EXTRACTION OF COPPER AND ZINC

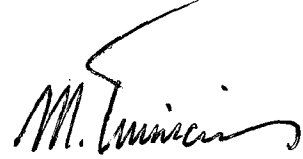FROM

BRASS-MELTING DROSS


A MASTER THESIS


SUBMITTED TO THE DEPARTMENT OF METALLURGICAL ENGINEERING

AND THE COMMITTEE ON THE FACULTY OF ENGINEERING

OF MIDDLE EAST TECHNICAL UNIVERSITY

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS

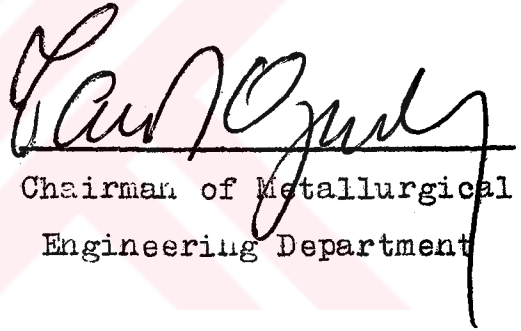FOR THE DEGREE OF

MASTER OF SCIENCE


By

Sadık Tezer

February 1974

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opinion it is fully adequate, in scope and quality,
as a thesis for the degree of Master of Science.

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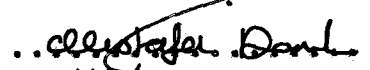Chairman of Metallurgical
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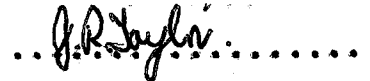
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# ABSTRACT

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The variables affecting the extraction of copper and zinc from brass-melting dross of MKE Kırıkkale Brass Factory were investigated.

To. produce copper and zinc, leach-electrolysis method was used. The dross was roasted first, then was leached with dilute sulphuric acid, and was purified. Subsequently the solution was electrolyzed using platinum electrodes.

Roasting and leaching temperatures, their durations, particle size of the dross, liquid to solids ratio, and acid concentration effected the dissolution of copper and zinc during processing. These effects were investigated seperately and it was found that optimum conditions were: 180 grams of $H_2SO_4$ per 100 grams of dross, liquid to solids ratio 6, 180 minutes of roasting and leaching times respectively, $800^{\circ}C$ of roasting temperature, leaching temperature $60^{\circ}C$, and 0.147 mm. particle size.

Key Words: Brass-Dross, Copper and Zinc Extraction, Leaching.

# ÖZÜ

Bu çalışmada, MKE Kırıkkale Pirinç Fabrikası baca küllerinden bakır ve çinko özütlenmesinde etkin değişkenler incelenmiştir.

Bakır ve çinko üretmek için sıyırma - elektroliz yönteminden yararlanılmıştır. Baca külleri önce kavrulmuş, sonra seyreltik sülfirik asit ile sıyrılmış ve arıtılmıştır. Son işlem olarak çözelti platin elektrodlar yardımıyla elektroliz edilmiştir.

Kavurma ve sıyırma temperatür ile zamanları, baca külü tanecik büyüklüğü, sıvı-katı oranı ve asit derişimi işlem sırasında bakır ve çinkonun çözünürlüğünü etkilemiştir. Bu etkenler birbirinden bağımsız olarak incelenmiş ve en uygun (optimum) koşullar: 100 gram baca külü için 180 gr. $H_2SO_4$, sıvı-katı oranı 6, kavurma zamanı 180 dakika, sıyırma zamanı 180 dakika, kavurma temperatürü $800^{\circ}C$, sıyırma temperatürü $60^{\circ}C$ ve baca külü tanecik büyüklüğü 0.147 mm. olarak saptanmıştır.

Anahtar Kelimeler: Baca Külü, Bakır ve Çinko Özütlenmesi, Sıyırma.

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## INTRODUCTION

Most of the copper and zinc used today for various
purposes are extracted from the ores or concentrates of
these two metals by pyrometallurgical methods of
extraction and through hydrometallurgical processes.

At various stages of extraction, and later during
the manufacture of alloys involving these metals some
copper and zinc are lost to waste products like slags
and dross. With the rising price of metals and increasing
world demand there is an intensive research effort to
either device new processes or establish the best
combination of known methods for the recovery of these
metals from such waste products.

Lost copper alloys contain readily oxidizable
elements, such as, zinc, tin, aluminum, magnesium, and
manganese. Upon melting the oxides separate almost
completely from the melt and form a dross. In some
alloys, such as high zinc brasses and aluminum bronze,
however the separation of the oxide phase is difficult
due to the effects like high surface tension. Thus, the
dross may en**trap** a considerable amount of metal,
resulting in high melting losses.

The brass factory operated by MKE at Kirikkale
produces a large amount of dross the analysis of which
is given in Table 1.

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Table 1 - Chemical Analysis of MKE Brass Dross

| Elements | (wt %) |
|---|---|
| Cu | 20.36 |
| Zn | 43.70 |
| $SiO_2$ | 6.94 |
| $Al_2O_3$ | 4.42 |
| Pb | 1.91 |
| $Fe_2O_3$ | 0.70 |
| Not accounted for | 5.23 |

This thesis is concerned with the winning of copper and zinc from brass-melting dross of MKE Kırıkkale Brass Factory. Following brief outline of extraction methods is pertinent to this study.

## A- METHODS OF COPPER PRODUCTION

Copper may be extracted from its ores and concentrates either by smelting or by leaching. In general, copper ores rarely contain more than 1 or 2 per cent copper. Table 2 presents the common copper minerals occuring in copper ores more often.

### a) Pyrometallurgical Extraction

Amongst these, the ores containing the sulfide group minerals are amenable to pyrometallurgical treatment, owing, mainly, to the exothermic character of the reactions leading to their decomposition. A typical flow-sheet for copper smelting is given in Figure 1.
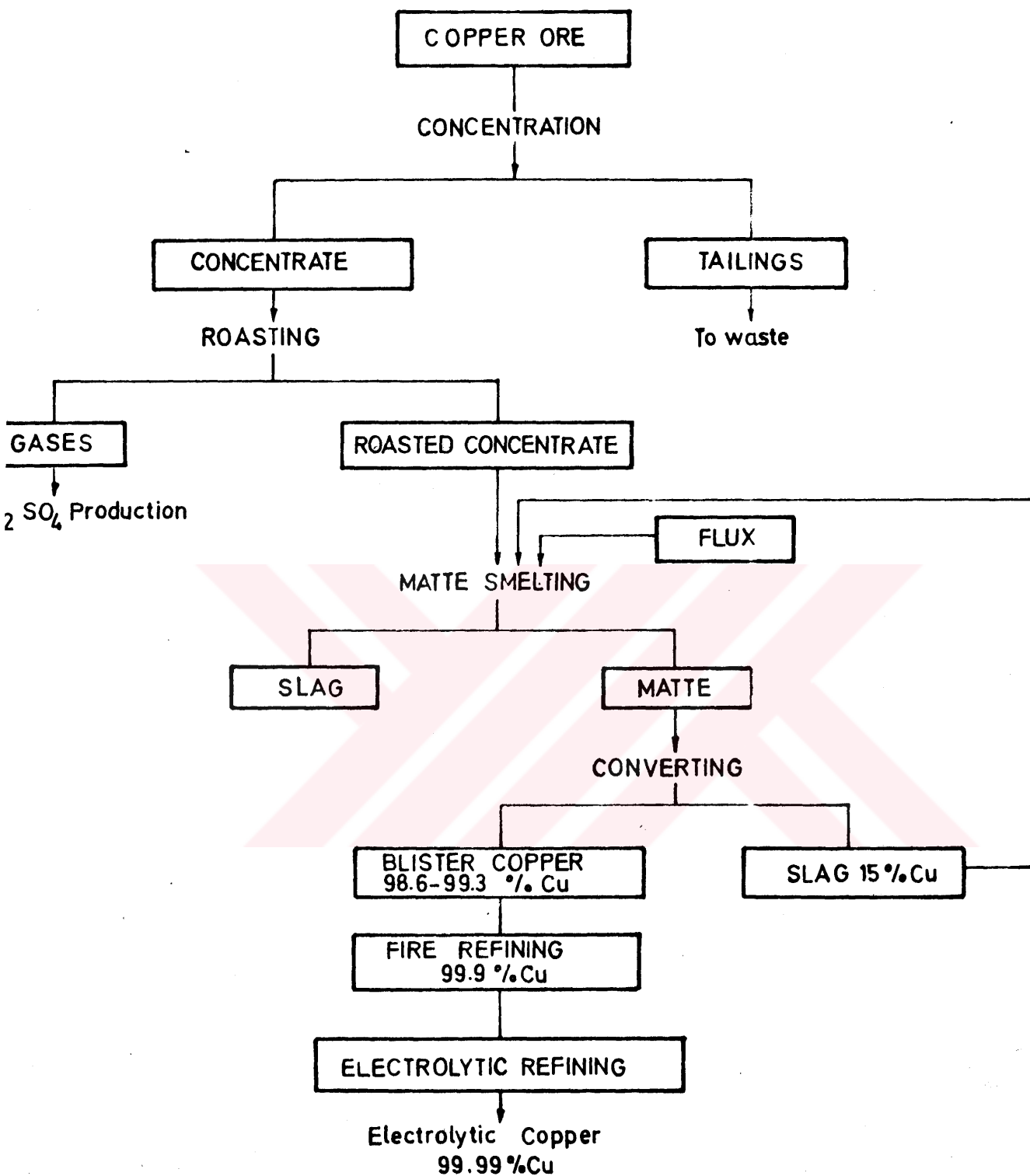
FIG. 1-A SIMPLIFIED FLOW-SHEET FOR COPPER SMELTING.

## Table 2 - Important Copper Minerals

| Mineral | Chemical Formula | Copper content per cent |
|---|---|---|
| Bornite | $5Cu_2S.Fe_2S_3$ | 55.6 |
| Chalcopyrite | $CuFeS_2$ | 34.6 |
| Chalcocite | $Cu_2S$ | 79.9 |
| Covellite | $CuS$ | 66.5 |
| Azurite | $2CuCO_3.Cu(OH)_2$ | 55.1 |
| Cuprite | $Cu_2O$ | 88.8 |
| Tenorite | $CuO$ | 79.9 |
| Native copper | $Cu$ | up to 99.9 |

### b) Hydrometallurgical Extraction

Numerous methods are known for the extraction of copper by hydrometallurgical means. The unit steps which are common to all these methods, however, are the same and can be listed as follows.

1- Bringing the ore, or any intermediate product to a state suitable for dissolution. This is usually roasting, or calcining and can be omitted when the material at hand contains the metal sought in a soluble form.

2- Leaching in a suitable solvent.

3- Purification of the leach solution.

4- Precipitation of the metal either by chemical or by electrochemical methods.

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## 1- Roasting

Roasting is applied in either one of the following forms, oxidizing, reducing, sulfatizing or chloridizing, depending upon the final desirable form of copper. Figure 2 shows a roasting phase diagram for copper at $700^\circ C^{(1)}$, plotted on $\log P_{SO_2}$ - $\log P_{O_2}$ coordinates. The diagram has been drawn for unit activities of condensed phases, i.e., for pure Cu-S-O system. The location of lines depicting the bivariant equilibria would shift both as a function of temperature and dilution with metals like iron, nickel and cobalt capable of forming Metal-S-O systems.

Neglecting, for a moment, the aforementioned dilution effects, the diagram in Figure 2 can be used to predict the phase changes that will take place upon roasting at constant temperature. The dashed line shown in Figure 2 is a commercial roasting course along which the roasted gases analyze $P_{SO_2} + P_{O_2} \cong 0.21$ atm. corresponding to the situation when roasting is conducted with normal air. As seen from the diagram hypothetical ore containing CuS only would undergo the following changes upon roasting at $700^\circ C$:

$$CuS_2 \xrightarrow{a} CuS \xrightarrow{b} Cu \xrightarrow{c} Cu_2O \xrightarrow{d} CuO.CuSO_4 \xrightarrow{e} CuSO_4 \xrightarrow{f}$$
$$CuO.CuSO_4 \xrightarrow{g} CuO.$$
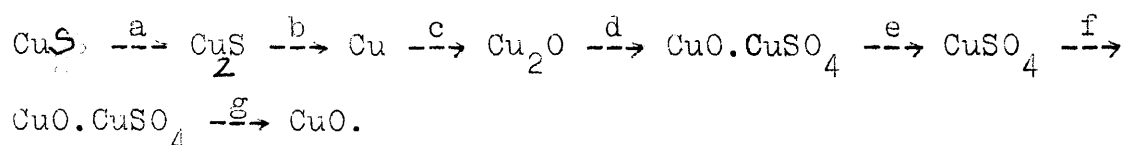
Combining the proper kinetic data with the information given in Figure 2 one may be able to stop in the predominance area of $Cu_2O$ or $CuSO_4$ or CuO and thus be in a position of controlling the products of roasting.

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## 2- Leaching

An ore that is considered suitable for leaching is one that does not respond well to gravity concentration, flotation, or other simple processes.

Solvents for leaching include both acids and bases, as well as some salts, but sulphuric acid is by far the most widely used. This is due partly to its effectiveness as a solvent, and partly to its wide availability and low cost. It is easy to handle and losses in process are low.

There are some necessary reagents in leaching which, like ferrous and ferric sulphate, assist in the dissolution reactions without acting as the principal solvent. Ferric sulphate helps dissolve a number of copper sulfides, and ferrous sulphate acts as a depolarizing agent in copper electrolysis.

The reactions by which copper minerals given in Table 2 dissolved in leaching, either with sulphuric acid or sulphuric acid plus ferric iron, are as follows:

<u>Azurite</u>:

$$Cu_3(OH)_2 \cdot (CO_3)_2 + 3H_2SO_4 = 3CuSO_4 + 2CO_2 + 4H_2O$$
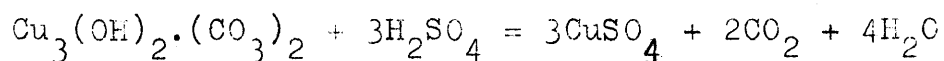
<u>Bornite</u>: Practically all the copper can be dissolved from bornite by leaching with hot acid plus ferrite sulphate.

<u>Chalcopyrite</u>: Only part of the copper in chalcopyrite is soluble in acid plus ferric iron, and

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even to get this solubility, fine grinding, heating of solutions, and a long contact time are required.

### Chalcocite:

$$Cu_2S + Fe_2(SO_4)_3 = CuS + CuSO_4 + 2FeSO_4$$
$$CuS + Fe_2(SO_4)_3 = CuSO_4 + 2FeSO_4 + S$$
___
$$Cu_2S + 2Fe_2(SO_4)_3 = 2CuSO_4 + 4FeSO_4 + S$$

### Covellite:

$$CuS + Fe_2(SO_4)_3 = CuSO_4 + 2FeSO_4 + S$$

### Cuprite:

$$Cu_2O + H_2SO_4 = CuSO_4 + Cu + H_2O$$
$$Cu + Fe_2(SO_4)_3 = CuSO_4 + 2FeSO_4$$
___
$$Cu_2O + H_2SO_4 + Fe_2(SO_4)_3 = 2CuSO_4 + H_2O + 2FeSO_4$$

### Tenorite:

$$CuO + H_2SO_4 = CuSO_4 + H_2O$$
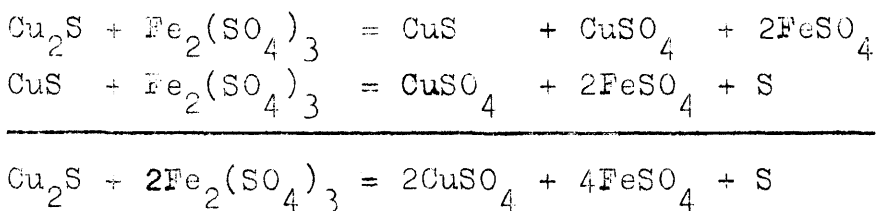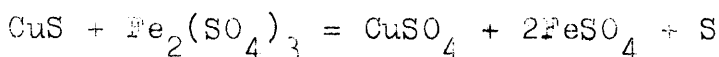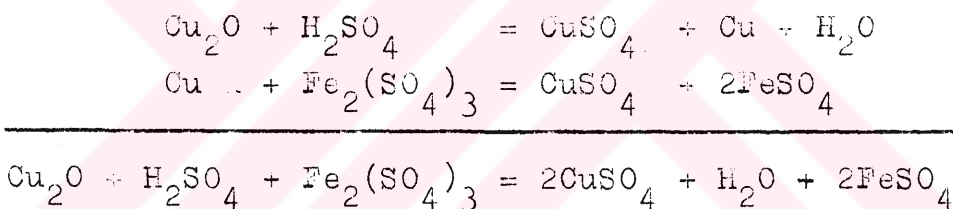
Leaching of copper is conditioned by number of factors, all of them common to the leaching of other metals as well:

    a- Particle size to which the ore is ground
    b- Composition and strength of the solvent
    c- Time of contact
    d- Temperature of the solvent

In addition to these factors, the physical character of the ore and its origin of formation importance.

