Cu²⁺ amount was calculated.

1 ml of 0.05 M EDTA & 3.177 mg of Cu^{++}

4.2.5 Anode casting for matte refining :

The matte obtained from I. C. C., Chatolla was melted in a graphite crucible in a forced draught pit furnace after which it was cast into anodes of sizes 8cm x 8cm $\frac{1}{2}$ cm. Copper wire of 3 mm diameter was previously impregnated in the mould to act as a hook for hanging anodes when cast. Casting was done in sand moulds.

4.2.6 Design and fabrication of Electrorefining Cell :

An electrorefining cell with control panel, as shown in Fig. 4.1, was designed and fabricated out of porous sheets and joined as water tight compartment by means of Chloroform and "Debecivo" adhesive. The cell had two tanks and the electrodes were hung by means of hooks made from copper ~~wires~~ ^{that} could slide over the bus bar as shown in Fig. 4.2. The electric circuit was completed as shown in Fig. 4.3.

4.27 Matte Refining :

The anodes were cast from matte and cathodes were cut from pure copper sheets. These were arranged in the cell, as shown in Fig. 4.5, with voltmeters and ammeters in the circuit.

The following variables were studied to obtain optimum conditions for electrorefining:

(1) Effect of current density :

The electrolytic cell was set on and the current drawn was varied. The area of cathode exposed to electrolyte was

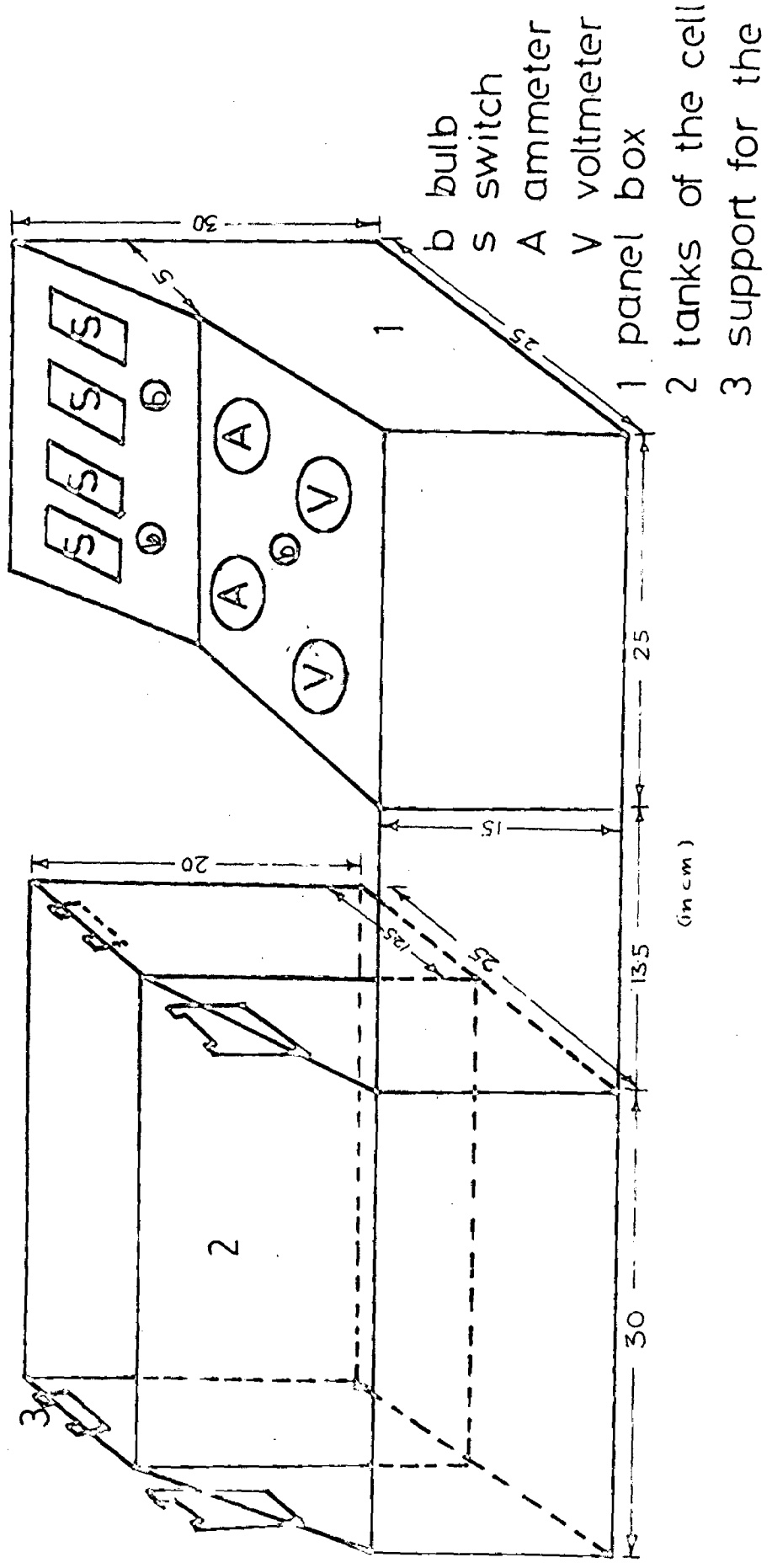
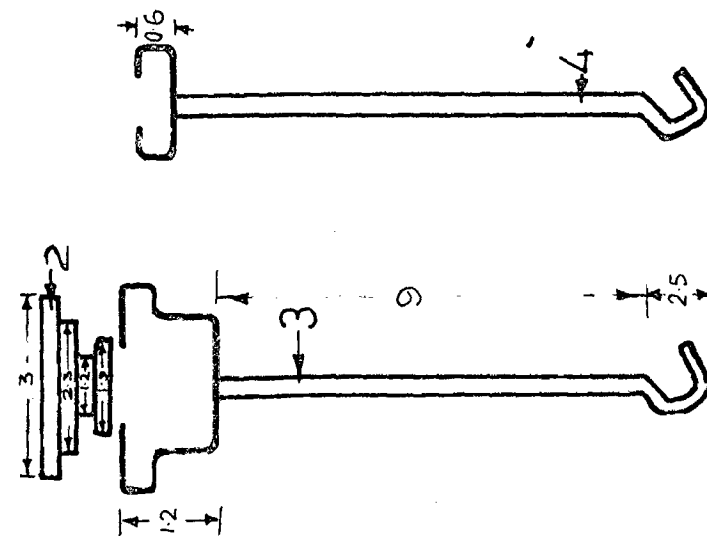
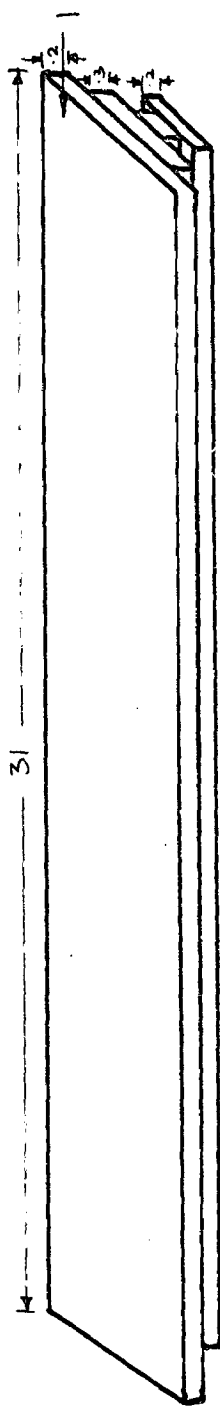


FIG.4.1 ELECTROLYSIS CELL WITH PANEL BOX

(in cm)