The object of crushing and grinding for leaching is obviously to permit contact of solvent and mineral, and subsequent removal of solution in a reasonable time.

Choice of strength of solution and solvent is a question of balancing several factors. Practically, the acidity of liquors used for copper leaching is less than 10 per cent. In copper leaching, this acid can not be neutralized completely because compounds of iron and aluminum precipitate from solutions that are too nearly neutral.

Time of contact is a very important factor, especially when leaching slowly soluble sulphides. Usually "time of contact" includes only that time during which fresh leach liquor is brought into contact with the ore.

Temperature is important since the solubility of copper sulphides is raised appreciably by increasing the temperature of the solvent carrying ferric iron.

3- Purification of the Leach Solution

Various means have been developed to purify leach solutions prior to eventual recovery of the metals. The electrolytic and the various chemical methods of precipitation have been applied to several metals.

Iron is removed from the solution by pH adjustments according to the diagram given in Figure 3. Any ferrous iron present is first oxidized to the ferric state with manganese dioxide and by hydrolysing the ferric sulphate:

$$2FeSO_4 + MnO_2 + 2H_2SO_4 = Fe_2(SO_4)_3 + MnSO_4 + 2H_2O$$

$$Fe_2(SO_4)_3 + 2H_2O = 2Fe(OH)SO_4 + H_2SO_4$$
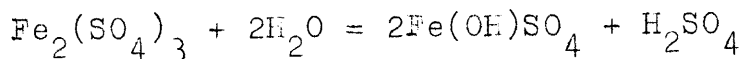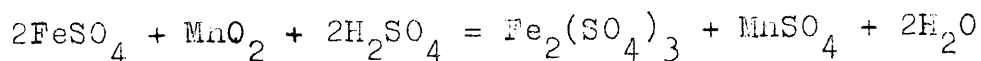
4- Winning of Copper from Leach Solution

Electrolytic recovery of copper from leach solutions is effected with insoluble anodes which are commonly rolled antimonial lead. The current causes copper to plate out on the cathode, and the electrolyte is continuously depleted in copper. Impurities are removed before electrolysis; therefore there is no build-up in the cell. The spent electrolyte is simply used over again as the solvent in leaching.

The electrolytes contain about 24 to 26 grams per liter of copper and 20 to 48 grams per liter of sulphuric acid. Copper deposition efficiencies are at their best when the electrolyte contains more than 20 grams per liter of copper, but a solution of 60 grams per liter of copper and 10 grams per liter of acid does not contain sufficient acid for good conductivity.[4]

Current densities used range from 0.6 to 1.3 amp. per sq. dm., although densities up to 2.1 amp. per sq. dm. have been used successfully.[4] Current density must be carefully chosen to balance several factors but, in
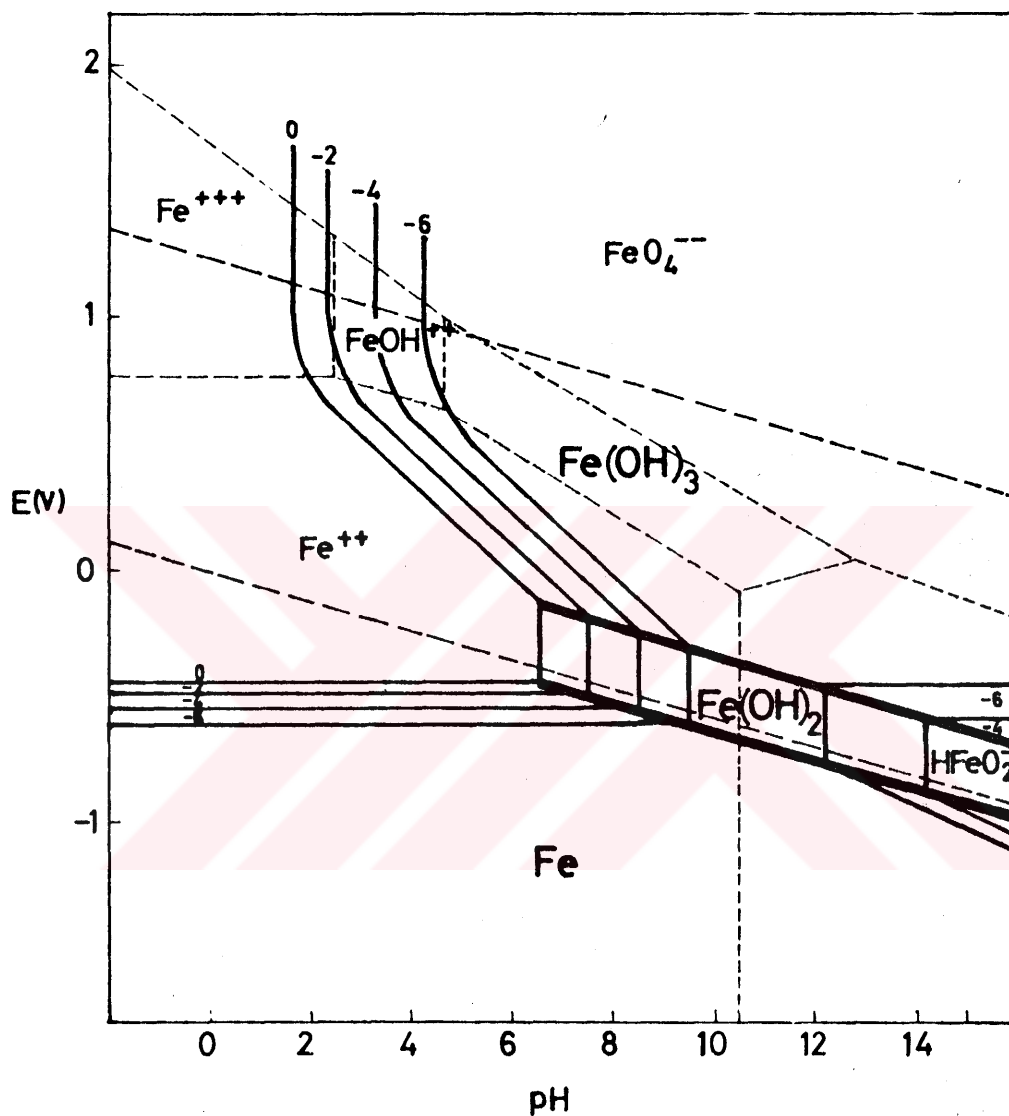
FIG.3_THE POURBAIX DIAGRAM FOR THE
SYSTEM IRON-WATER AT 25°C

general, slow deposition at low current densities favors better condition of the final deposit and higher current efficiency. It is possible under certain conditions to deposit a copper powder by running current density very high.

Current efficiency is simply the ratio of the amount of metal deposited in a unit of time to the amounts that should have been deposited according to Faraday's Law. One ampere-hour should yield 1.186 grams of copper at 100 per cent efficiency. Losses of current can occur because of poor connections, leakage in various parts of the circuit, insufficient circulation of electrolyte (which may cause hydrogen to form at the cathode), or actual short-circuiting of electrodes through "tree" formation.

In addition to electrowinning there are some chemical methods of precipitation, and they are used to recover copper when the electrolytic recovery is not desired. Obviously there are a considerable number of theoretically possible precipitants, but only three are in actual use. These are:

    1- Precipitation by iron, usually called cementation

    2- Precipitation as cuprous chloride by metallic copper from solutions carrying chlorine

    3- Precipitation from ammonia solutions by decomposing and driving off the solvent.

A simplified flow-sheet for copper hydrometallurgy is given in Figure 4.
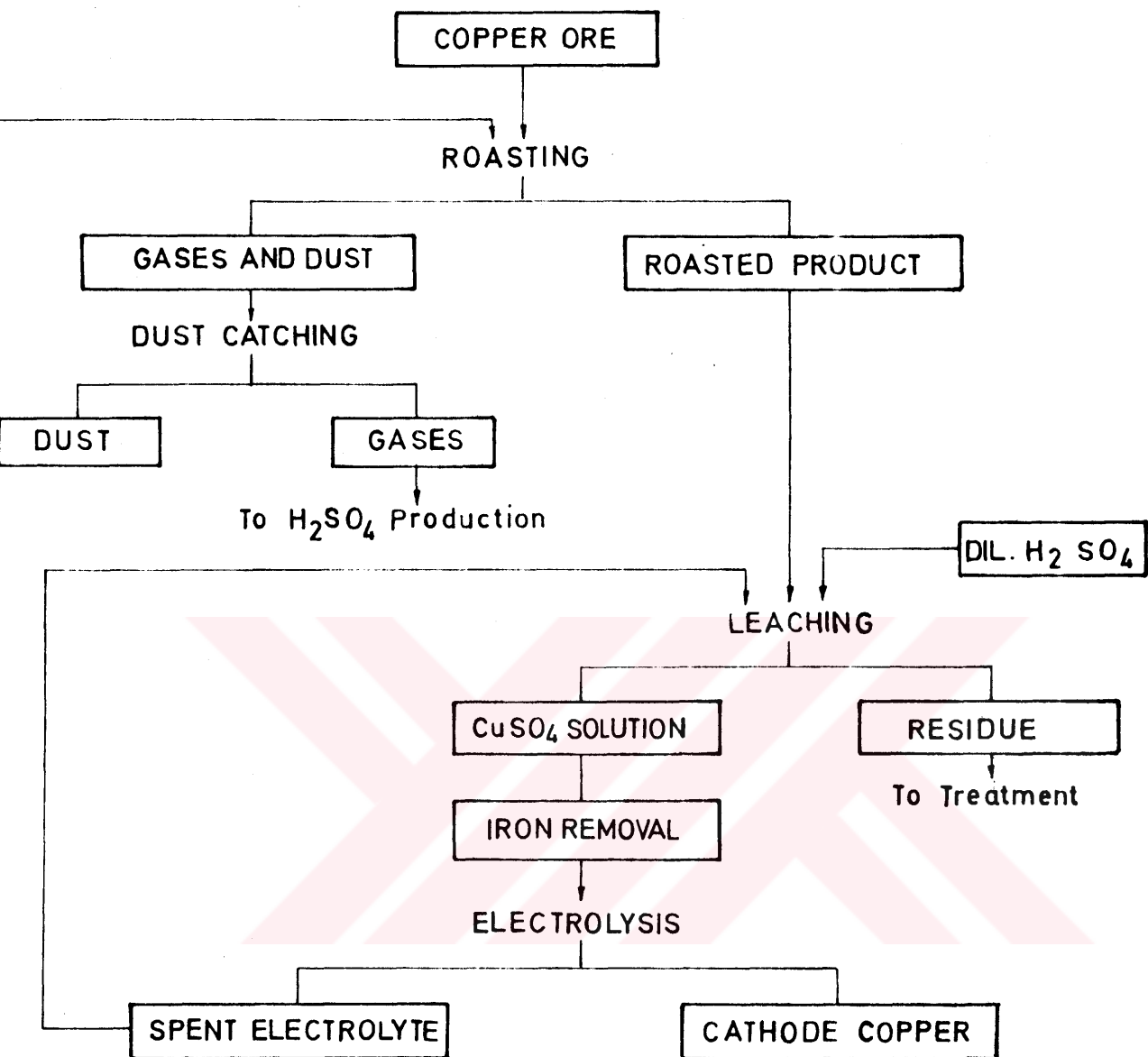
FIG. 4—A SIMPLIFIED FLOW-SHEET FOR COPPER HYDROMETALLURGY.

## B- METHODS OF ZINC PRODUCTION

Zinc is found in nature as a few minerals. The principal among them is zinc sulphide, ZnS, known as sphalerite or zinc blende, and its variety marmatite which is an isomorphic mixture of zinc and iron sulphides (Zn, Fe)S. Next in importance are zinc carbonate $ZnCO_3$ known as smithsonite, and zinc silicate, $Zn_2SiO_4.H_2O$, called hemimorphite or calamine. The other minerals occur seldom and are of no commercial value.

The metallurgy of zinc is divided into two fields: pyrometallurgy and hydrometallurgy. The former is mainly presented by the distillation processes, and the latter by the electrolytic processes.

### 1- Roasting of Zinc Ores

The main purpose of roasting zinc ores or concentrates is to convert the zinc sulphide to zinc oxide and to expel the sulphur dioxide gas. Accordingly, the principal reaction of concentrate roasting is:

$$2ZnS + 3O_2 = 2ZnO + 2SO_2 + 223.6 \text{ kcal.}$$
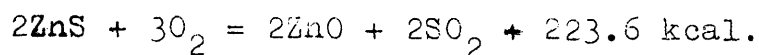
The ignition point of zinc sulphide depends on its mineralogical composition and grain size. For practical purposes it may be assumed that the zinc sulphide concentrate ignites at anywhere between $550^{\circ}C$ and $600^{\circ}C$. The rate of combustion increases with increasing temperature and decreases as more sulphur is burned out, for the reason that the oxide film forming on the surface of each grain shuts out oxygen.

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The heat balance of the roasting operation is made up of the heat input from the combustion of the sulphides and the heat losses to the surroundings. As the rate of combustion is reduced, heat input per unit time is reduced too and at certain moment of time it becomes equal to heat losses. It is at this moment that the spontaneous burning of the sulphides ceases. Too high a temperature of roasting may cause the particles to sinter or fuse, which fact would hamper the inflow of air to the sulphides and the rate of combustion of the sulphur would drop rapidly.

In roasting, some of the zinc sulphide is oxidized to zinc sulphate, which may be expressed by the following equations:

$$2SO_2 + O_2 = 2SO_3 + 45.2 \text{ kcal}$$

$$ZnO + SO_3 = ZnSO_4 + 55.6 \text{ kcal}$$
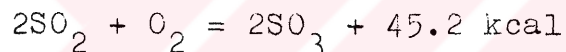
The impurities contained in the zinc concentrate are oxidized in roasting to form $Fe_2O_3$, CuO, CdO, $Sb_2O_3$, and $As_2O_3$. The oxides of arsenic and antimony partly pass of as fumes, and are partly oxidized to higher and less volatile oxides.

The acid oxides $SO_3$, $As_2O_5$, $Sb_2O_5$, $Fe_2O_3$, $SiO_2$ etc, react with the basic oxides and carbonates, i.e., CdO, FeO, CuO, PbO, $CaCO_3$ and $MgCO_3$ to form respective zinc sulphates, arsenates, antimonates, ferrites and silicates. All of the reactions here do not reach completion owing to the fact that either the reacting materials are not present in stoichiometric proportions,

or contact between them is upset, or the rate of
interaction is too low. The most detrimental secondary
reactions in roasting are those producing ferrites of
zinc and cadmium and silicates of lead and zinc. The
latter, reacting with the sulphuric acid in the
subsequent leaching, form colloidal silicic acid which
hampers filtration and settling. Zinc ferrite, on its
part, reacts with sulphuric acid but slowly, and the
zinc fixed in it does not practically pass into solution.
At low temperatures, the rate of zinc ferrite formation
is insignificant, but it rapidly increases at above
$650^{\circ}$C. The largest quantity of zinc ferrite is produced
in roasting zinc concentrates containing marmatite for
the reason that in marmatite sulphides of zinc and iron
make up an isomorphic mixture.

2- Leaching of Roasted Product

The primary purpose of leaching a zinc concentrate
is to dissolve the zinc oxide:

$$ZnO + H_2SO_4 = ZnSO_4 + H_2O$$

Being a simple process in itself, it is
complicated, however, by the simultaneous dissolving of
unwanted elements and compounds which have an adverse
effect on the electrolysis and recovery of zinc. For this
reason, a two-prong approach has to be taken to the
leaching operation: firstly, to minimize the amount of
impurities passing into solution; secondly, to purify
the solution.

Many of the impurities can be reduced in amount
or eliminated by neutralizing the zinc sulphate solution
with zinc oxide, with the formation and precipitation of
ferric hydroxide. This method is commonly called "iron
purification" and is usually carried out simultaneously
with leaching. To this end, any ferrous iron present is
first oxidized to the ferric state with manganese
dioxide and by hydrolysing the ferric sulphate:

$$2FeSO_4 + MnO_2 + 2H_2SO_4 = Fe_2(SO_4)_3 + MnSO_4 + 2H_2O$$

$$Fe_2(SO_4)_3 + 2H_2O = 2Fe(OH)SO_4 + H_2SO_4$$
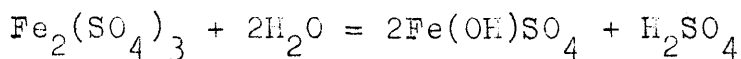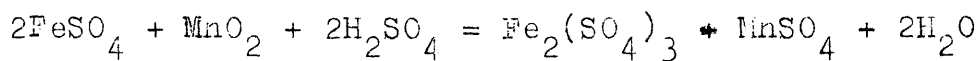
The first reaction is possible in an acid medium,
therefore, the iron has to be oxidized at the beginning
of the leaching operation. The second reaction is
feasible only at the end of the leaching when the acid
has been depleted and the solution is almost neutral.

The arsenic and antimony are removed from the
solution simultaneously with iron.

The principal reaction of copper and cadmium
elimination is that of electrolytic reduction: both
copper and cadmium are below zinc in the electromotive
series, and zinc replaces them:

$$Cu^{2+} + Zn = Cu + Zn^{2+}$$

$$Cd^{2+} + Zn = Cd + Zn^{2+}$$

The purification may be carried out with zinc dust. More zinc must be added than is required theoretically to precipitate the copper and cadmium present for the reason that some of the zinc is dissolved due to the reduction of hydrogen ions. The removal may be enhanced by increasing the temperature of the solution.

The clarified solution may be further treated for the removal of cobalt with sodium xanthogenate and blue vitriol.

The purified solution may be treated for the elimination of chlorine which may come from running water or chlorine-bearing recycled materials. The removal of chlorine is based on the precipitation of nearly insoluble chlorides of copper, silver or mercury. Copper purification is used in most cases; the reagent is freshly deposited cement copper.

The harmful effects of some impurities may be moderated by the addition of surface-active materials to the electrolyte. These addition agents may be glue, goulac and various organic substances. Most often, up to 0.1 gram of glue per litre is added for the purpose. This, however, does not make solution purification unnecessary.

The complete recovery of zinc requires an excess of sulphuric acid. On the other hand, the solution should be neutral towards the end of the leaching operation if the iron is to be withdrawn successfully. To meet these requirements the leaching operation is

carried out in two stages (double leaching). First, roasted ore is treated with a slightly acid solution of $ZnSO_4$ containing about 100 to 130 grams of zinc per litre and 1 to 5 grams of free sulphuric acid per litre. The acid present will not leach out all of the zinc, only some of it will pass into the solution which will be neutral and therefore clean of iron. This stage is called the neutral leach. The insoluble residue of the neutral stage still carries much zinc, and it is re-treated by depleted electrolyte containing about 100 grams of $H_2SO_4$ per litre in the second stage called the acid leach. Towards the end of the second stage, the concentration of sulphuric acid in the solution drops to 1-5 grams per litre, and it is used for neutral leaching.

The rate of leaching depends on the concentration of sulphuric acid. As it is higher in the acid than in the neutral leach, the bulk of the zinc passes into solution during the second stage. The other factors affecting the rate of leaching are temperature, the grain size of the roasted ore, agitation, etc.

As the temperature rises, the rate of leaching increases due to an increase in the rate of diffusion and the rate of chemical reactions between the sulphuric acid and the solid zinc compounds.

The grain size of the ore affects the rate of leaching above all for the reason that the coarse and fine particles differ in chemical composition. The coarse particles are mainly sintered zinc sulphides,

ferrites, and silicates which react with sulphuric acid
but slowly. Furthermore, the zinc contained in the larger
particles passes into solution more slowly than the
fines: in the coarse particles the surface of the zinc
compounds may be isolated from the solution by the
gangue, while in the fine particles it is exposed. As
the grain size decreases, the surface area of solids per
unit weight increases, and the rate of solution is
directly proportional to the surface area of the particles.
This is why coarse-grained material should preferably be
reground prior to leaching.

The agitation of the pulp consisting of solid
particles and solvent speeds up diffusion. The solid
particles should be always held in suspension for better
contact between their surface and the solvent.

The equipment for leaching may be either air-
operated or mechanical. In air-operated apparatus, the
pulp is agitated by compressed air, and in mechanical
equipment by a rotary stirrer.

The efficiency of filtering varies with the
composition of the zinc ore being treated, roasted and
leaching conditions. The roasting of ores high in silica
produces considerable quantities of zinc silicates,
their formation increasing directly with silica content,
and roasting temperatures.

The acid leach step destroys the zinc silicates
to form colloidal silicic acid:

$$MO.SiO_2 + H_2SO_4 + (n-1)H_2O = MSO_4 + SiO_2.nH_2O$$
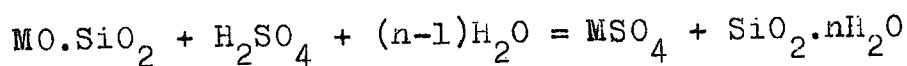
Colloidal silicic acid, depositing on the filtering medium, bridges the pores and reduces the rate of filtrate flow. This detrimental effect of silicic acid on filtering may be controlled by roasting at lower temperatures and by conducting the acid leach at reduced pH values. The heating of the pulp prior to filtering promotes the coagulation of silicic acid.

3- The Electrolysis of the Leach Solution

The purified neutral solution which contains ions $Zn^{2+}$, $SO_4^{2-}$, $H^+$ and $OH^-$ is subjected to electrolysis. Both ions of zinc and hydrogen can discharge at the cathode:

$$Zn^{2+} + 2e = Zn \quad , \quad E^0 = -0.76V$$

$$2H^+ + 2e = H_2 \quad , \quad E^0 = 0.00V$$
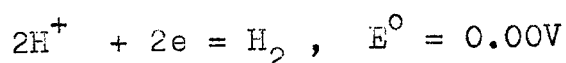
On the basis of their electrode potentials, it would appear that the electrolysis of zinc sulphate solution would result simply in the decomposition of water with the production of hydrogen at the cathode. This is not the case, however, and zinc is successfully recovered by electrolysis of aqueous electrolytes. The Pourbaix diagram for the system $Zn-H_2O$ at $25^0C$ is given in Figure 6.

The explanation lies in that the actual potential to deposit hydrogen at a zinc electrode is much higher

- 21 -
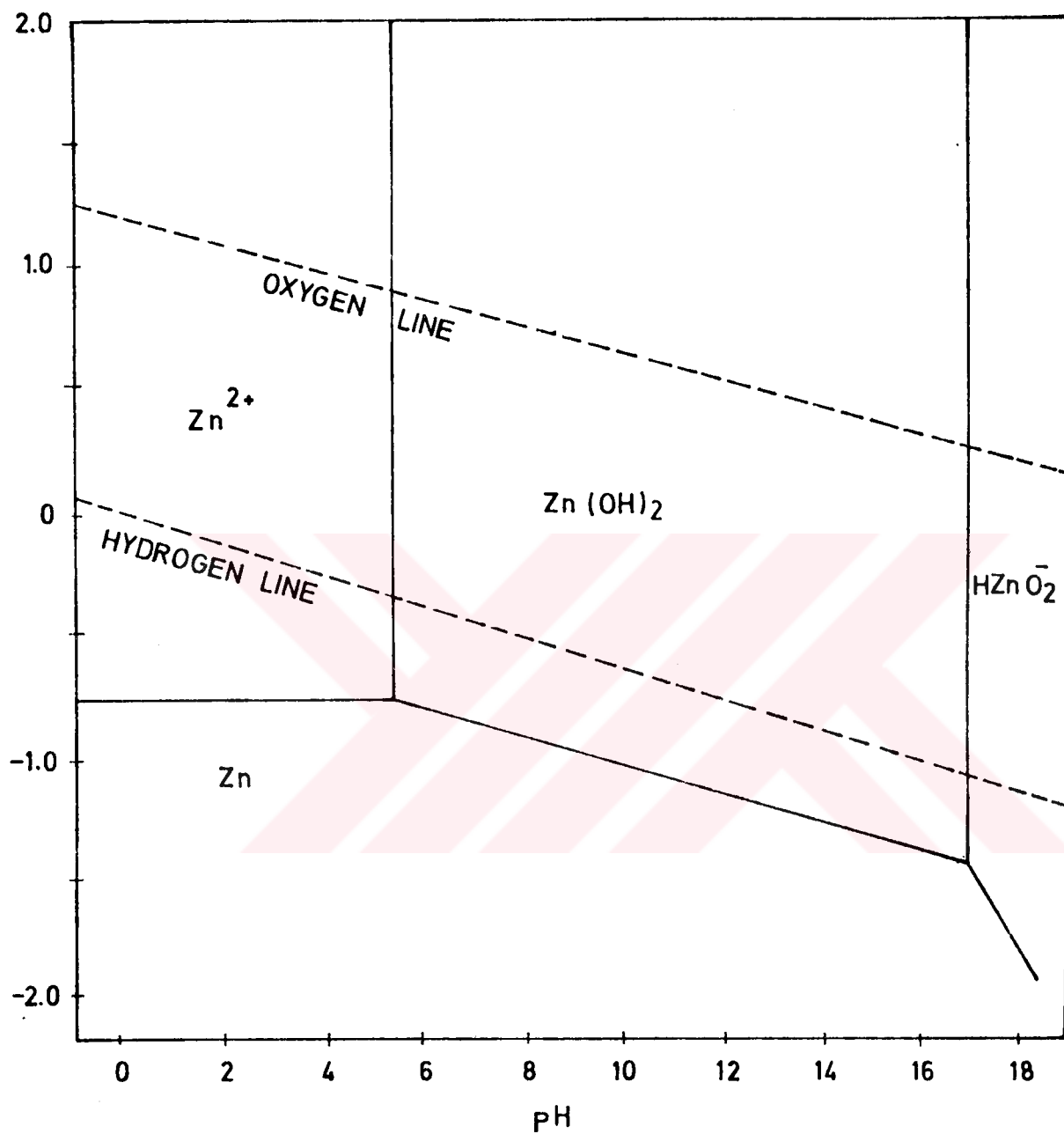
FIG. 5 - THE POURBAIX DIAGRAM FOR THE SYSTEM Zn-$H_2O$ AT 25°C, ASSUMING UNIT ACTIVITIES.

than the theoretical value. This difference is called the hydrogen overvoltage of a zinc electrode. The hydrogen overvoltage is due to the fact hydrogen ions have a lower rate of discharge than have zinc ions.

It is essential to reduce hydrogen production at the cathode, for this improves the current efficiency of electrolysis. To this end, all factors that tend to increase the hydrogen overvoltage on zinc should be utilized where possible.

The discharge potential of zinc ions is very close to that determined by the Nernst Equation:

$$E_{Zn} = E^O \pm (RT/nF)Lnf_{Zn}C_{Zn} \cong -0.76 + 0.029 \ logf_{Zn}C_{Zn}$$

where

$E^O$ = electrode potential;

$C_{Zn}$ = zinc concentration in electrolyte;

$f_{Zn}$ = activity of zinc ions.

The discharge potential of zinc ions grows more positive as their concentration (or, rather, their activity) in the solution increases.

The discharge potential of hydrogen ions is the sum of the equilibrium potential and overvoltage.

$$E_H = 0.058 \ logf_H C_H + \eta$$

where $\eta$ is the overvoltage, V.

As electrolysis progresses, the zinc concentration in it is reduced, its acidity increases, and current efficiency decreases, making the complete recovery of zinc from the electrolyte economically unattractive. The usual practice is to withdraw the electrolyte from the cell after about half the zinc has been recovered and the equivalent amount of free sulphuric acid has been regenerated. The depleted electrolyte is then used to leach roasted ore or concentrate. The zinc left in the spent electrolyte, is a ballast on the process. Therefore it is desirable to keep the amount of zinc left in the electrolyte to a minimum.

A simplified flow-sheet for zinc hydrometallurgy is given in Figure 6.

```
              ┌──────────────┐
              │   ZINC ORE   │
              └──────────────┘
                     │
                 ROASTING
          ┌──────────┴───────────────┐
  ┌────────────────┐        ┌──────────────────┐
  │ GASES AND DUST │        │ ROASTED PRODUCT  │
  └────────────────┘        └──────────────────┘
          │
   DUST CATCHING
    ┌─────┴─────┐
┌────────┐  ┌────────┐
│  DUST  │  │ GASES  │
└────────┘  └────────┘
                │
        To H₂SO₄ Production
```

To $H_2SO_4$ Production

┌──────────────┐
│ DIL. $H_2SO_4$ │
└──────────────┘

LEACHING

┌─────────────────┐        ┌──────────────┐
│ Zn SO₄ SOLUTION │        │   RESIDUE    │
└─────────────────┘        └──────────────┘

Zn $SO_4$ SOLUTION

┌──────────────┐
│ PURIFICATION │
└──────────────┘

ELECTROLYSIS

┌─────────────────────┐        ┌──────────────┐
│ SPENT  ELECTROLYTE  │        │ CATHODE ZINC │
└─────────────────────┘        └──────────────┘

CATHODE  ZINC MELTING

┌──────────────┐
│  SLAB ZINC   │
└──────────────┘
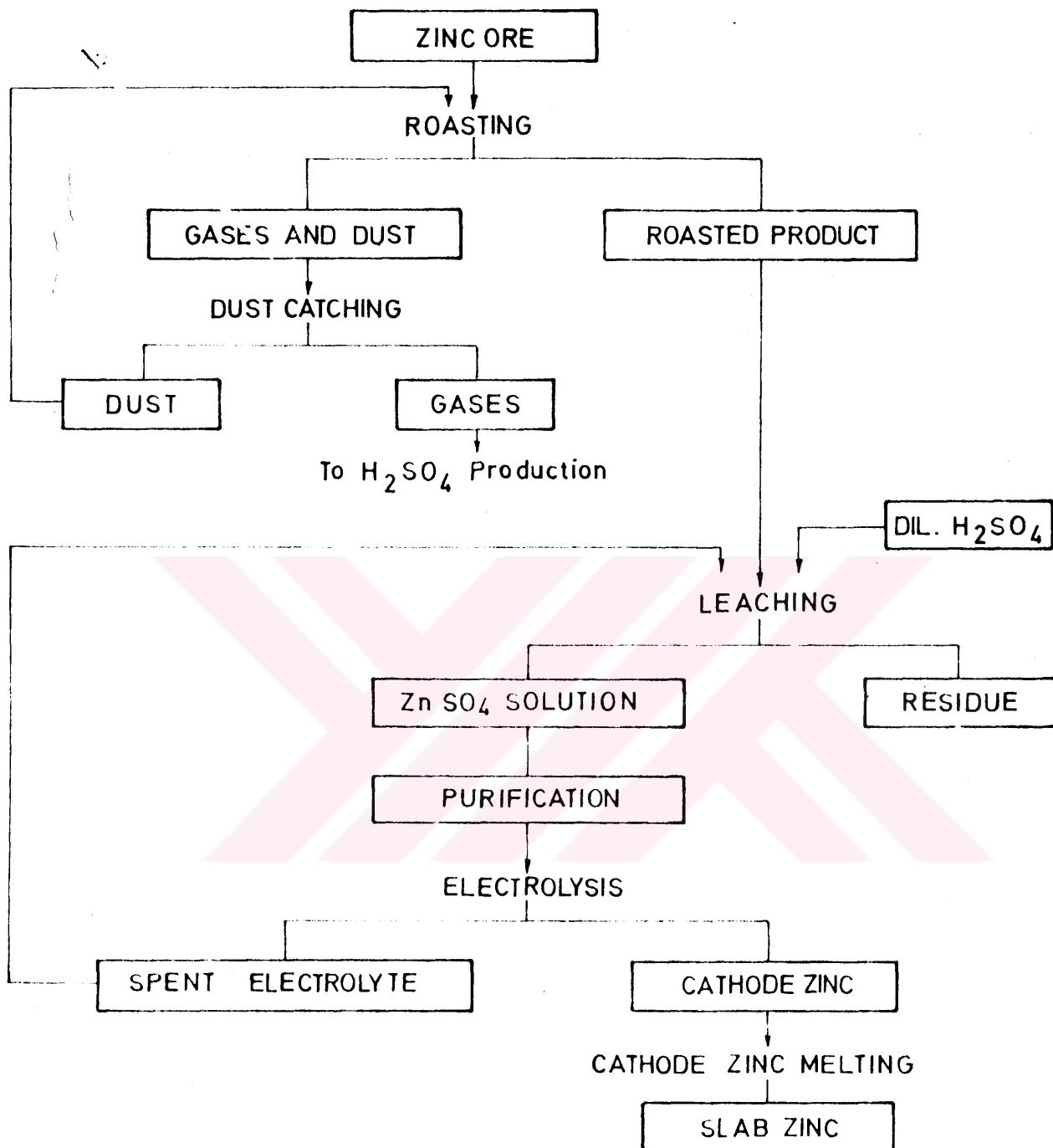
.6 - A SIMPLIFIED  FLOW-SHEET FOR ZINC HYDROMETALLURGY.