- 1 bus bar
- 2 cross-section of bus bar
- 3 hook for anode
- 4 hook for cathode

FIG4.2 BUS BAR & HOOKS

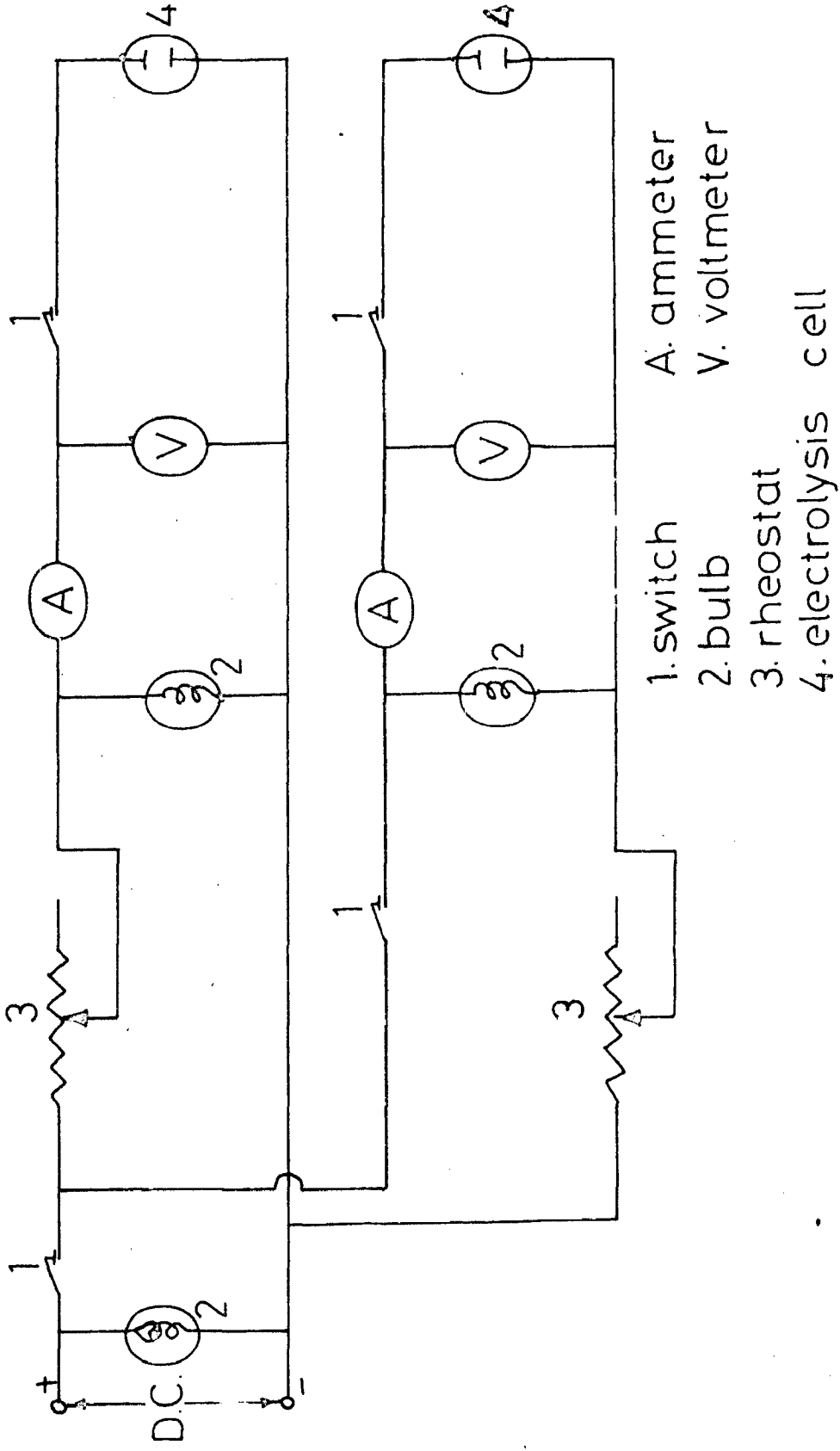


FIG. 4.3 ELECTRIC CIRCUIT OF THE ELECTROLYSIS CELL

kept constant by keeping electrode at fixed depth in electrolyte. The duration of electrolysis was kept constant for each observation and the current drawn was measured. Fig. 5.1 shows the cathodic current efficiency change with current density at three different concentrations of H_2SO_4 (50 g/L, 100 g/L and 150 g/L).

(ii) Effect of Electrode Distance :

The electrolysis cell was set on and the distance between electrodes varied keeping current density, concentration of electrolyte and duration of electrolysis constant. Such three sets of observations were taken with three different H_2SO_4 concentrations to find the effect of electrode distance on cathodic current efficiency (Shown in Fig. 5.2).

(iii) Effect of $CuSO_4$ concentration in electrolyte :

The concentration of $CuSO_4$ in electrolyte was varied keeping current density, H_2SO_4 concentration in electrolyte and electrode distance constant. Three sets of observations were taken at different concentrations of H_2SO_4 (shown in Fig. 5.3).

(iv) Effect of H_2SO_4 concentration in Electrolyte :

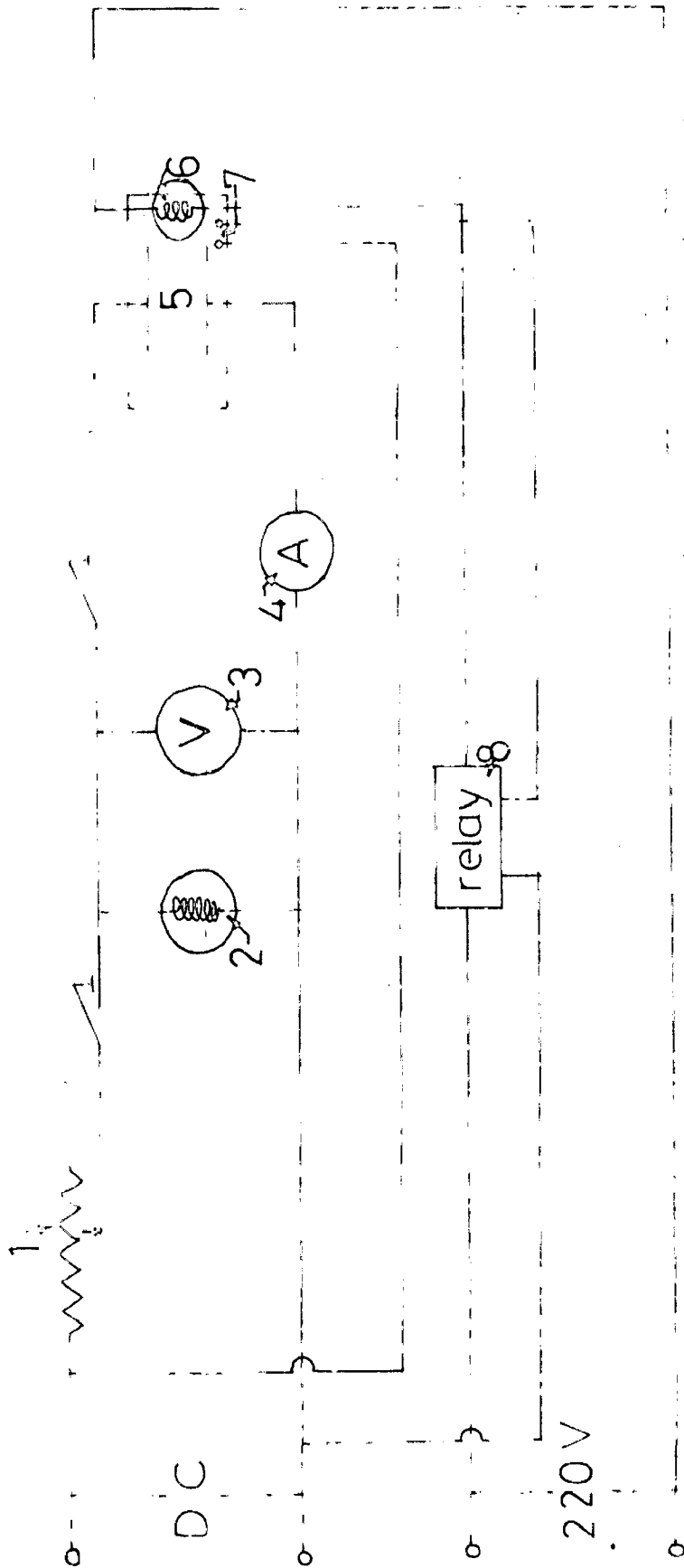
The concentration of H_2SO_4 in electrolyte was varied keeping current density, $CuSO_4$ concentration of electrolyte and electrode distance constant. Fig. 5.4 shows the cathodic current efficiency change with H_2SO_4 concentration of electrolyte at three different $CuSO_4$ concentrations.

(v) Effect of temperature :

The electrolyte in the electrolytic cell was heated by an electric bulb and bath temperature was automatically controlled by means of relay. The relay circuit is shown in Fig. 4.4. Readings for copper deposition were taken at room temperature and then upwards, at intervals of 10°C , keeping other variables constant for one set of observations. Fig. 5.5 shows the cathodic current efficiency change with temperature at three different H_2SO_4 concentrations.

(vi) Effect of H_2SO_4 concentration without any CuSO_4 in electrolyte.

Observations were taken by setting on the cell and keeping all the other variables constant except H_2SO_4 concentration in the electrolyte (shown in Fig. 5.6).



- 1. rheostat
- 2. bulb
- 3. voltmeter
- 4. ammeter

- 5. electrolysis cell
- 6. heating bulb
- 7. H contact thermo-meter
- 8. switching relay

FIG. 4.4 AUTOMATIC TEMPERATURE CONTROL CIRCUIT

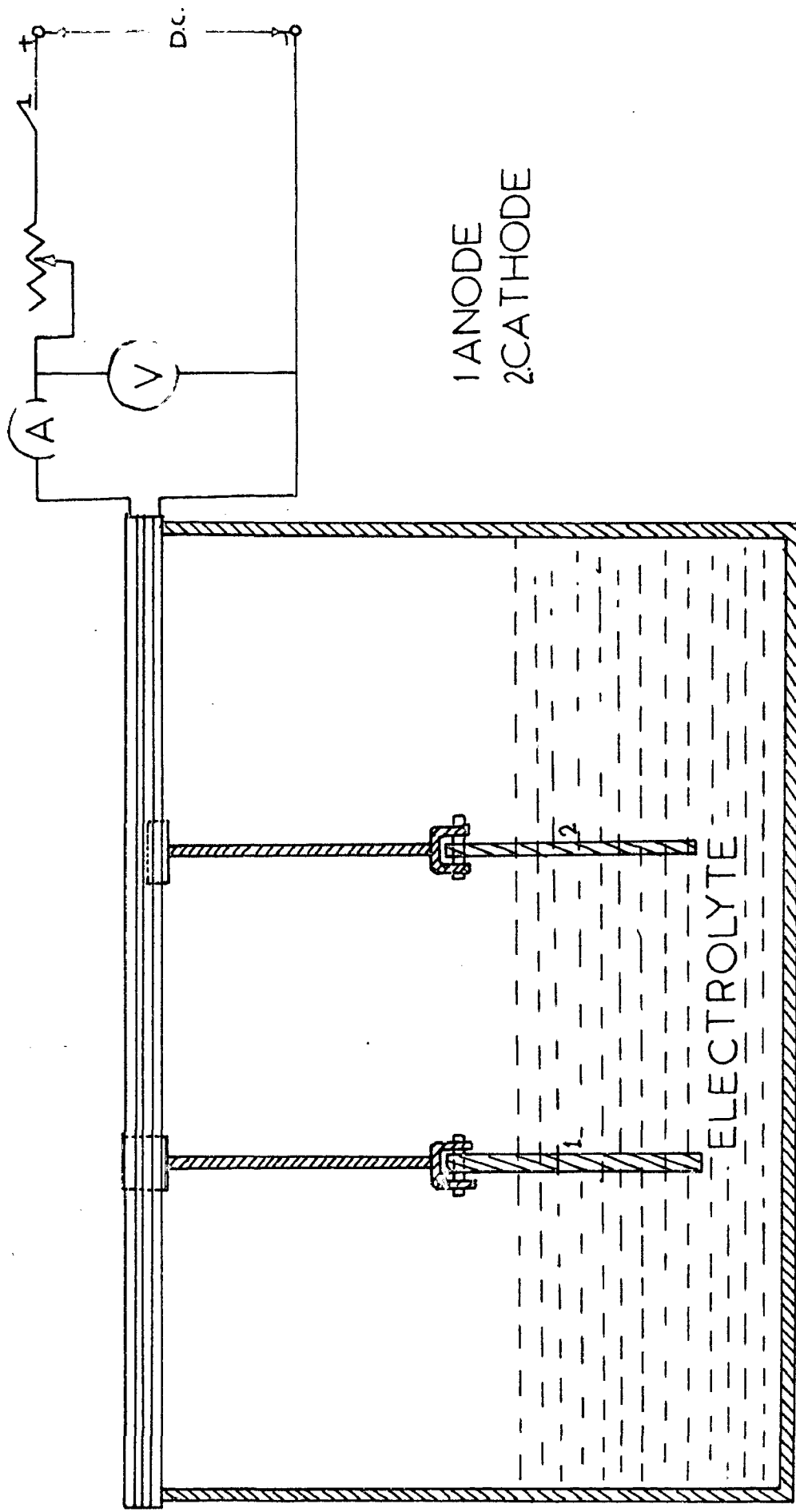


FIG.4.5 CROSS-SECTIONAL VIEW OF ELECTROLYSIS CELL

Chapter 5

OBSERVATIONS AND RESULTS :

5.1 Flotation :

Table 5.1

Weight of pine oil (Frother)	0.52 g/L
Weight of Potassium ethyl Xanthate	0.32 g/L
pH	9.2
Temperature	30°C
Weight of slag	150 g/L
Conditioning time	3 minutes
Frothing time	5 minutes
Percentage of Cu in Slag	31
Particle size	170 ⁺ /300 ⁺
Copper percent in concentrate	11.3

5.2 Matte Refining :

(1) Influence of Current density on cathodic efficiency in electrolysis of copper matte :

Table 5.2

Distance between electrodes	3 Cm
Time of electrolysis	6 hrs.
Temperature of bath	30 ± 2°C
Area of cathode inside the electrolyte	±0.760 dm ²
Volume of water taken	±2.5 L.

Concentration of CuSO_4 in electrolyte 30 g/L
 Concentration of H_2SO_4 in electrolyte 50 g/L

Sl. No.	Current (amp.)	Current density (amp/dm ²)	Weight of copper deposited (gm)	Current efficiency (%)
1	2	3	4	5
1	0.1	0.130	0.4732	66.3
2	0.4	0.522	1.9132	67.2
3	0.7	0.912	2.0504	57.2
4	1.0	1.30	3.1104	42.3
5	1.3	1.69	3.1472	33.9

Table 5.3

Distance between electrodes 3 cms.
 Time of electrolysis 6 hours
 Temperature of bath $30^\circ \pm 2^\circ\text{C}$
 Area of cathode inside the electrolyte 0.766 dm²
 Volume of water taken 2.5 Litres
 Concentration of CuSO_4 in electrolyte 30 gms/Litre
 Concentration of H_2SO_4 in electrolyte 100 gms/Litre

Sl. No.	Current (in amp.)	Current density (amp)	Weight of copper deposited (in gm)	Current efficiency, % (A/F)
1	0.1	0.130	0.8692	77.1
2	0.4	0.522	2.0024	73.1
3	0.7	0.912	2.9102	53.3
4	1.0	1.30	3.0333	42.5
5	1.3	1.69	3.1920	34.5