25-A

C H A P T E R  II

EXPERIMENTAL PROCEDURE

A- GENERAL PROCEDURE

The experiments of this study were designed to
determine the proper working conditions for the
extraction of copper and zinc from brass dross. For this
purpose, the dross was crushed in a jaw crusher for size
reduction. Later, these smaller pieces were ground in
roller and gyratory crushers in order to obtain a
material fine enough for subsequent roasting experiments;
the ground product was subjected to size classification
and the copper and zinc content of each size group were
determined in order to eliminate errors which might have
arised due to heterogeneous metal distribution.

Roasting experiments were performed in order to
convert metallic copper into copper oxide which is more
soluble in $H_2SO_4$ than the former. For roasting a 100 gm.
portion of ground dross was placed in a rectangular
silica tray and inserted into a "Gallenkamp" muffle
furnace, heated with resistance-heating elements. An air
pump was fitted to the furnace to provide necessary air.
The temperatures within this furnace were measured and
maintained constant to $\mp 5^{o}C$ by means of built-in
temperature measuring and controlling devices.

At the end of each roasting run, the trays were taken out from the furnace, cooled to room temperature, weighed and leached in water acidulated with sulphuric acid. In all leaching experiments the aim was to determine the optimum conditions of leaching time, leaching temperature, liquid to solids ratio and concentration of the sulphuric acid which are effective for complete dissolution.

Leaching experiments were performed in 2 lt pyrex-beakers. The stirring of the leach solutions were effected by an electrically operated device, while the temperatures during leaching were kept constant by the use of a Haake Water Bath. For each leaching experiment the roasted product was placed in the beaker, the proper amount of water was added, and commercial $H_2SO_4$ (sp.gr.1.815 - 1.820, 90%) was employed as the solvent. Upon termination of leaching the leach solution was filtered, the copper and zinc concentrations were determined analytically.

B- CHEMICAL ANALYSIS

Qualitative Analysis: Qualitative analysis of the samples were done by using atomic spectroscopy method.

Quantitative Analysis: The elements observed in qualitative analysis were analyzed quantitatively by combining gravimetric, electrolytic and atomic absorption methods. Details of these analysis are given below.

a) Tin: Dissolve 5 grams of the sample in 40 cc. of dil. $HNO_3$ (2:1), cover immediately with a watch glass, and when violent action ceases, boil until no more red

fumes are given off. Place the beaker on a water bath and digest for 0.5 hour. Dilute with 50 cc. of water and filter at once, if the alloy contains phosphorus, washing very thoroughly with 2% $HNO_3$.

Test the last drops of the filtrate with a little potassium ferrocyanide or ammonium sulphide solution, neither solution should give any precipitate, place the filter paper and contents in a weighed porcelain crucible smoke off the paper and ignite for 15 minutes in the full heat of a burner. Cool in a desiccator and weight. This represents $SnO_2$ + $Sb_2O_4$ + $P_2O_5$, together with traces of Fe, Cu and Pb. The P and Sb are separetely determined, calculated to oxides and subtracted from the above weight. The remainder is $SnO_2$. Calculate to Sn by multiplying with the factor 0.7877.

b) <u>Copper and Lead</u>: Dilute the filtrate from the Sn determination to approximately 200 cc. and add conc. $HNO_3$ until the solution contains approximately 10%. Then add 1 cc. of conc. $H_2SO_4$. Electrolyze the solution in a beaker, starting with a current of 2 amperes and gradually working up to 3 amperes, as the blue color of the solution disappears. By using stationary platinum electrodes, continue the electrolysis for 45 minutes. At the end of this time stop the rotation of the electrode but do not turn off the electrolysis current. Lower the beaker and shut off the current just before the electrodes come out of the solution. Quickly wash the electrodes with a stream of distilled water from a wash bottle. Remove and immerse immediately in methyl alcohol. Then burn off the alcohol in the air, keeping

the electrode in constant motion. Cool in a desiccator and weigh. The cathode contains the Cu in the metallic state and the anode contains the Pb as $PbO_2$. Calculate the latter to Pb by multiplying with the emprical factor 0.8643.

Test the solution for complete removal of Cu and Pb by further electrolysis with fresh electrodes and weigh any further deposit which may form.

c) Zinc: To the filtrate from The Cu and Pb determinations add 5 cc. (not more) of conc. $H_2SO_4$ and evaporate to the appearance of $SO_3$ fumes. Cool, rinse into a suitable beaker, and dilute to approximately 150 cc. Add 50 cc. of 30% NaOH solution and electrolyze the solution using a current of 3 amperes and 2.5 volts, and a cathode which has been plated with Cu. The cathode used previously in the determination of Cu is suitable. The Zn generally deposits out in 15 minutes. After weighing the deposit, however, dissolve off the Zn in dil. HCl (1:1), wash, dry and weigh, then electrolyze for 10 minutes more in the same solution to insure the complete removal of all Zn. The manipulation for this determination is exactly as in the Cu determination and the Zn is weighed as metallic zinc.

Because of difficulties encountered in electrolytic zinc determination, zinc was later analized by Atomic Absorption Method. For this purpose a Pye Unicam SP90 Atomic Absorption Spectrophotometer was used at a wavelength of 213.9 mµ . Details of analysis and sample preparation were given in the Unicam Absorption Method Zn1[15].

d) <u>Iron</u>: A 500 mg of the dross was placed in a [...]
beaker, wetted with a few drops of water, and 15 ml of
HCl was added. The sample was heated near to boiling,
any dark particles remaining undissolved was attacked
by a few drops of HF addition. Upon cooling the solution
was filtered, the filtrate was heated on a hot plate.
In order to reduce any ferric iron present to ferrous
state stannous chloride solution was added dropwise
until the yellow color of the solution has disappeared.
The excess of stannous chloride was absorbed by 10 ml
of mercuric chloride solution addition. The volumetric
determination of iron after this stage consisted in
putting 10 ml 1:5 $H_2SO_4$, 5 ml $H_3PO_4$, and a few drops of
diphenylamine barium sulfonate salt indicator to the
solution and titrating it with 0.1 N potassium dichromate
to the end point.

C H A P T E R  III


RESULTS


Experimental data obtained in **this** work, by
using the methods described in previous chapter, are
presented in Tables 3 through 11. These data are
summarized in graphical form in Figures 7 through 20.
The data pertain the experimental findings on roasting,
leaching and extraction.


1- X-Ray Diffraction Pattern


The raw dross subjected to X-ray diffraction
analysis yielded the pattern **given** in Table 3. Upon
comparison with ASTM card files the peaks were identified
as shown in this Table.


Table 3 - X-Ray Diffraction Results

| 2θ | θ | Sinθ | I | I/I₁ | d | Peaks |
|---|---|---|---|---|---|---|
| 39.90 | 19.950 | 0.3420 | 2.8 | 16.6 | 3.3572 | - |
| 48.00 | 24.000 | 0.4067 | 10.8 | 64.0 | 2.8162 | ZnO |
| 52.20 | 26.100 | 0.4410 | 8.6 | 50.9 | 2.6037 | ZnO |
| 55.10 | 27.550 | 0.4670 | 16.9 | 100.0 | 2.4765 | ZnO |
| 73.65 | 36.825 | 0.6000 | 4.0 | 23.61 | 1.9111 | - |
| 89.60 | 44.800 | 0.7060 | 4.5 | 26.70 | 1.6256 | - |
| 101.60 | 50.800 | 0.7760 | 4.3 | 25.40 | 1.4781 | - |
| 112.30 | 56.150 | 0.8310 | 5.0 | 29.60 | 1.3792 | - |
| 114.80 | 57.400 | 0.8450 | 2.5 | 14.80 | 1.3597 | - |
| 135.40 | 67.700 | 0.9270 | 1.5 | 8.86 | 1.2381 | - |

Other peaks couldn't be identified.

## 2- Copper and Zinc Distribution as a Function of Particle Size

The ground dross was screened to pass through different sieves. The copper and zinc content of four size groups were determined as shown in Table 4.

### Table 4 - Copper and Zinc Distribution in Raw Ground Dross

| Particle Size mm. | Copper wt % | Zinc wt % |
| --- | --- | --- |
| 0.589 | 19.62 | 43.70 |
| 0.295 | 20.36 | 43.75 |
| 0.147 | 20.04 | 43.67 |
| 0.053 | 20.00 | 43.70 |

The copper and zinc percentages given represent an **average** of three determinations on each size group in order to ensure reproducibility.

## 3- Effect of Roasting Temperature

100 gram portions of dross were placed in silica trays and roasted for three hours at temperatures $500^{\circ}C$, $600^{\circ}C$, $700^{\circ}C$, and $800^{\circ}C$. The particle size was 0.147 mm. Each roasting product was cooled and later leached three hours at room temperature in water containing 105 gr. sulphuric acid with a liquid to solids ratio of 4/1. The copper and zinc extraction results from these samples as a function of roasting temperature are shown

in Table 5. Later 0.295 mm. particle size for copper extraction and 0.589 mm. particle size for zinc extraction were examined under **same** roasting and leaching conditions to determine the effect of roasting temperature. These results are also tabulated in Table 5.

Table 5- Effect of Roasting Temperature on
Copper and Zinc Extractions.

| Roasting Temp. ($^{o}$C) | Particle Size (mm.) | | | |
|---|---|---|---|---|
| | 0.147 | 0.295 | 0.147 | 0.589 |
| | Cu Extraction(%) | | Zn Extraction(%) | |
| 500 | 45 | 39 | 27 | 32 |
| 600 | 58 | 47 | 30 | 35 |
| 700 | 65 | 50 | 81 | 47 |
| 800 | 72 | 40 | 83 | 47 |

The data given in Table 5 are shown graphically in Figures 7 and 8 where copper and zinc extraction are plotted versus temperature of roasting, respectively. These figures indicate that roasting around 700-800$^{o}$C is very effective in taking most of the charged copper into solution and roasting around 700$^{o}$C is effective for zinc.

4- Effect of Particle Size

Copper and zinc extraction through leaching from charge prepared with nine different size groups are listed in Table 6, and shown graphically in Figure 9 and 10. It is apparent that higher the size reduction
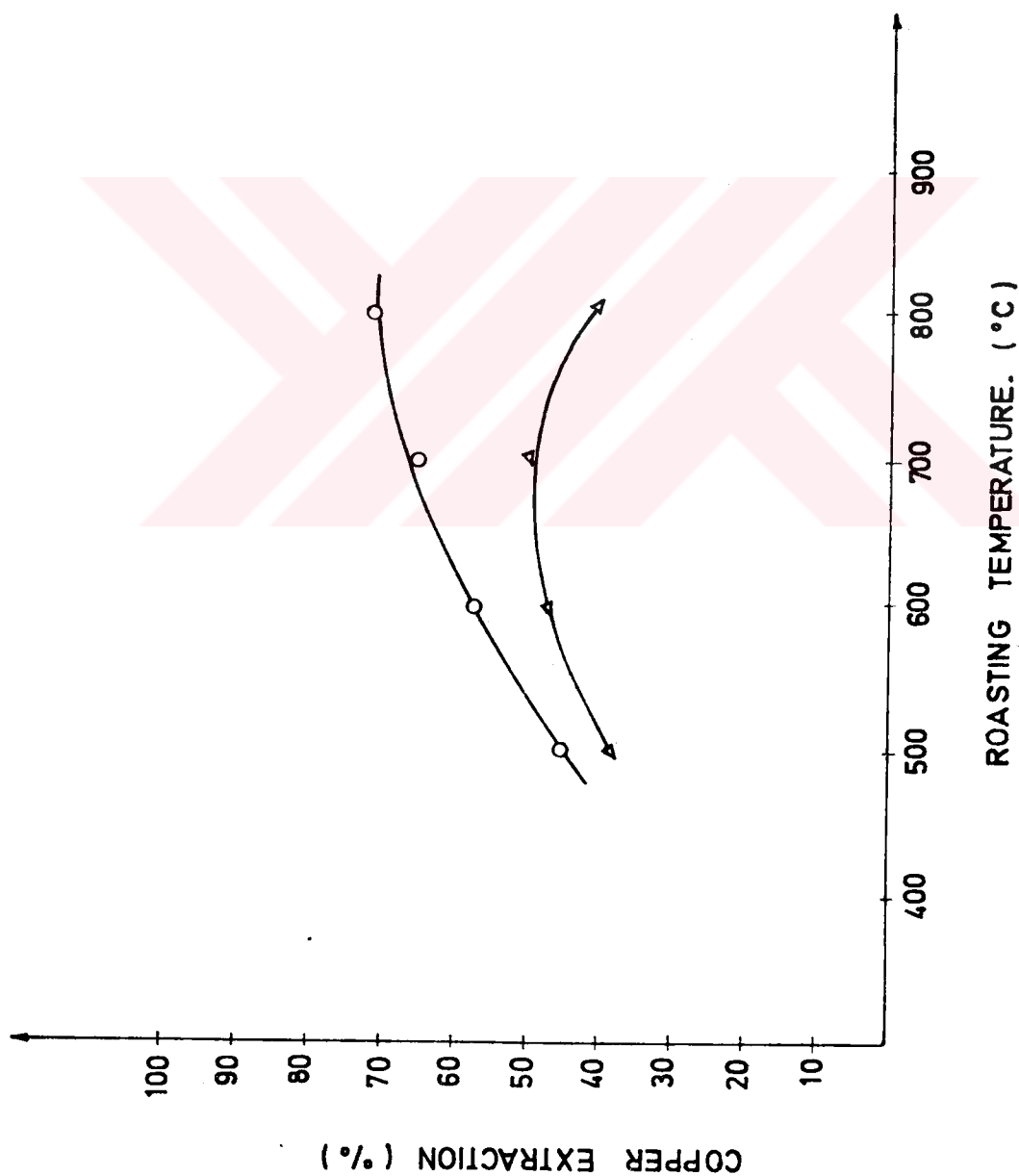
PARTICLE SIZE =
Δ =   0.295 mm.
ο =   0.147 mm.
LEACHING TIME   = 3 hr.
LEACHING TEMP.   = 25 °C.
LIQUID/SOLIDS   = 4/1.
$H_2SO_4$   = 105 gr.
ROASTING TIME   = 3 hr.