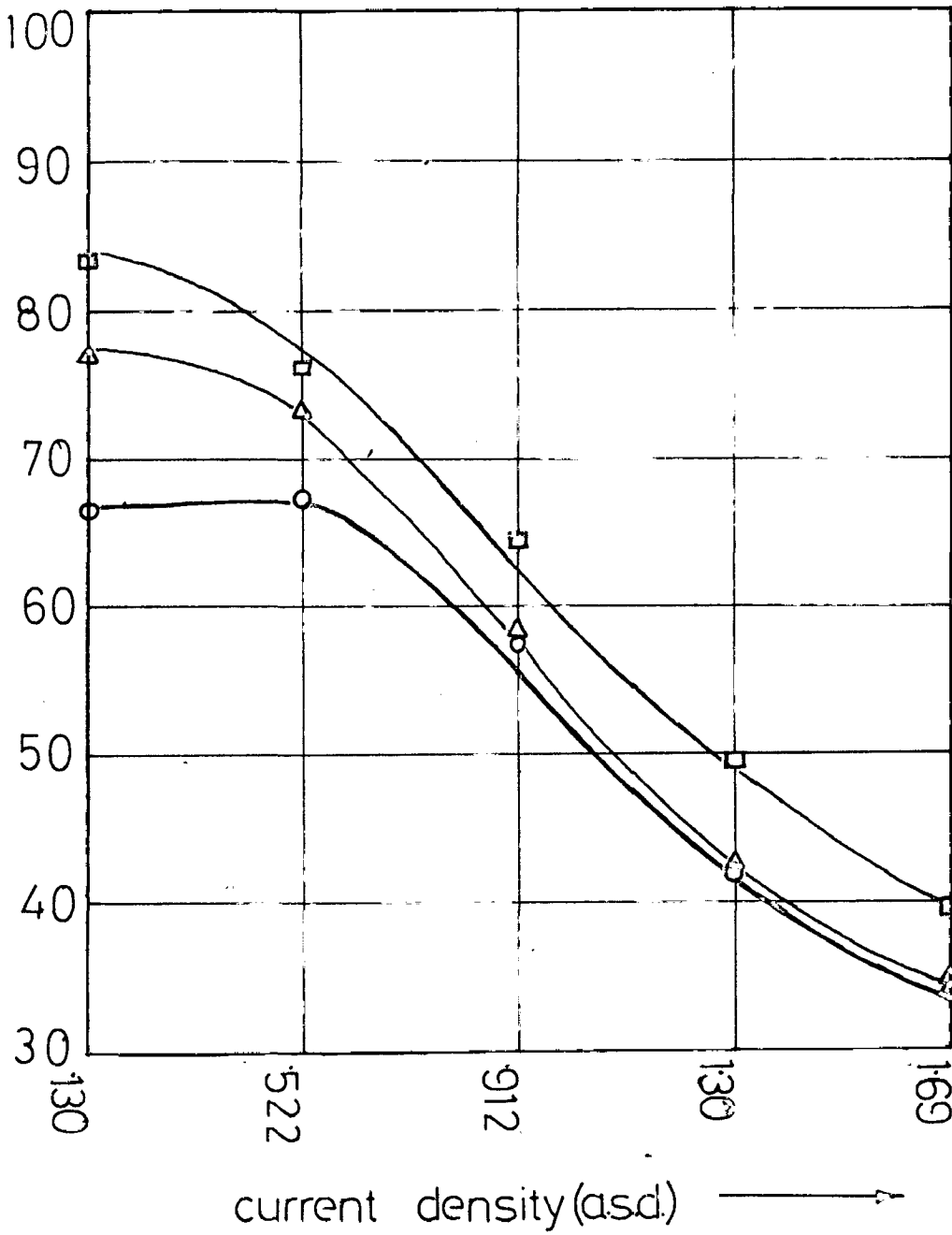
Table 5.4

Distance between electrodes	3 cms.
Time of electrolysis	6 hours.
Temperature of bath	30 \pm 2 $^{\circ}$ C
Area of cathode inside the electrolyte	0.766 dm 2
Volume of water taken	2.5 Litres
Concentration of CuSO $_4$ in electrolyte	30 gms/Litre
Concentration of H $_2$ SO $_4$ in electrolyte	= 150 gms/Litre

Sl.No.	Current (in amp.)	Current density (asd)	Weight of copper deposited (in gms)	Current efficiency, n (in %)
1	0.1	0.130	0.5966	83.6
2	0.4	0.522	2.1732	76.2
3	0.7	0.912	3.3234	64.7
4	1.0	1.30	3.5580	49.8
5	1.3	1.69	3.7012	39.9

(2) Influence of Electrode distance on cathodic efficiency
in electrolysis of copper matte :

○ 50g/l } H_2SO_4
 ▲ 100g/l } CONCENTR.
 □ 150g/l } ATION



6.5.] EFFECT OF CURRENT DENSITY

Table 5.5

Time of electrolysis	6 hrs.
Temperature of bath	30 ± 2°C
Area of cathode inside the electrolyte	0.766 dm ²
Volume of water taken	2.5 L
Current density	0.522 asd
Concentration of CuSO ₄ in electrolyte	30 g/L
Concentration of H ₂ SO ₄ in electrolyte	50 g/L

Sl. No.	Electrode distance (cm.)	Weight of Copper deposited (gms.)	Current Efficiency, η (%)
1	2.0	1.6098	59.6
2	2.5	1.8082	63.4
3	3.0	1.9132	67.2
4	4.0	1.4508	51.1
5	5.0	1.1322	39.2
6	6.0	1.0304	36.2

Table 5.6

Time of electrolysis	6 hours
Temperature of bath	$30 \pm 2^{\circ}\text{C}$
Area of cathode inside the electrolyte	0.766 dm^2
Volume of water taken	2.5 Litres
Current density	$0.4/766 \text{ ASD} = 0.522 \text{ ASD}$
Concentration of CuSO_4 in electrolyte	30 gms/Litre
Concentration of H_2SO_4 in electrolyte	100 gms/Litre

Sl. No.	Electrode distance (in cms.)	Weight of copper deposited (in gms).	Current efficiency, η (In %)
1	2.0	1.7576	61.6
2	2.5	1.9343	67.9
3	3.0	2.0024	73.1
4	4.0	1.5916	53.9
5	5.0	1.1118	38.9
6	6.0	1.0432	36.7

Table 5.7

Time of electrolysis	6 hours.
Temperature of bath	30.2°C
Area of cathode inside the electrolyte	0.766 dm ²
Volume of water taken	2.5 Litre
Current	0.4 amp.
Current density	0.4/0.766 amp/cm ² = 0.522 amp/cm ²
Concentration of CuSO ₄ in electrolyte	30 gms/Litre
Concentration of H ₂ SO ₄ in electrolyte	150 gms/Litre

Sl. No.	Electrode distance (in cm.)	Weight of copper deposited (in gms.)	Current efficiency, n (in %)
1	2.0	1.0902	66.3
2	2.5	2.1134	73.7
3	3.0	2.1732	76.2
4	4.0	1.9264	67.7
5	5.0	1.2100	42.6
6	6.0	1.0006	33.1