COPPER EXTRACTION (%)

ROASTING TEMPERATURE. (°C)

FIG.7- THE EXTRACTION OF COPPER (%) AS A FUNCTION OF ROASTING TEMPERATURE.(°C)

FIG.8- THE EXTRACTION OF ZINC (%) AS A FUNCTION OF ROASTING TEMPERATURE(°C)
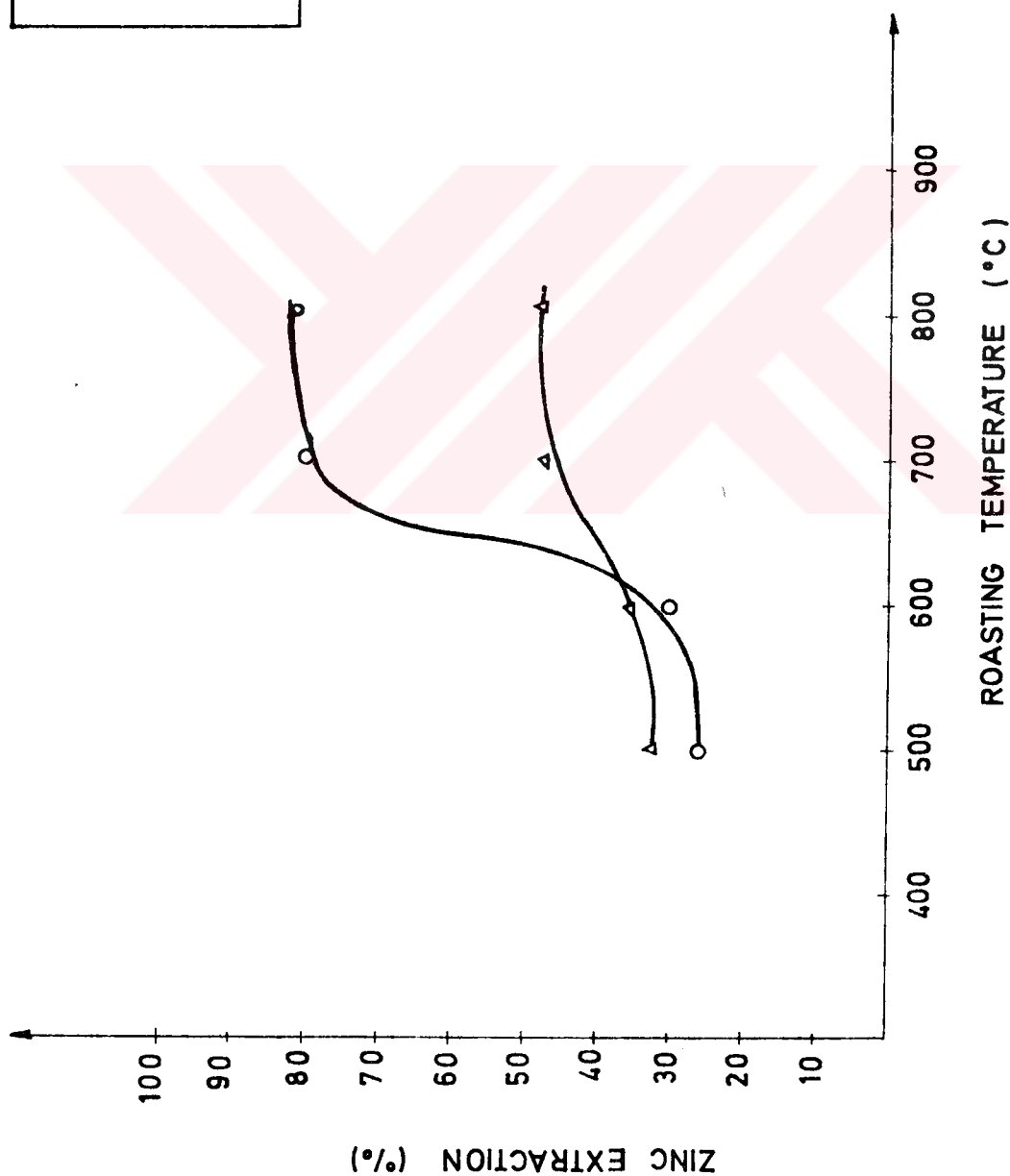
PARTICLE SIZE =
  o = 0.147 mm.
  Δ = 0.589 mm.
LEACHING TIME = 3 hr.
LEACHING TEMP = 25°C
LIQUID/SOLIDS = 4/1
$H_2SO_4$ = 105gr.
ROASTING TIME = 3hr.

FIG. 9- THE EXTRACTION OF COPPER (%) AS A FUNCTION OF PARTICLE SIZE. (mm.)

NO ROASTING
LEACHING TIME = 3 hr.
LEACHING. TEMP. = 25°C
LIQUID / SOLIDS = 4/1
$H_2SO_4$ = 105 gr.

PARTICLE SIZE ( x $10^{-2}$ mm.)

COPPER EXTRACTION (%)

35
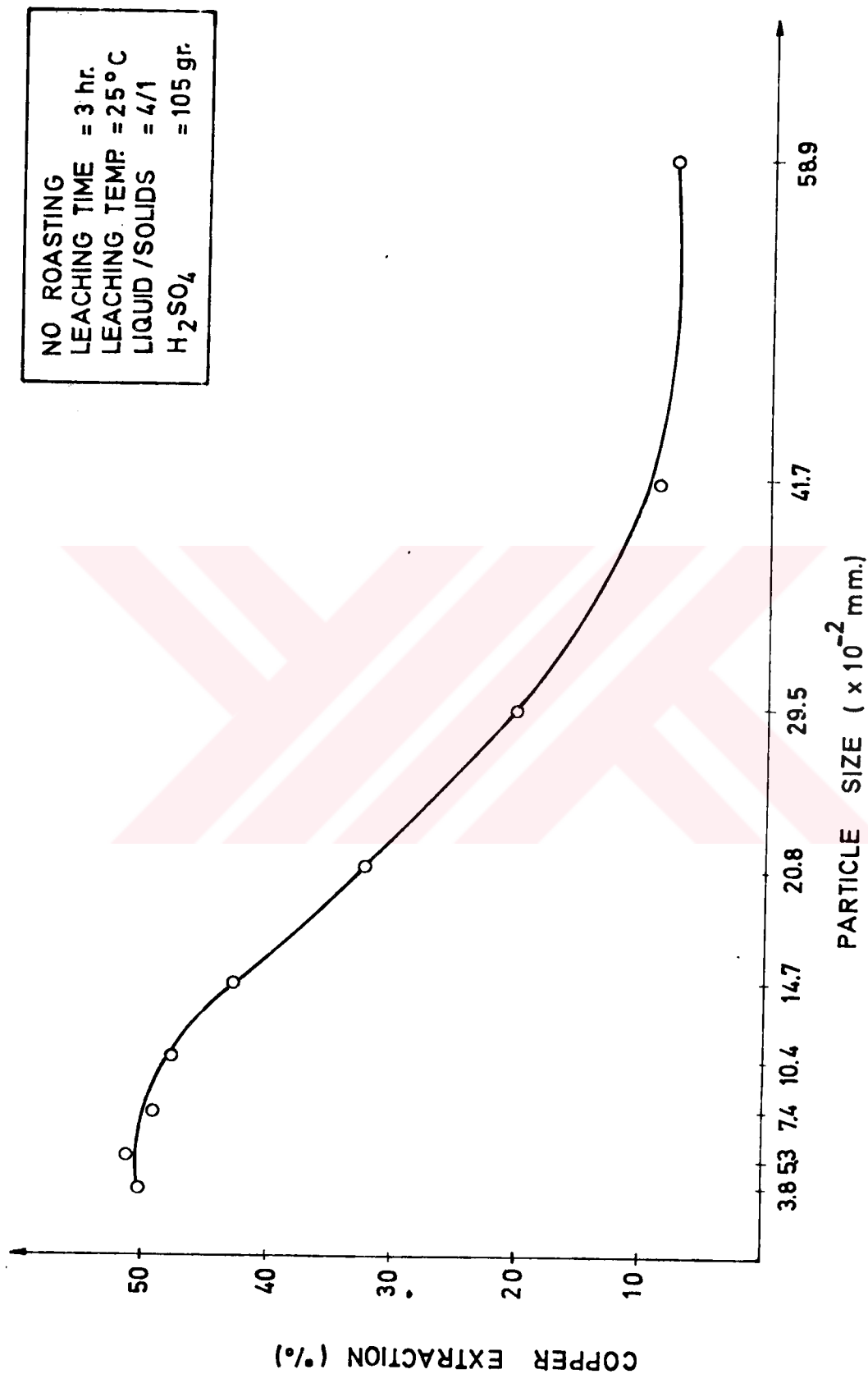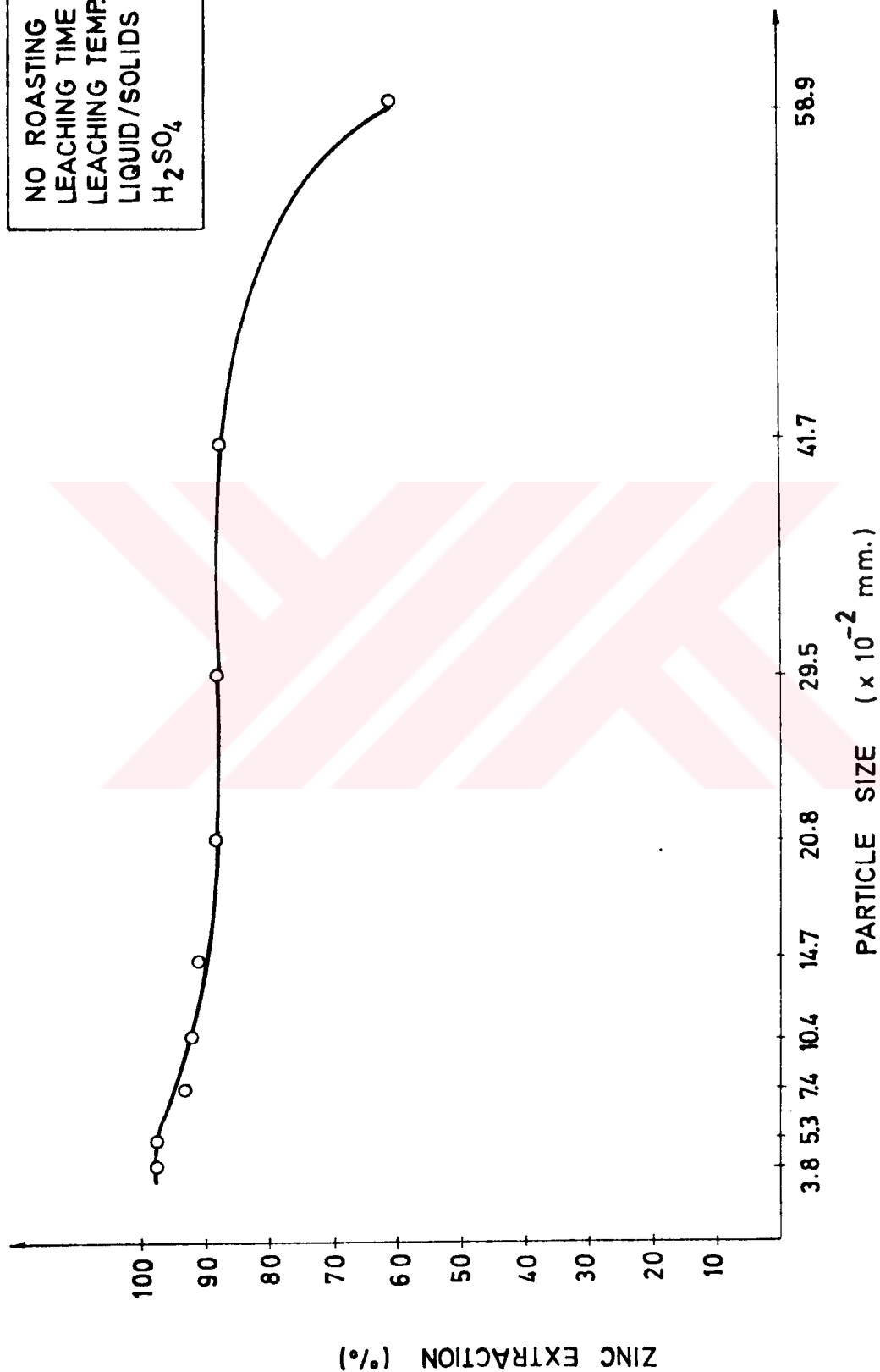
FIG. 10 – THE EXTRACTION OF ZINC (%) AS A FUNCTION OF PARTICLE SIZE (mm.)

NO ROASTING
LEACHING TIME = 3 hr.
LEACHING TEMP. = 25°C
LIQUID/SOLIDS = 4/1
$H_2SO_4$ = 105 gr.

ZINC EXTRACTION (%)

PARTICLE SIZE ($\times 10^{-2}$ mm.)

greater the ability of copper and zinc to undergo the leaching action hence we obtain higher extractions at smaller particle sizes. The unroasted dross was leached three hours at room temperature in water containing 105 grams sulphuric acid with a liquid to solids ratio of 4/1.

Table 6- Effect of Particle Size on Copper and
Zinc Extractions

| Particle Size mm. | Copper wt % | Zinc wt % |
|---|---|---|
| 0.589 | 8.5 | 60.50 |
| 0.417 | 9.0 | 88.80 |
| 0.295 | 20.1 | 89.00 |
| 0.208 | 32.5 | 89.10 |
| 0.147 | 43.0 | 91.60 |
| 0.104 | 48.0 | 92.60 |
| 0.074 | 49.0 | 93.40 |
| 0.053 | 51.0 | 98.00 |
| 0.038 | 50.0 | 98.00 |

5- Effect of Roasting Time

One of the most important factors influencing the economy of this process is the retention time. Therefore a charge containing 100 gr. ground dross with a particle size of 0.147 mm. was subjected to roasting for different reaction periods at 800$^{o}$C. The dross was leached three hours at room temperature in water containing 105 gr. of sulphuric acid with a liquid

to solids of 4/1. The copper and zinc extraction results
at the end of these durations are listed in Table 7.

Table 7 - Effect of Roasting Time on Copper and
Zinc Extractions

| Roasting Time (minutes) | Copper Extraction (wt %) | Zinc Extraction (wt %) |
|:---:|:---:|:---:|
| 90 | 53 | 62 |
| 120 | 64 | 75 |
| 150 | 70 | 78 |
| 180 | 72 | 81 |
| 210 | 72 | 81 |

Data in Table 7 is shown graphically in Figures
11 and 12. The curves exhibit two distinct portions.
There is increasing copper extraction up to 180 minutes
of roasting, after which the extraction remains more
or less constant at 72% for Cu and 81% for Zn. There-
fore one can choose the optimum roasting time as three
hours at $800^{\circ}C$.