○ 50 g/l
 △ 100 g/l
 □ 150 g/l

} H_2SO_4
 CONCENTRATION

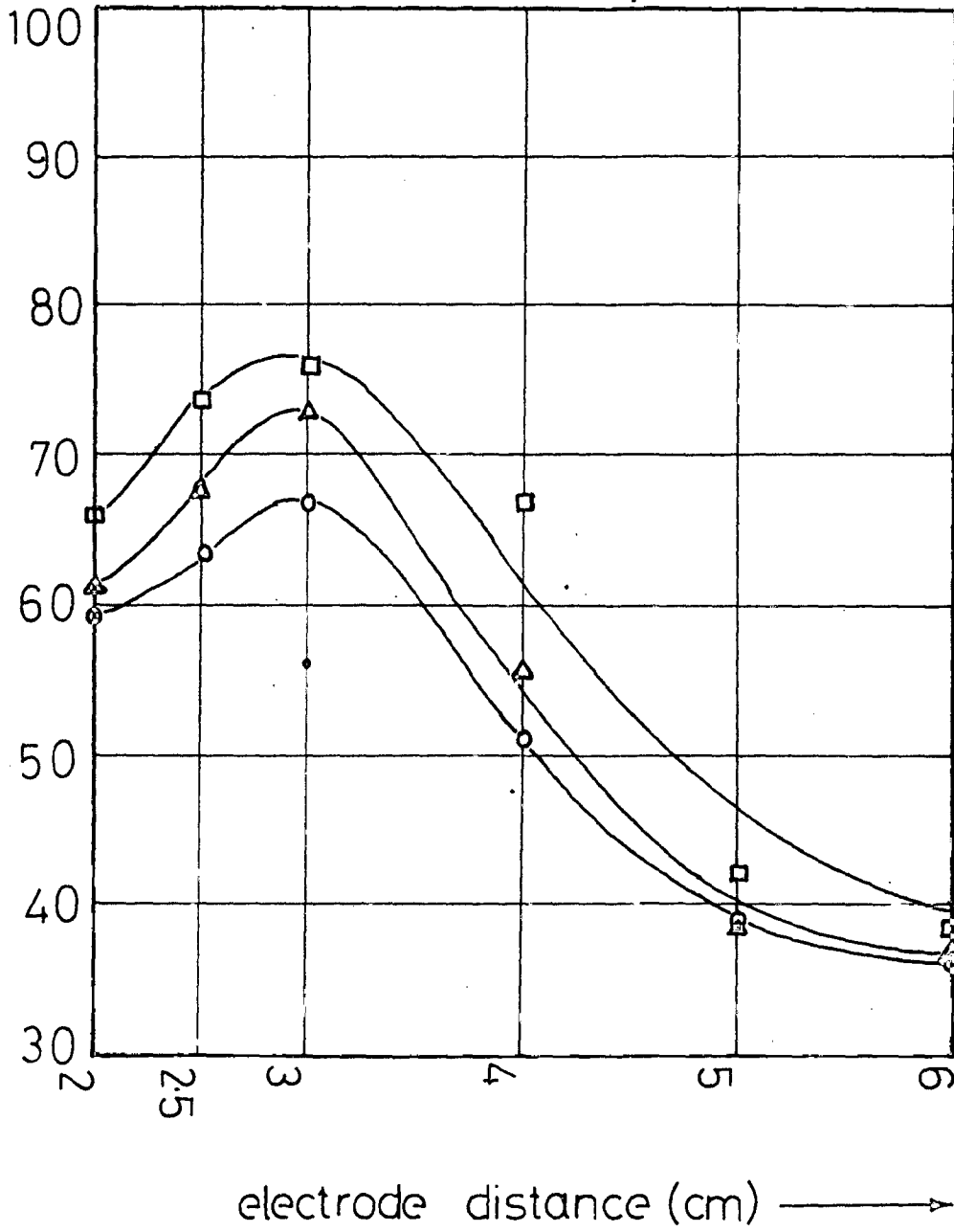


FIG.5.2 EFFECT OF ELECTRODE DISTANCE

(3) Influence of $CuSO_4$ concentration on cathodic efficiency :

Table 5.8

Distance between electrodes	3 Cm.
Time of electrolysis	6 hrs.
Temperature of bath	$30 \pm 2^\circ C$
Area of cathode inside the electrolyte	0.766 cm^2
Volume of water taken	2.5 L
Current density	0.522 amp
Concentration of H_2SO_4 in electrolyte	50 g/L

Sl. No.	Concentration of $CuSO_4$ (g/L)	Weight of copper deposited (gms.)	Cathodic efficiency, η (%)
1	10	1.2868	45.2
2	20	1.7602	61.7
3	30	1.9132	67.2
4	40	1.9372	67.9
5	50	1.9434	68.3

Table 5.9

Distance between electrodes	3 cms.
Time of electrolysis	6 hrs.
Temperature of bath	$30 \pm 2^\circ C$
Area of cathode inside the electrolyte	0.766 cm^2
Volume of water taken	2.5 Litres
Current density	0.522 amp
Concentration of H_2SO_4 in electrolyte	50 g/L

Sl. No.	Concentration of CuSO_4 (in g/L)	Weight of copper deposited (in gms.)	Current efficiency, η (in %)
1	10	1.3172	46.1
2	20	1.8006	63.2
3	30	2.0824	73.1
4	40	2.1504	75.6
6	50	2.2006	77.2

Table 5.10

Distance between electrodes	3 Cm.
Time of electrolysis	6 hrs.
Temperature of bath	$30 \pm 2^\circ\text{C}$
Area of cathode inside the electrolyte	0.766 dm^2
Volume of water taken	2.5 Litres
Current density	0.522, asd
Concentration of H_2SO_4 in electrolyte	150 gms/Litre

Sl. No.	Concentration of CuSO_4 (g/L)	Weight of copper deposited (in gms.)	Current efficiency, η (in %)
1	10	1.3762	40.3
2	20	1.9614	65.6
3	30	2.1732	76.2
4	40	2.2002	79.2
5	50	2.2716	79.8

○ 50 g/l } H₂SO₄
△ 100 g/l } CONCENT-
□ 150 g/l } TRATION

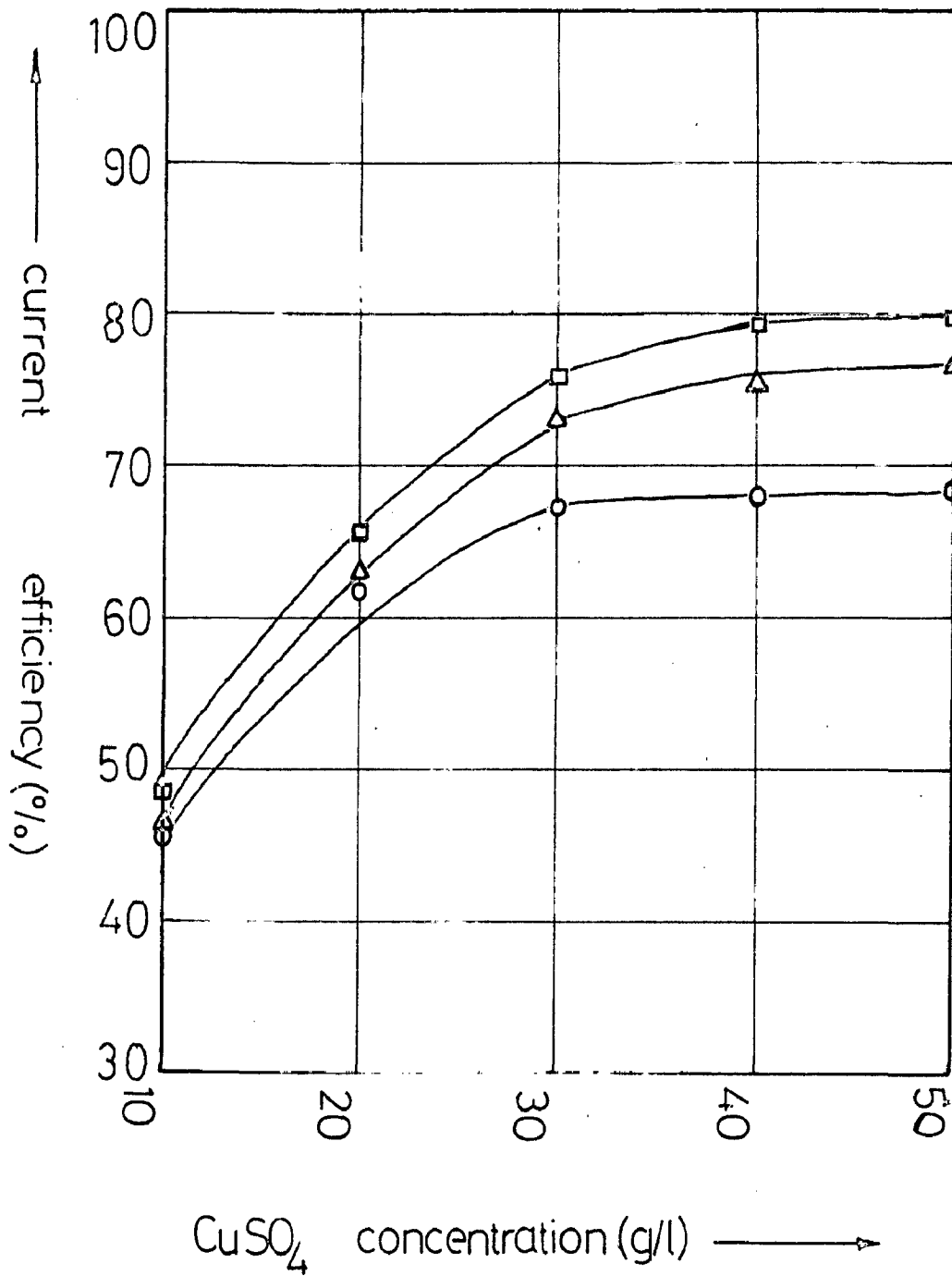


FIG. 5.3 EFFECT OF CuSO₄ CONCENTRATION

(4) Influence of H_2SO_4 concentration on Cathodic Efficiency :

Table 5.11

Distance between electrodes	3 cm.
Time of electrolysis	6 hrs.
Temperature of bath	$30 \pm 2^\circ C$
Area of cathode inside the electrolyte	0.766 dm^2
Volume of water taken	2.5 L
Current density	0.522 amp
Concentration of $CuSO_4$ in electrolyte	30 g/L

Sl. No.	Concentration of H_2SO_4 (g/L)	Weight of copper deposited (gm)	Current efficiency, η (%)
1	50	1.9132	67.2
2	100	2.0824	73.1
3	150	2.1732	76.2
4	200	1.9906	66.8
5	250	1.7812	59.0

Table 5.12

Distance between electrodes	3 cms.
Time of electrolysis	6 hrs.
Temperature of bath	$30 \pm 2^\circ C$
Area of cathode inside the electrolyte	0.766 dm^2
Volume of water taken	2.5 Litres
Current density	0.522 amp
Concentration of $CuSO_4$ in electrolyte	40 gms/Litre

Sl. No.	Concentration of H_2SO_4 (g/L)	Weight of copper deposited (gms.)	Current efficiency, η (in %)
1	50	1.9372	67.9
2	100	2.1504	75.6
3	150	2.2602	79.2
4	200	1.9902	69.9
5	250	1.7862	62.7

Table 5.13

Distance between electrolyte	3 cms.
Time of electrolysis	6 hrs.
Temperature of bath	30 \pm 2 ^o C
Area of cathode inside the electrolyte	0.1766 dm ²
Volume of water taken	2.5 Litres
Current density	0.522 amp
Concentration of $CuSO_4$ in electrolyte	50 gms/Litres

Sl. No.	Concentration of H_2SO_4 (g/L)	Weight of copper deposited (gms)	Current efficiency, η (in %)
1	50	1.9434	68.3
2	100	2.2006	77.2
3	150	2.2716	79.8
4	200	2.0402	71.6
5	250	1.7938	62.1

○ 30 g/l } CuSO_4
△ 40 g/l } CONCENTRATION
□ 50 g/l }

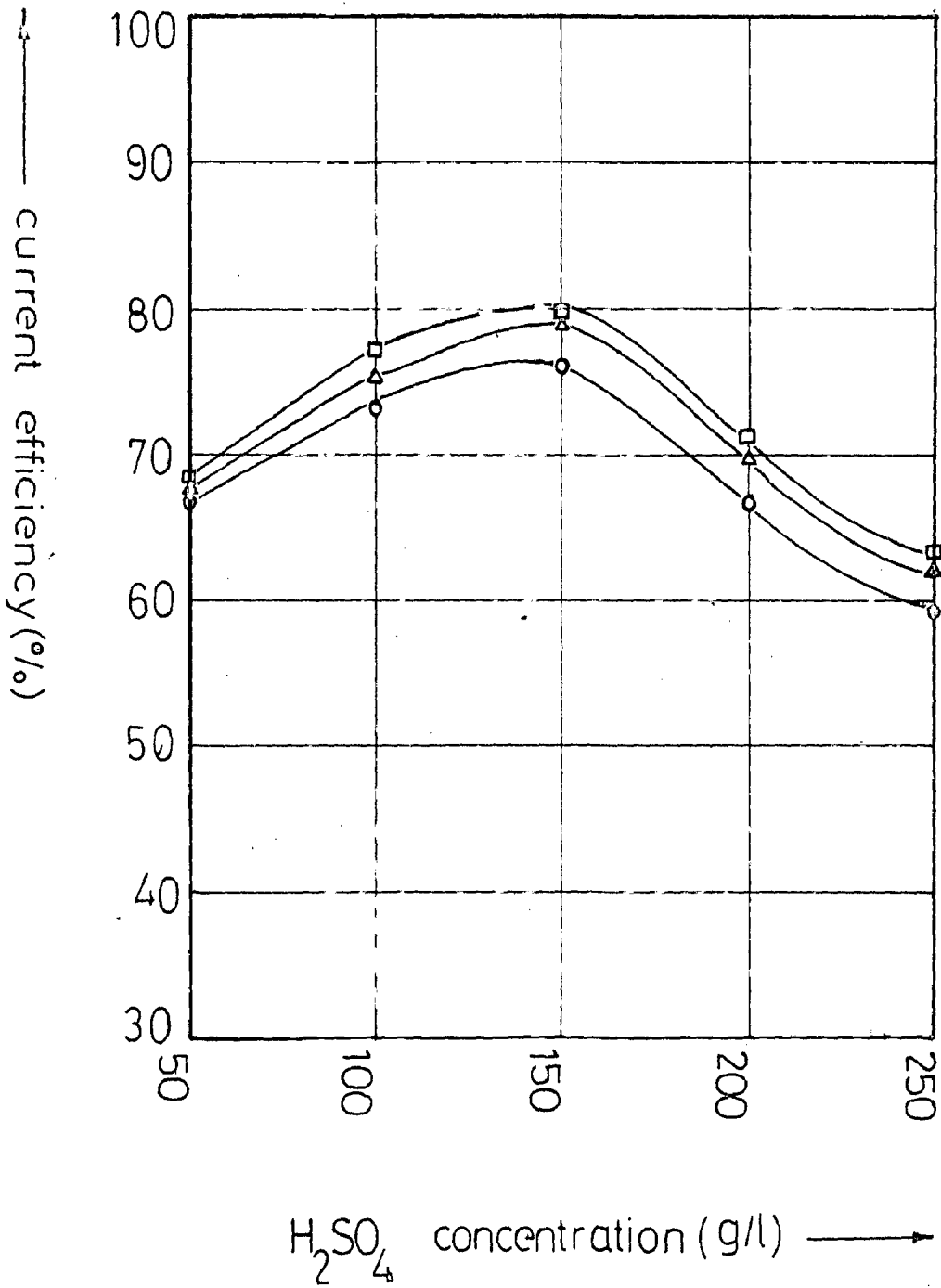


FIG.5.4 EFFECT OF H_2SO_4 CONCENTRATION

(5) Influence of temperature on cathodic efficiency in electrolysis of copper sulfate

Table 5.14

Distance between electrodes	3 cm.
Time of electrolysis	6 hrs.
Area of cathode inside the electrolyte	0.766 cm ²
Volume of water taken	2.5 L
Current density	0.522 amp
Concentration of CuSO ₄ in electrolyte	30 g/L
Concentration of H ₂ SO ₄ in electrolyte	50 g/L

Sl. No.	Temperature (°C)	Weight of copper deposited (gms)	Current efficiency, η (in %)
1	30	1.9132	69.2
2	40	1.9904	69.6
3	50	2.1412	73.6
4	60	2.3520	82.7

Table 5.15

Distance between electrodes	3 cm.
Time of electrolysis	6 hrs.
Area of cathode inside the electrolyte	0.766 cm ²
Volume of water taken	2.5 Litres
Current density	0.522 amp
Concentration of CuSO ₄ in electrolyte	30 g/L
Concentration of H ₂ SO ₄ in electrolyte	100 g/L