The data presented until here were designed to
determine the optimum conditions of roasting for the
extraction. The recovery of the metal consists of three
steps: (a) a successful roasting, (b) bringing metals
into an aqueous solution, and (c) electrolytic
deposition of materials. Two sets of experiments, the
data of which are presented below, were performed to
determine the working conditions for (b).
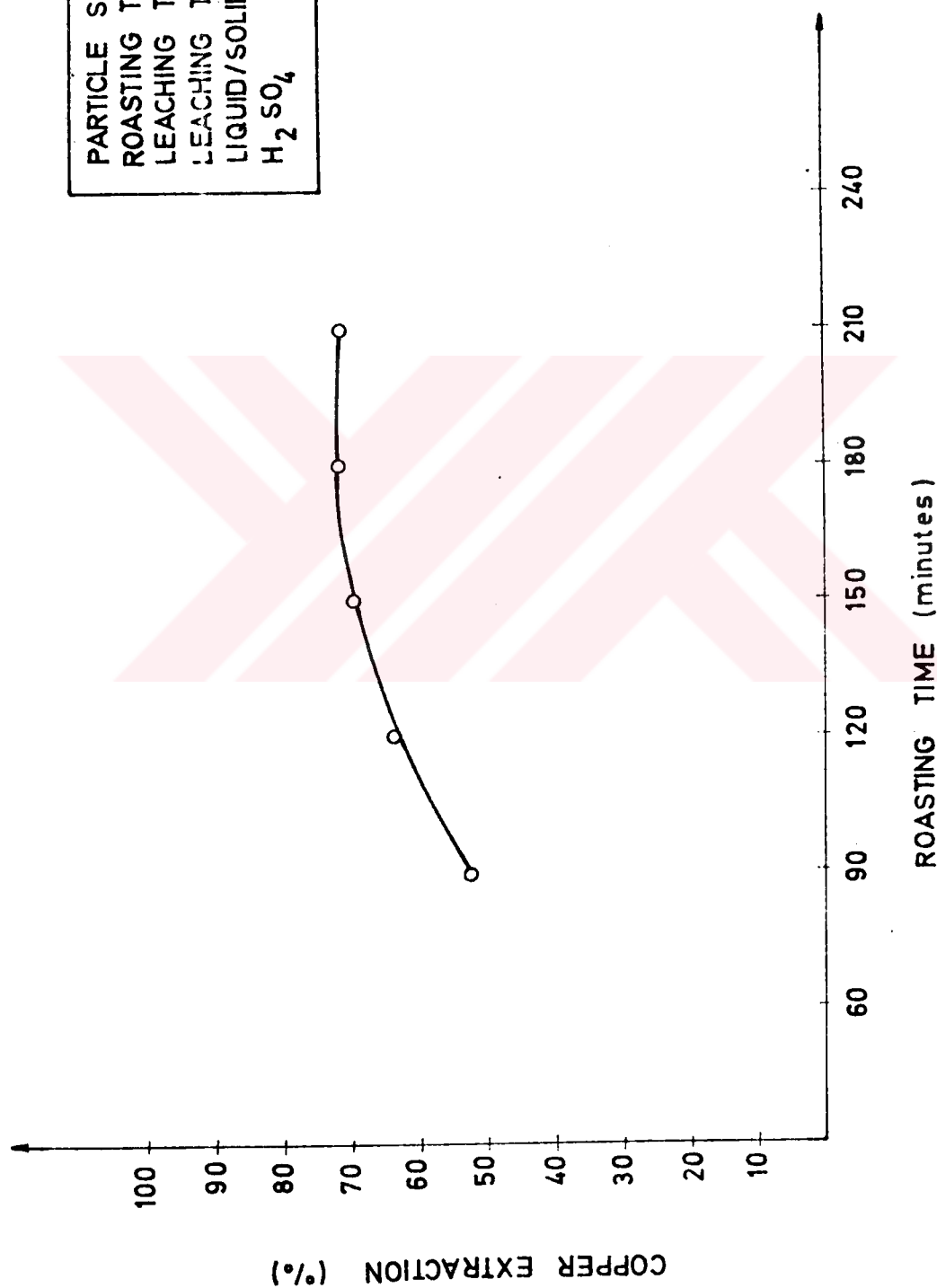
FIG. 11_ THE EXTRACTION OF COPPER (%)AS A FUNCTION OF ROASTING TIME (min)

PARTICLE SIZE = 0.147 mm.
ROASTING TEMP. = 800°C
LEACHING TIME. = 3 hr.
LEACHING TEMP. = 25°C
LIQUID/SOLIDS = 4/1
$H_2SO_4$ = 105 gr.

ROASTING TIME (minutes)

COPPER EXTRACTION (%)

PARTICLE SIZE = 0.147 mm.
ROASTING TEMP. = 800 °C
LEACHING TIME = 3 hr.
LEACHING TEMP. = 25 °C
LIQUID / SOLIDS = 4/1
$H_2SO_4$ = 105 gr.

ZINC EXTRACTION (%)

ROASTING TIME (minutes).
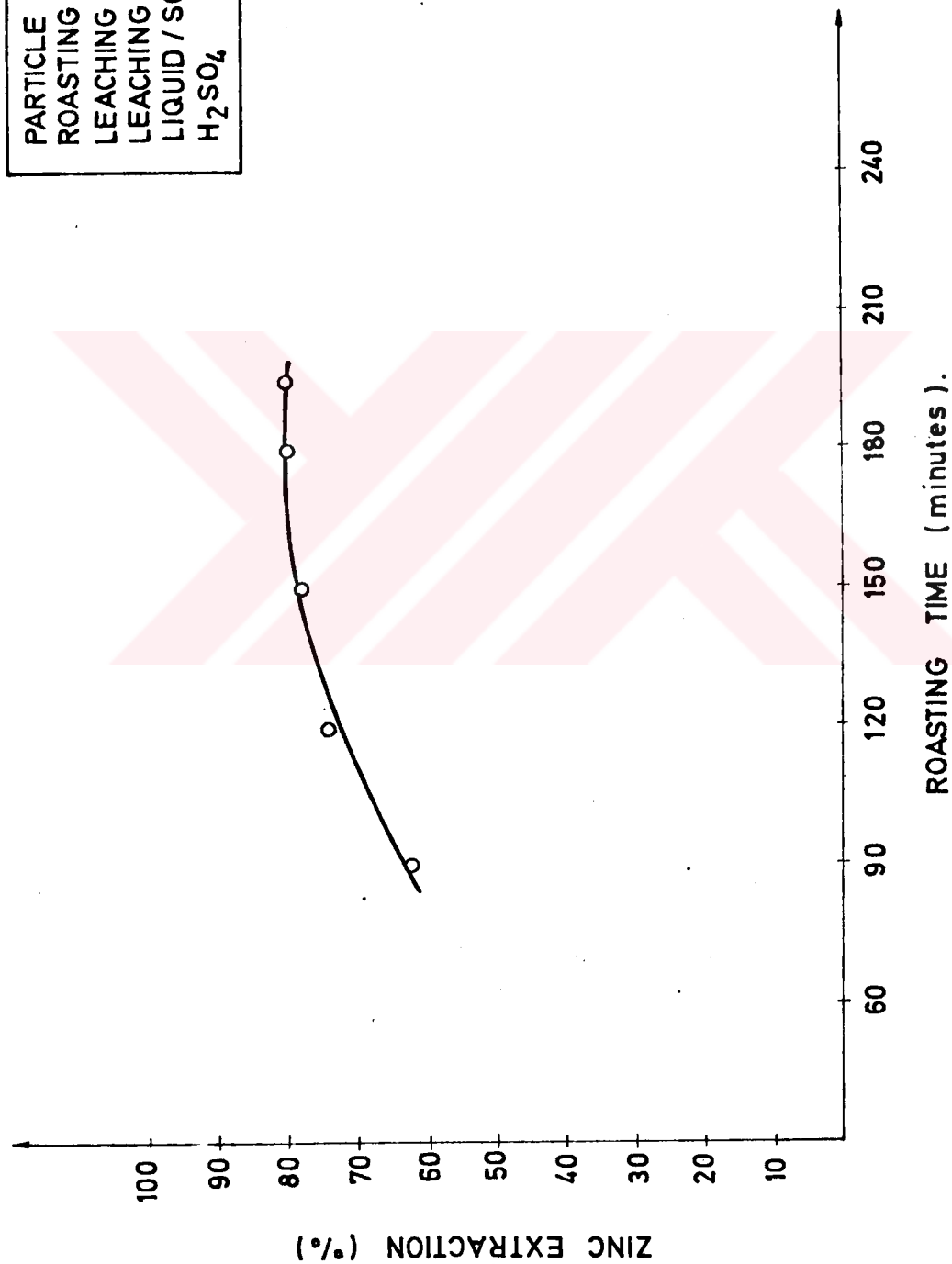
FIG.12_THE EXTRACTION OF ZINC (%) AS A FUNCTION OF ROASTING TIME (minutes)

40

## 6- Effect of Leach Solution Acidity on Extraction

A charge containing 100 grams of dross was roasted at 800°C for three hours. Upon cooling the product was leached in six different solutions, these were the solutions containing 105, 125, 140, 165, 180, and 197 grams $H_2SO_4$ in 400 ml solution. The leaching temperature was 25°C, and the leaching time was 3 hours. The particle size was 0.147 and 0.417 mm. for Cu extraction and 0.147 for Zn extraction. The results are tabulated in Table 8.

### Table 8 - Effect of Leach Solution Acidity on Copper and Zinc Extraction

| $H_2SO_4$ (gr.) | Particle Size (mm.) | | Zinc Extraction (wt %) |
|---|---|---|---|
| | 0.147 | 0.417 | |
| | Copper Extraction (wt %) | | |
| 105 | 71 | 58 | 67 |
| 125 | 58 | 42 | 64 |
| 140 | 55 | 45 | 63 |
| 165 | 50 | 66 | 65 |
| 180 | 93 | 74 | 74 |
| 197 | 94 | 74 | 74 |

The data shown in Table 8 is plotted in Figures 13 and 14 showing copper and zinc extractions as a function of sulphuric acid content of leach solution respectively. These figures reveal that an optimum of about 180 grams $H_2SO_4$ gives highest copper and zinc dissolution.
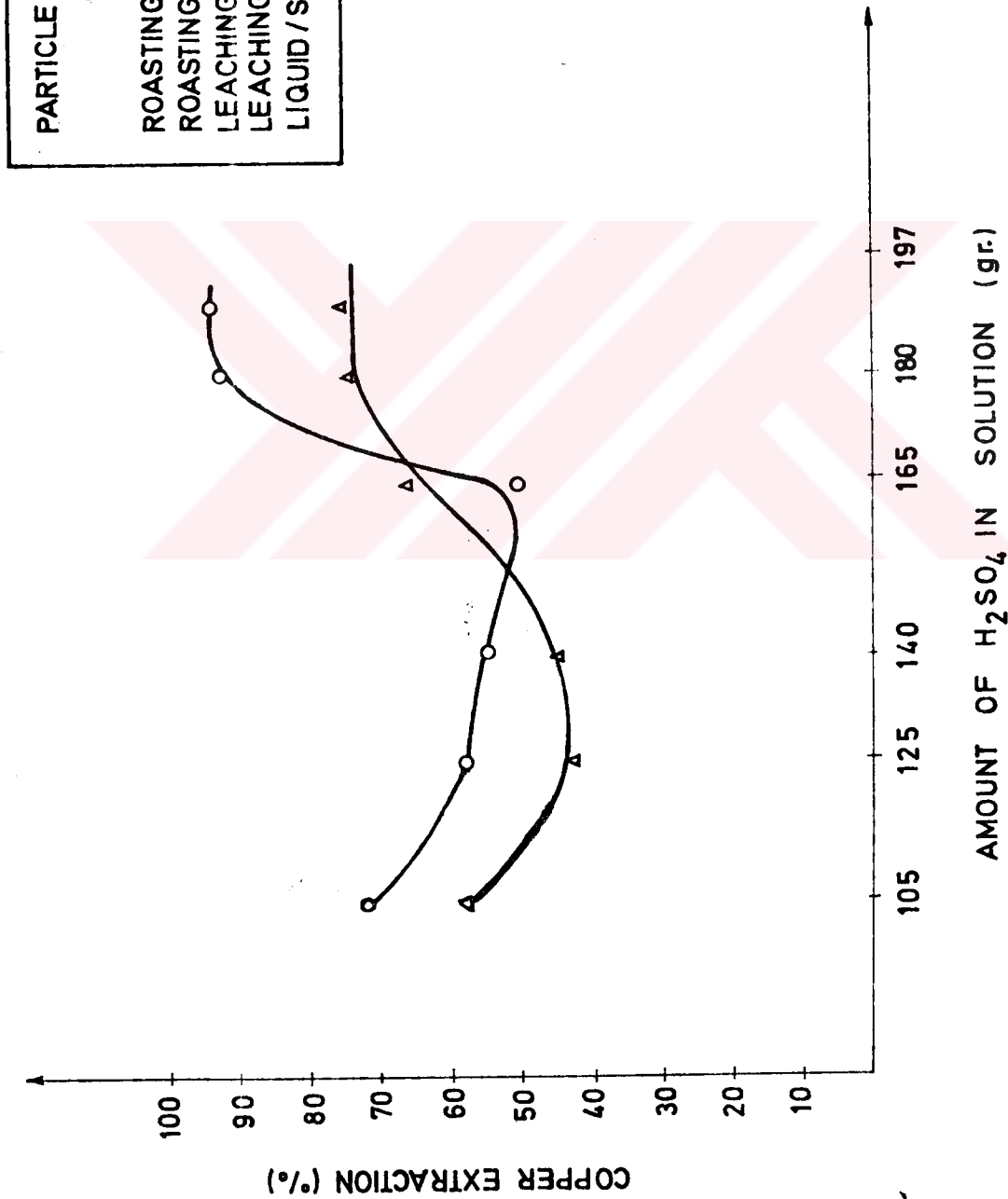
FIG.13-THE EXTRACTION OF COPPER (%) AS A FUNCTION OF LEACH SOLUTION ACIDITY (gr.$H_2SO_4$)
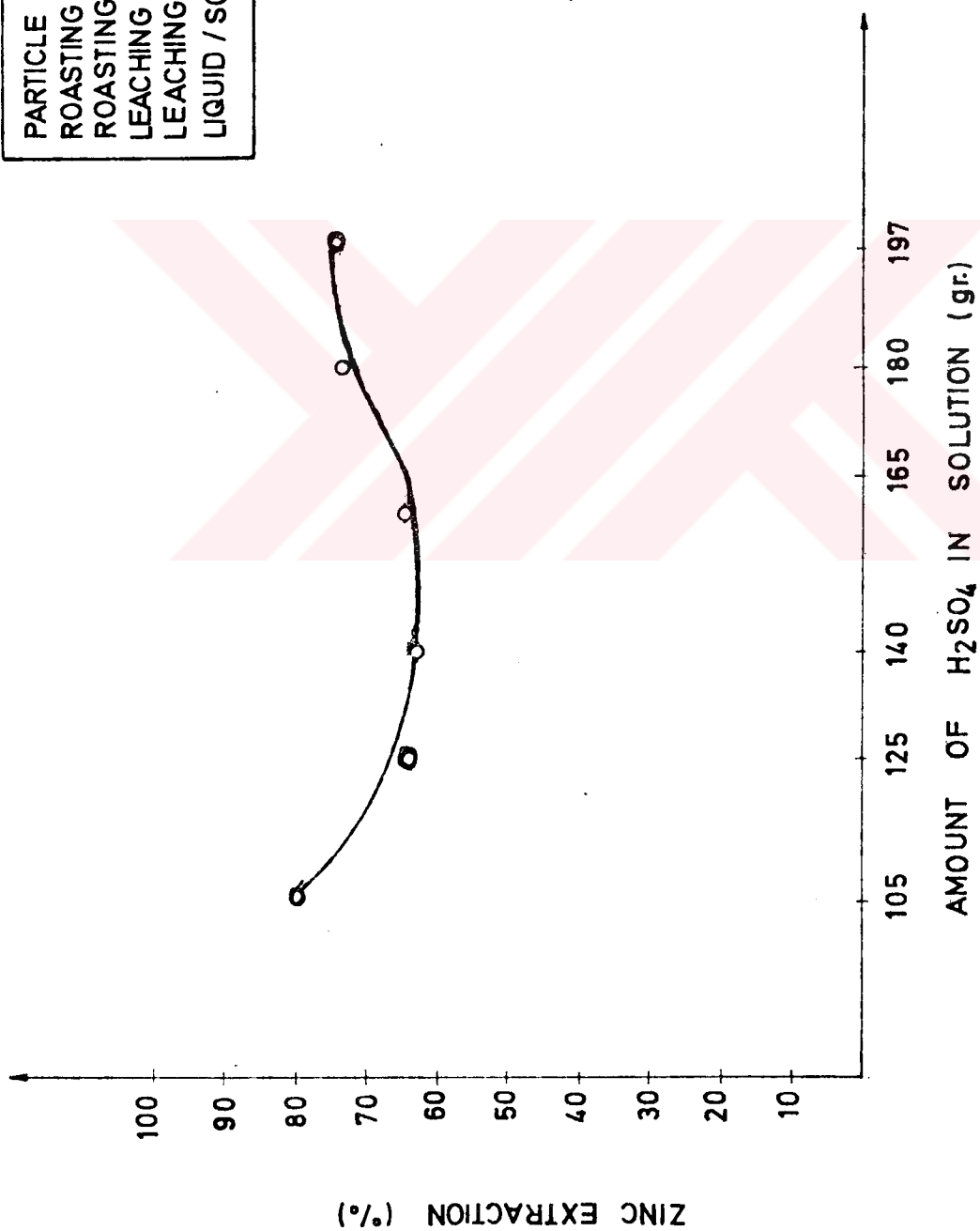
PARTICLE SIZE =
O = 0.147 mm.
△ = 0.417 mm.
ROASTING TEMP = 800°C
ROASTING TIME = 3 hr.
LEACHING TEMP = 25°C
LEACHING TIME = 3 hr.
LIQUID/SOLIDS = 4/1

AMOUNT OF $H_2SO_4$ IN SOLUTION (gr.)