Sl. No.	Temperature (°C)	Weight of copper deposited (gms)	Current efficiency, η (in %)
1	30	2.0024	73.1
2	40	2.1002	73.7
3	50	2.1302	74.9
4	60	2.3626	83.0

Table 5.16

Distance between electrodes	3 cms.
Time of electrolysis	6 hrs.
Area of cathode inside the electrolyte	0.766 dm ²
Volume of water taken	2.5 Litres
Current density	0.822 amp
Concentration of H ₂ SO ₄ in electrolyte	150 g/L
Concentration of CuSO ₄ in electrolyte	30 g/L

Sl. No.	Temperature (°C)	Weight of copper deposited (gms)	Current efficiency, η (in %)
1	30	2.1732	76.2
2	40	2.1900	77.1
3	50	2.4004	84.3
4	60	2.5404	89.1

○ 50 g/l } H₂SO₄
△ 100 g/l } CONCENTR.
□ 150 g/l } ATION

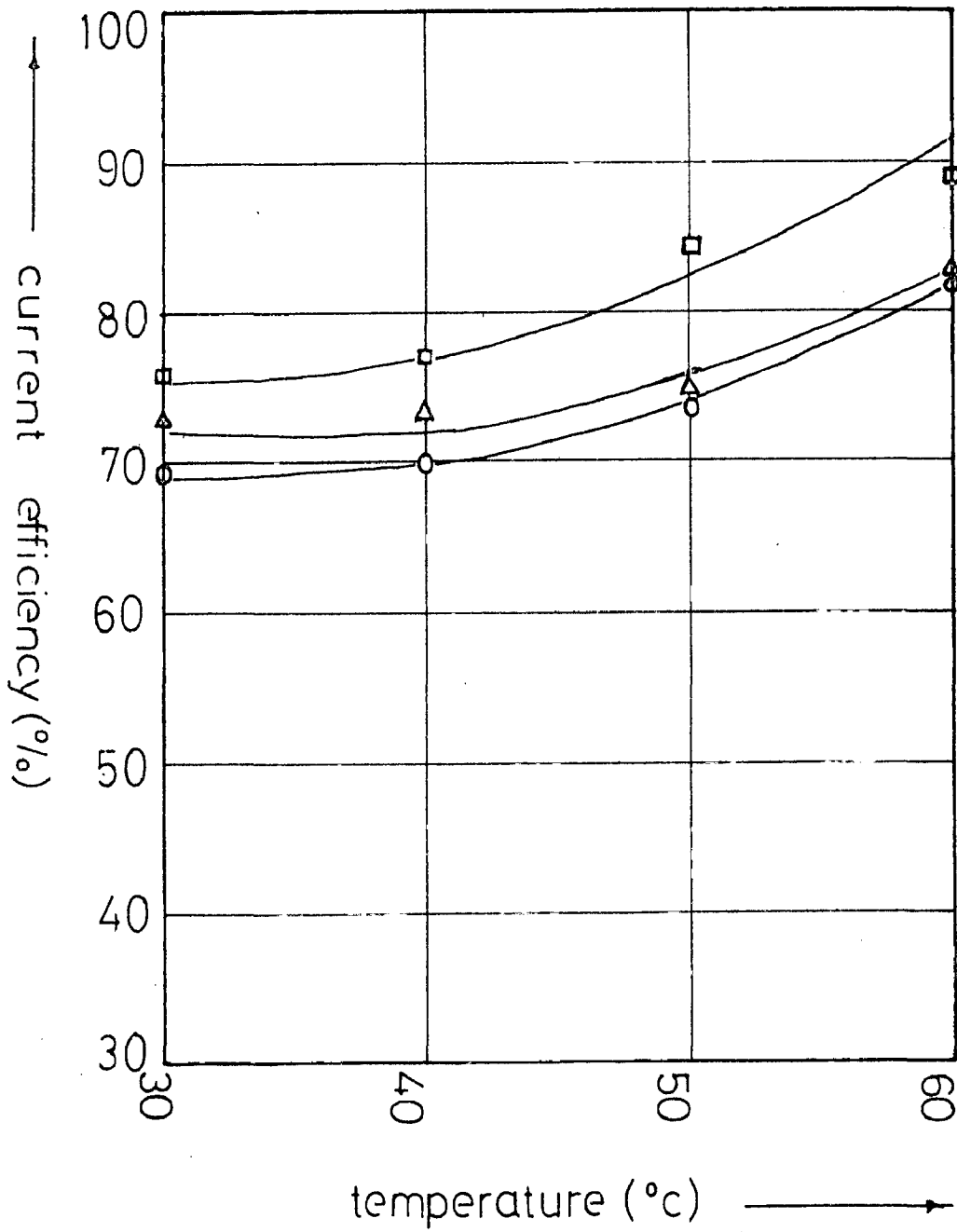


FIG.5.5 EFFECT OF TEMPERATURE

(6) Influence of H_2SO_4 concentration without any $CuSO_4$ in electrolyte on cathodic efficiency :

Table 5.17

Distance between electrodes	3 cm.
Time of electrolysis	6 hrs.
Temperature of bath	$30 \pm 2^\circ C$
Area of cathode inside the electrolyte	0.766 cm^2
Volume of water taken	2.5 Litres
Current density	0.522 amp

Sl. No.	H_2SO_4 concentration (g/L)	Weight of copper deposited (gm)	Current efficiency, η (in %)
1	25	0.8552	30.0
2	50	0.9294	32.6
3	75	0.9370	32.9
4	100	0.9370	32.5