COPPER EXTRACTION (%)

PARTICLE SIZE = 0.147 mm.
ROASTING TEMP = 800°C
ROASTING TIME = 3 hr.
LEACHING TEMP = 25°C
LEACHING TIME = 3 hr.
LIQUID / SOLIDS = 4/1

ZINC EXTRACTION (%)

AMOUNT OF $H_2SO_4$ IN SOLUTION (gr.)

FIG.14_ THE EXTRACTION OF ZINC(%) AS A FUNCTION OF LEACH SOLUTION ACIDITY ( gr $H_2SO_4$ )

## 7- Effect of Leaching Time

A charge containing 100 grams of dross with a particle size of 0.147 mm. were roasted three hours at $800^{\circ}$C. Upon cooling the product was leached at about $40^{\circ}$C in 400 ml. solution which contains 180 grams of sulphuric acid for 120, 150, 180 and 210 minutes. The results are tabulated on Table 9.

### Table 9 - Effect of Leaching Time on Copper and Zinc Extractions

| Leaching Time (minutes) | Copper Extraction (wt %) | Zinc Extraction (wt %) |
|---|---|---|
| 120 | 70.78 | 69.00 |
| 150 | 86.24 | 73.00 |
| 180 | 91.00 | 75.00 |
| 210 | 91.00 | 75.00 |

Above data is plotted in Figures 15 and 16 where copper and zinc dissolution is shown as a function of leaching time respectively. These figures show that at the end of three hours of leaching, virtually all copper goes into leach solution, and at the same time 75.00% zinc goes into leach solution.

## 8- Effect of Liquid to Solids Ratio

A charge containing 100 grams of dross with a particle size of 0.147 mm. were roasted three hours at $800^{\circ}$C. Upon cooling the product were leached at about
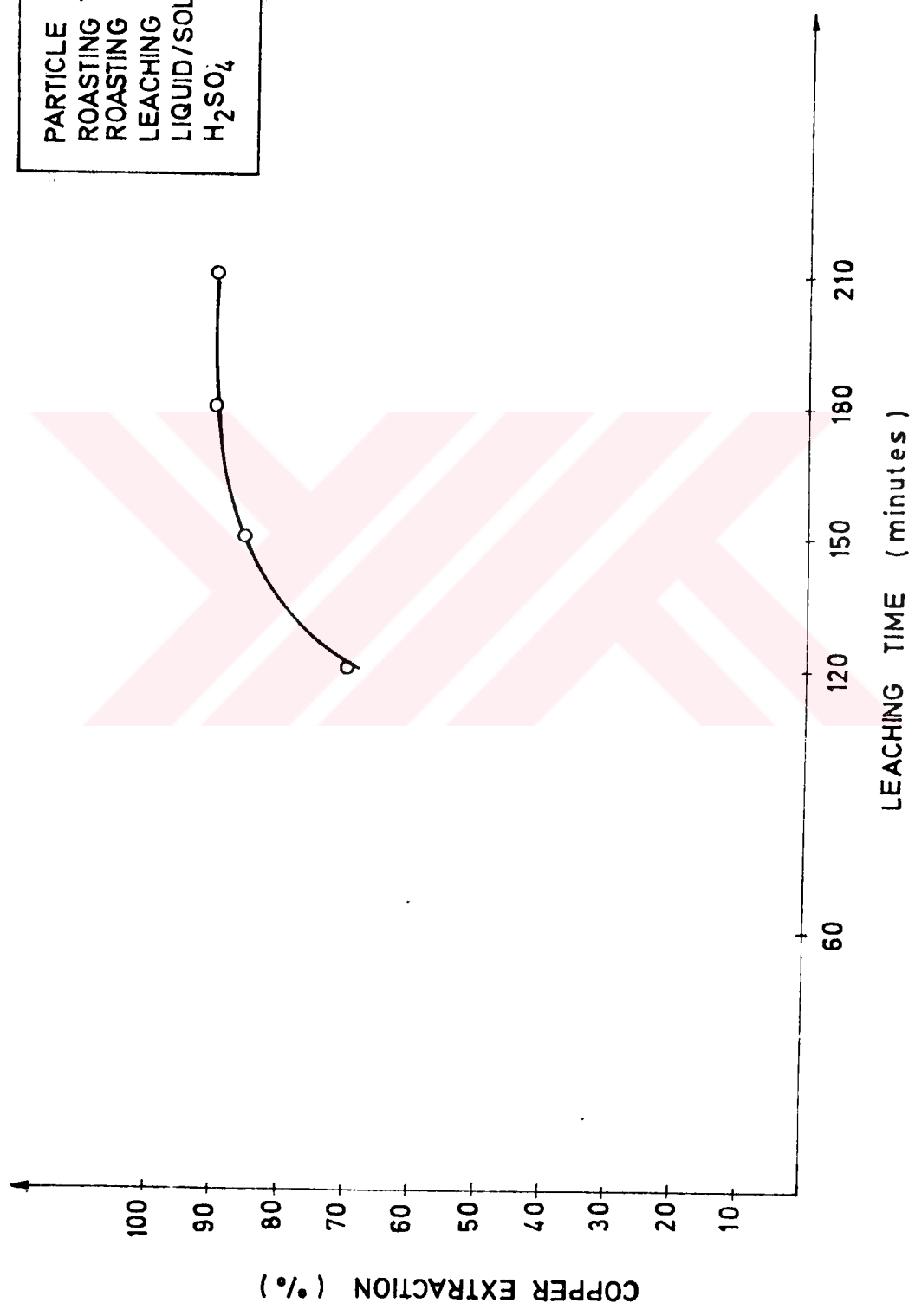
PARTICLE SIZE = 0.147 mm.
ROASTING TEMP. = 800°C
ROASTING TIME. = 3 hr.
LEACHING TEMP. = 40°C
LIQUID/SOLIDS = 4/1
H₂SO₄ = 180 gr.

FIG.15- THE EXTRACTION OF COPPER (%) AS A FUNCTION OF LEACHING TIME (minutes)

FIG.16-THE EXTRACTION OF ZINC (%) AS A FUNCTION OF LEACHING TIME (minutes)

PARTICLE SIZE = 0.147 mm.
ROASTING TEMP. = 800°C
ROASTING TIME. = 3 hr.
LEACHING TEMP.= 40° C
LIQUID/SOLIDS. = 4/1
$H_2SO_4$ = 180 gr.

ZINC EXTRACTION (%)

LEACHING TIME (minutes)

46

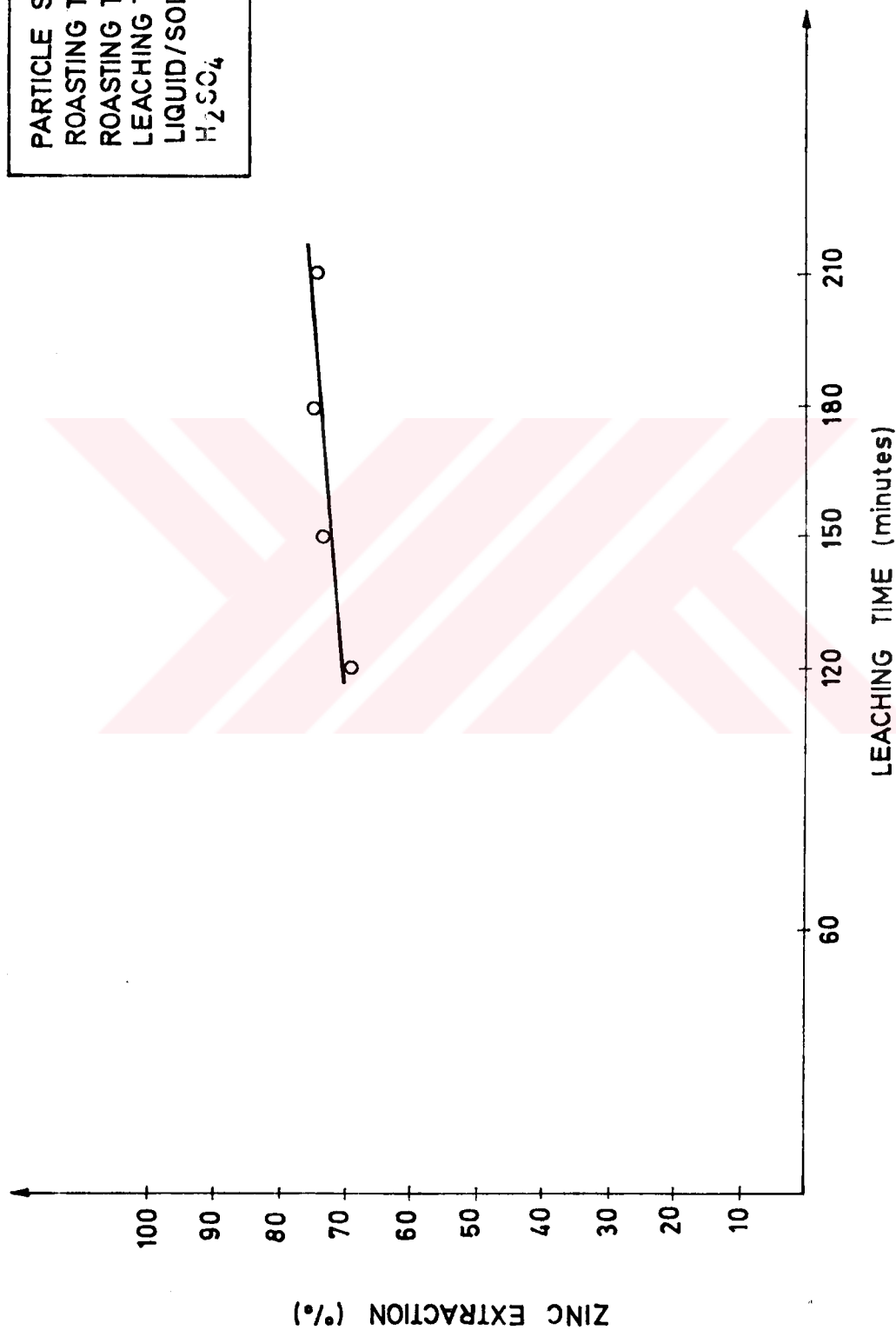45°C in a solution that contains 180 gr. sulphuric acid for three hours. The results are tabulated in Table 10.

Table 10 - Effect of Liquid to Solids Ratio on Copper and Zinc Extraction

| Liquid/Solids | Copper Extraction (wt %) | Zinc Extraction (wt %) |
|---------------|--------------------------|------------------------|
| 1/2 | 40.00 | 25.00 |
| 2/1 | 60.00 | 55.00 |
| 4/1 | 86.00 | 75.00 |
| 6/1 | 98.00 | 77.70 |
| 8/1 | 98.10 | 77.80 |

The data shown in Table 10 is plotted in Figures 17 and 18 where copper and zinc dissolution is shown as a function of liquid to solids ratio respectively. These figures show that with a liquid to solids ratio of 6 virtually all copper goes into leach solution, and with the same ratio around 77.70% zinc goes into leach solution.

9- Effect of Leach Temperature

A charge containing 100 grams of dross with a particle size of 0.295 mm. were roasted three hours at about 800°C. Upon cooling the product was leached for three hours in 400 ml. solution that contains 180 grams sulphuric acid in it. The leaching temperatures were 25, 40, 50, 60 and 65°C. The results are tabulated on Table 11.
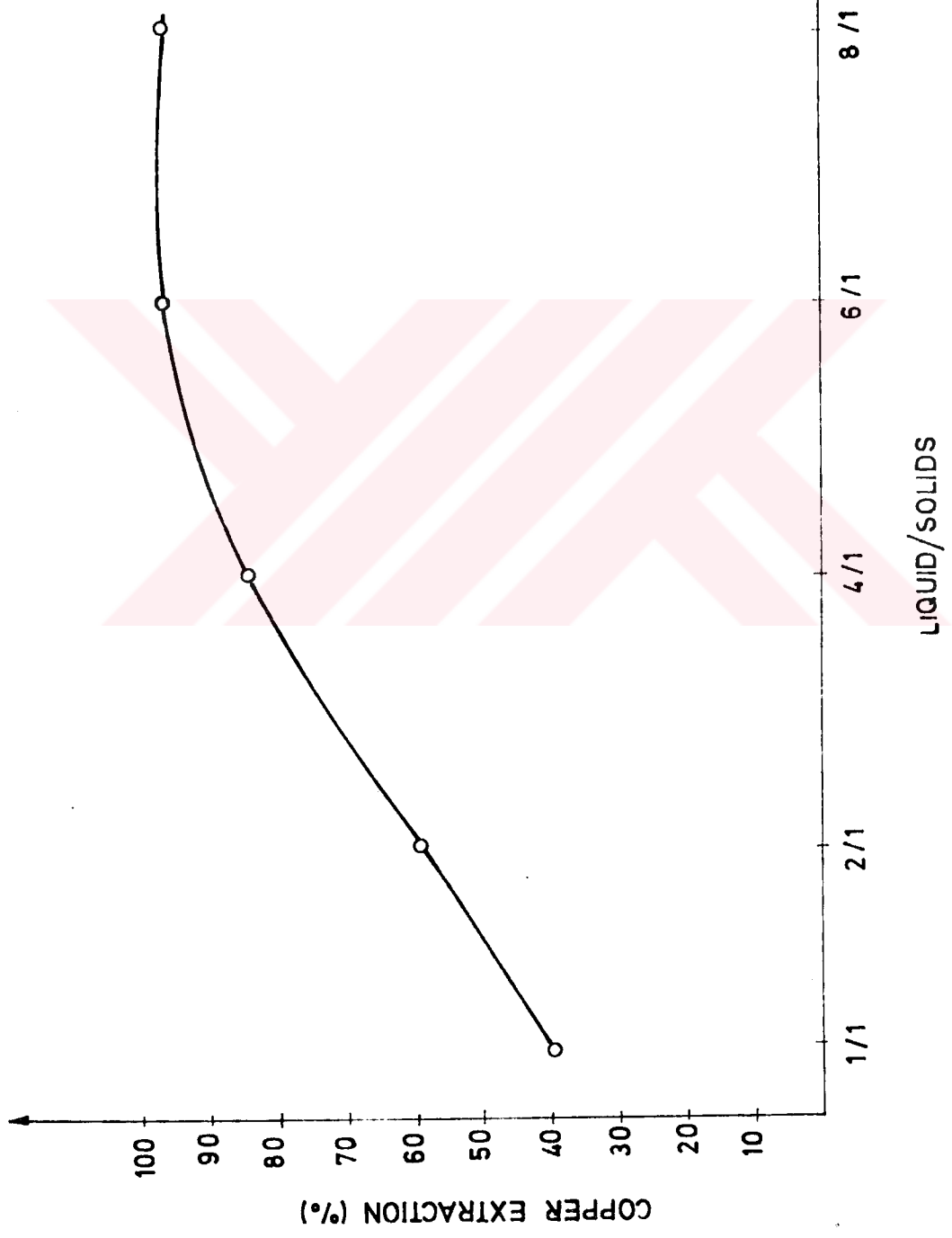
FIG. 17 — THE EXTRACTION OF COPPER (%) AS A FUNCTION OF LIQUID TO SOLIDS RATIO.

PARTICLE SIZE = 0.147 mm.
ROASTING TEMP. = 800°C
ROASTING TIME = 3 hr.
LEACHING TEMP = 45°C
LEACHING TIME = 3 hr.
H₂SO₄ = 180 gr.

COPPER EXTRACTION (%)

LIQUID/SOLIDS

FIG. 18 - THE EXTRACTION OF ZINC (%) AS A FUNCTION OF LIQUID TO SOLIDS RATIO.

Conditions shown on plot:

PARTICLE SIZE = 0.147 mm.
ROASTING TEMP. = 800°C
ROASTING TIME. = 3 hr.
LEACHING TEMP = 45°C
LEACHING TIME. = 3 hr.
$H_2SO_4$ = 180 gr.