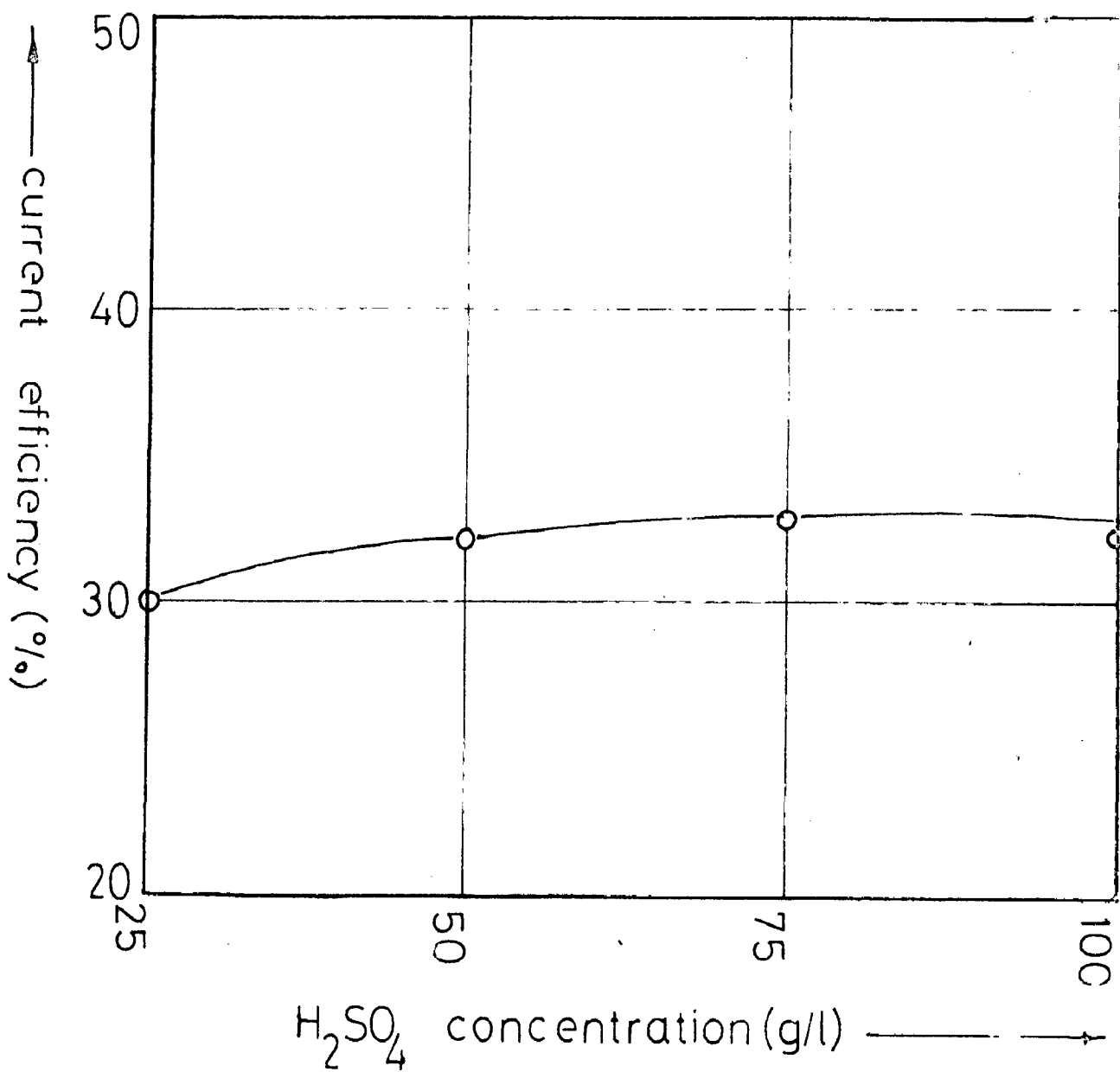


FIG.5.6 EFFECT OF H_2SO_4 CONCENTRATION WITHOUT ANY $CuSO_4$

Chapter 6

DISCUSSIONS
MATTE REFINING

(i) Influence of Current Density :

As the current density was increased (from 0.130 to 3.69 A/cm^2) at bath temperature of $30 \pm 2^\circ C$, cathodic current efficiency was found to decrease as evident from fig. 5.1. The decrease in current efficiency with increase in current density may be attributed to the reduction of Cu^{++} ions to Cu^+ at the cathode,



(ii) Influence of electrode distance :

As the inter-polar distance was increased (from 2 to 6 cm) the current efficiency was found to increase up to an inter-polar distance of about 3 cm. and then it went on decreasing. Also with change in concentration of H_2SO_4 (50 g/L, 100 g/L and 150 g/L) it has been seen that there is an increase in current efficiency corresponding to the same inter-polar distance. The increase in current efficiency upto about 3 cm. distance may be attributed to the decreased interference to impurities with increasing volume of electrolyte between the electrodes. But as the inter-polar distance is increased further, cathodic current efficiency decreases probably due to the predominant effect of resistance of electrolyte in between the two electrodes .

(iii) Influence of $CuSO_4$ concentration :

From the fig. 5.3 it is inferred that cathodic

current efficiency increases as the concentration of CuSO_4 in solution increases from 10 to 50 g/L. It assumes a constant value after this around 40 g/L concentration of CuSO_4 . This may be attributed to the increase in Cu^{++} ion concentration and after 40 g/L concentration the negligible change in current efficiency may be due to complete saturation of Cu^{++} ions in the electrolyte.

(iv) Influence of H_2SO_4 concentration :

It is evident from the Fig. 5.4 that cathodic current efficiency increases with the increase in H_2SO_4 concentration upto 150 g/L. After this it decreases slowly. This may be attributed to the dissolution of deposited copper at the cathode with higher concentration of H_2SO_4 . Also with the change in concentration of CuSO_4 (30 g/L, 40 g/L and 50 g/L) it has been seen that there is an increase in current efficiency as the concentration of CuSO_4 increases.

(v) Influence of temperature :

It is seen from the Fig. 5.5 that the efficiency increases with increasing temperature. The maximum current efficiency is obtained at the temperature of 60°C . This increase in current efficiency with temperature may be attributed to the dissociation of more CuSO_4 in solution at higher temperatures and thus contributing more Cu^{++} ions in solution.

(vi) Influence of H_2SO_4 without any $CuSO_4$ in electrolyte :

With the concentrations of 25, 50, 75 and 100 g/L of H_2SO_4 it is found that the cathodic current efficiencies nearly remain constant and are very low (ranging from 30.0 to 32.5 percent) as compared to electrolyte bath having $CuSO_4$. This may be attributed to the slow dissolution of matte in solution and thus less concentration of Cu^{++} ions.

Flotation :

It has been possible to obtain around 11.3 percent copper in the concentrate by using flotation technique involving selective flotation of oxides and sulphides present in the fine ground slag. For the most efficient flotation following conditions were found to be most suitable for 150 gm of slag sample :

1, C. C. of Potassium Ethyl Xanthate (0.32 g/L)

1, C. C. of pine oil as frother (0.32 g/L)

pH 9.2

Conditioning time 3 minutes

particle size 175/300 μ

Frothing time 5 minutes

Increasing the quantity of collector to overabundant levels results in decreased recovery due to the fact that slag particles are also floated which decreases the selectivity of copper during flotation. Also with increasing frothing agent, recovery decreases as the solution becomes

saturated with frother. Increasing the time for conditioning and frothing cannot effect in anyway the recovery of copper from slag but the decrease in conditioning and frothing time affect as the recovery will not be complete due to incomplete flotation.

This flotation concentrate can be smelted giving a proper grade of matte which can be directly electrorefined to give highest recovery of copper from the slag.

Chapter 7

CONCLUSIONS

Direct electrorefining technique for the recovery of copper from matte can be used in practice. This reduces the steps of conventional process with less capital cost and ease in performance. This process is economical in case when the electricity is cheaply and easily available.

In the present study current efficiency is taken as a measure for the recovery of copper from the matte. The influence of various variables on cathodic current efficiency is studied and the optimum conditions are obtained for a particular matte composition. It is found that maximum cathodic current efficiency i.e., maximum recovery of copper is obtained for

- (i) Current density of 0.150 A/cm^2 ,
- (ii) Electrode distance of 3.0 cm,
- (iii) Bath composition of 40 g/L CuSO_4 and 150 g/L H_2SO_4 concentration.

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It is also found that the cathodic current efficiency increases with the increase in temperature.

From the studies on slag obtained from I.C.C. plants it can be concluded that it is possible to concentrate the slag for recovery of copper from it.

Optimum conditions for selective flotation of oxide and sulphide copper in slag have been obtained and a concentrate with around 11.3 percent copper has been obtained.

This concentrate can be smelted to give proper grade of matte which can directly be electrorefined for the recovery of copper.

Chapter 8

SCOPE FOR FUTURE WORK

There is considerable scope for future work, especially in matte refining which is still in its infancy and has yet to undergo a commercial breakthrough. Some suggestions regarding the advance study of this process may be as follows :

(i) The use of ultrasonic stirring :

This method involves mounting an ultrasonic vibrator in the tank of an electrolytic bath to irradiate the electrodes thereby increasing the rate of metal depositing.

(ii) The use of Diaphragm Cell :

The use of a diaphragm cell is required where the anode is corroded in a chloride bath to give maximum efficiency for dissolution. The cathode copper would not be contaminated by the chloride and the cathode efficiency can be maintained at high level.

(iii) Recovery of precious metals from the slime :

Studies can be made on treating copper refinery slimes to recover and separate precious metals like Au, Ag, Se, Te, As, Bi etc. are dissolved in matte during smelting.

(iv) Purification and circulation of electrolyte :

Impurities could be removed and enough copper ions must be added to bring the copper ions of the electrolyte to the original level by purification and circulation of electrolyte.

(v) Studies may be done in pilot plant stage to find the economic feasibility of direct refining process studied by the author.

(vi) Conditions of smelting the concentrate for getting suitable composition of matte can also be studied.

The present work can also be extended to other metal mattes as well, notable among them are a range of Nickel mattes. Further, other variables can be studied like influence of stirring, additive agents like glue and gelatine.

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