Axes: ZINC EXTRACTION (%) vs LIQUID/SOLIDS
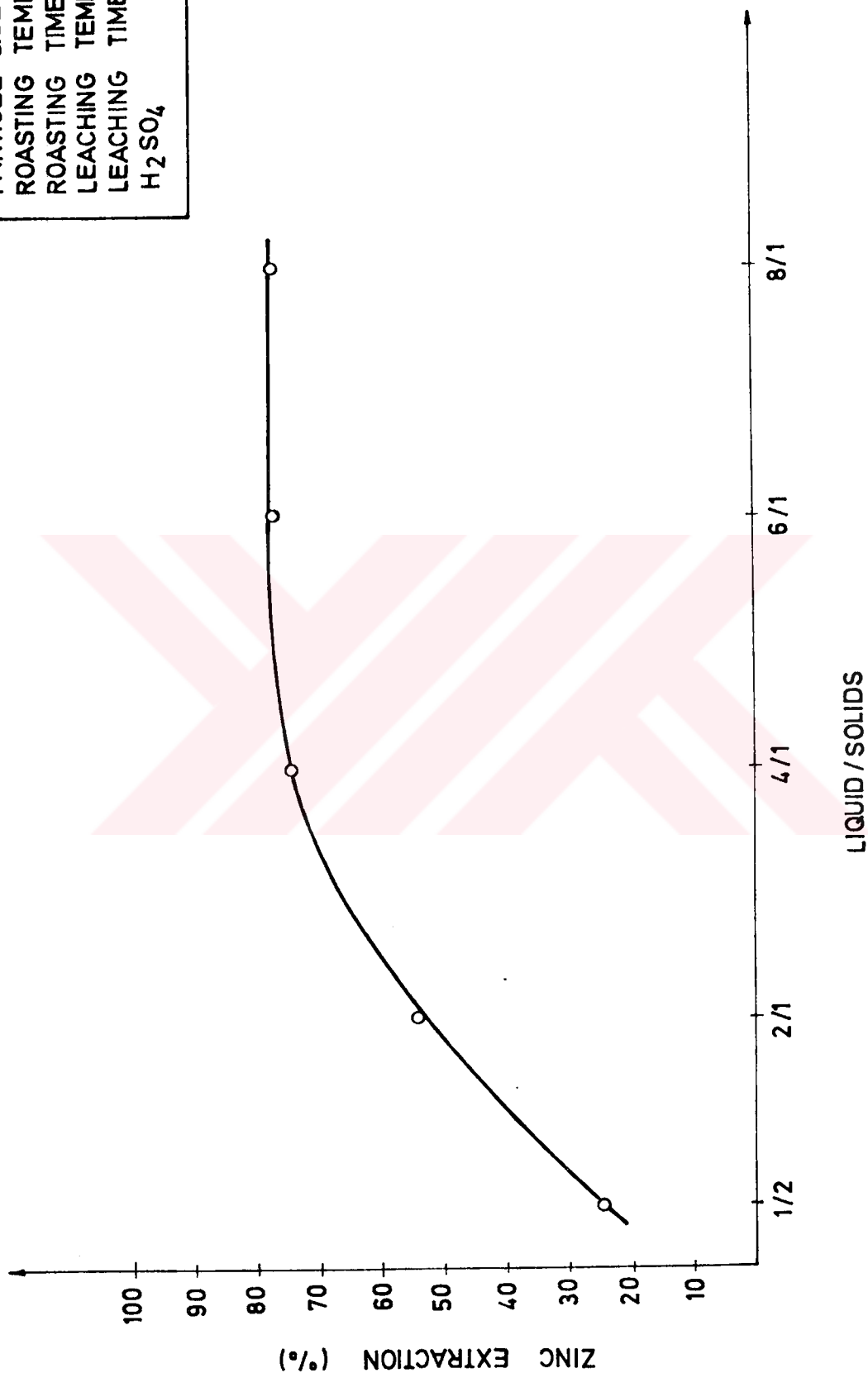
Table 11 - Effect of Leach Temperature on Copper
and Zinc Extractions

| Leaching Temperature ($^{\circ}$C) | Cu Extraction (wt %) | Zn Extraction (wt %) |
|---|---|---|
| 25 | 72.90 | 72.05 |
| 40 | 87.85 | 75.55 |
| 50 | 95.00 | 76.70 |
| 60 | 97.85 | 78.90 |
| 65 | 97.90 | 78.95 |

The data shown in Table 11 is plotted in
Figures 19 and 20 where copper and zinc extraction is
shown as a function of leaching temperature
respectively. These figures show that at a temperature
of 60$^{\circ}$C most of the copper present goes into leach
solution, and about 78.90% zinc goes into leach
solution.

PARTICLE SIZE = 0.147 mm.
ROASTING TEMP. = 800°C
ROASTING TIME. = 3 hr.
LEACHING TIME = 3 hr
LIQUID / SOLIDS = 4/1
$H_2SO_4$ = 180 gr.

COPPER EXTRACTION (%)

LEACHING TEMPERATURE (°C)

FIG.19_ THE EXTRACTION OF COPPER (%) AS A FUNCTION OF LEACHING TEMPERATURE (°C).

FIG. 20 - THE EXTRACTION OF ZINC (%) AS A FUNCTION OF LEACHING TEMPERATURE.

PARTICLE SIZE = 0.147 mm.
ROASTING TEMP. = 800°C
ROASTING TIME. = 3 hr.
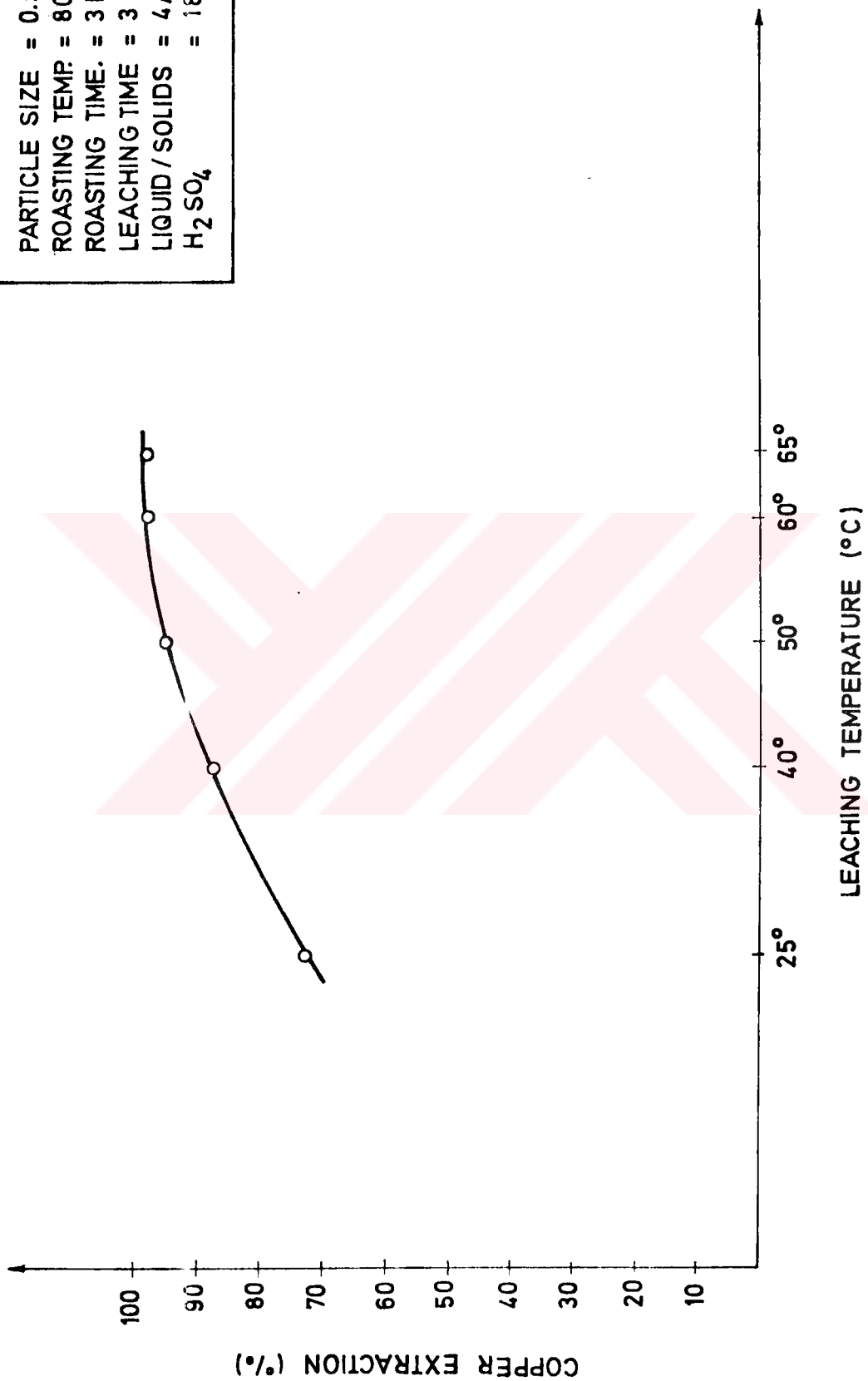LEACHING TIME. = 3 hr.
LIQUIDS/SOLIDS = 4/1
$H_2SO_4$ = 180 gr.
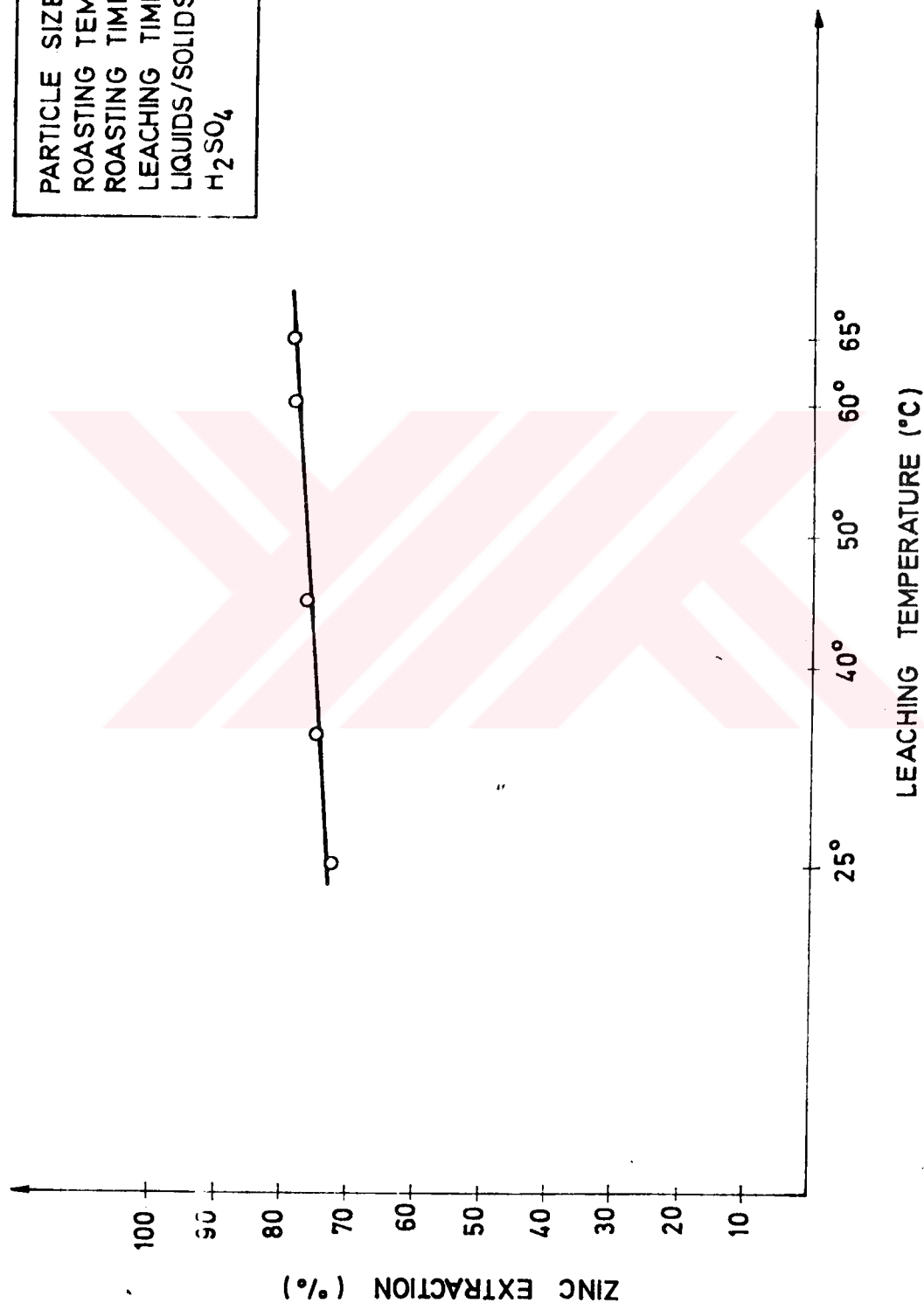
# C H A P T E R   IV

## DISCUSSION AND CONCLUSION

With the rising price of copper and zinc and increasing demand of these metals, new processes or combinations of known methods was established to recover copper and zinc from waste products such as slags and dross. It is important to have an idea about the proper working conditions for the extraction and it was our aim to determine them. In the determination of these variables, they were examined independently from each other, that is, one condition was changed and remaining variables were kept constant, and the optimum condition found is applicable under the conditions at that stage. In fact the variables are dependent on each other and any change in one of them effects the optimum condition. For instance it is possible to obtain a different optimum condition for particle size if we increase the leaching temperature from $25^{o}C$ to higher degrees or if we increase the leaching time. To determine the proper working conditions dependently on each other needs a very long time, therefore I limited the experiments and determine them as mentioned.

With the knowledge obtained in experiments and values given in Tables 1-11 and Figures 7-20 optimum conditions for copper extraction can be listed as follows:

1- Roasting Temperature: 800°C (from Fig. 7)

2- Particle Size        : 0.147 mm. (from Fig. 9)

3- Roasting Time        : 180 minutes (from Fig. 11)

4- Acid Concentration   : 180 grams of sulphuric
                          acid per 100 grams of
                          dross (from Fig. 13).

5- Leaching Time        : 180 minutes (from Fig. 15)

6- Liquid to Solids     :
   Ratio                : 6/1 (from Fig. 17)

7- Leaching Temperature: 60°C (from Fig. 19)


Similarly optimum conditions for zinc extraction
can be listed as follows:


1- Roasting Temperature: 25°C (from Fig. 10)

2- Particle Size        : 0.058 mm. (from Fig. 10)

3- Roasting Time        : 180 minutes (from Fig. 12)

4- Acid Concentration   : 180 grams of sulphuric
                          acid per 100 grams of
                          dross (from Fig. 14)

5- Leaching Time        : 180 minutes (from Fig. 16)

6- Liquid to Solids
   Ratio                : 6/1 (from Fig. 18)

7- Leaching Temperature: 60°C (from Fig. 20)


The first two optimum conditions, namely roasting
temperature and particle size, of copper and zinc
extractions are different from each other and others
are same. Therefore to select the proper working
conditions for the extraction of copper and zinc
together, the above conditions must be considered to
determine the most economical ones.

A simplified flow-sheet showing the proposed method of extraction is developed by considering bove factors, and it is given in Figure 21.

Figure 10 shows that it is possible to extract zinc up to 98% when no roasting takes place. In this condition about 50% of the copper was also extracted. To obtain better results for copper extraction the dross was roasted but in that case the amount of zinc extracted were decreased to lower values. At low temperatures the rate of zinc ferrite formation is insignificant, but it rapidly increases at above $650^{\circ}$C. But the formation of zinc ferrite ($ZnO.Fe_2O_3$) which is insoluble in the leach solution depends on the following factors:

a) Iron content of the dross;
b) The form of copper and zinc in the matrix;
c) Roasting method;
d) Roasting temperature;
e) Roasting time.

Since our dross contains a very small amount of $Fe_2O_3$ (about 0,70%) the zinc ferrite formation was insignificant, and an increase in zinc extraction was obtained as the roasting temperature was increased as shown in Figure 8.

Figures 9 and 10 show an increase in the per cent extraction of two metals as the particle size decreases. This was expected since the particle size
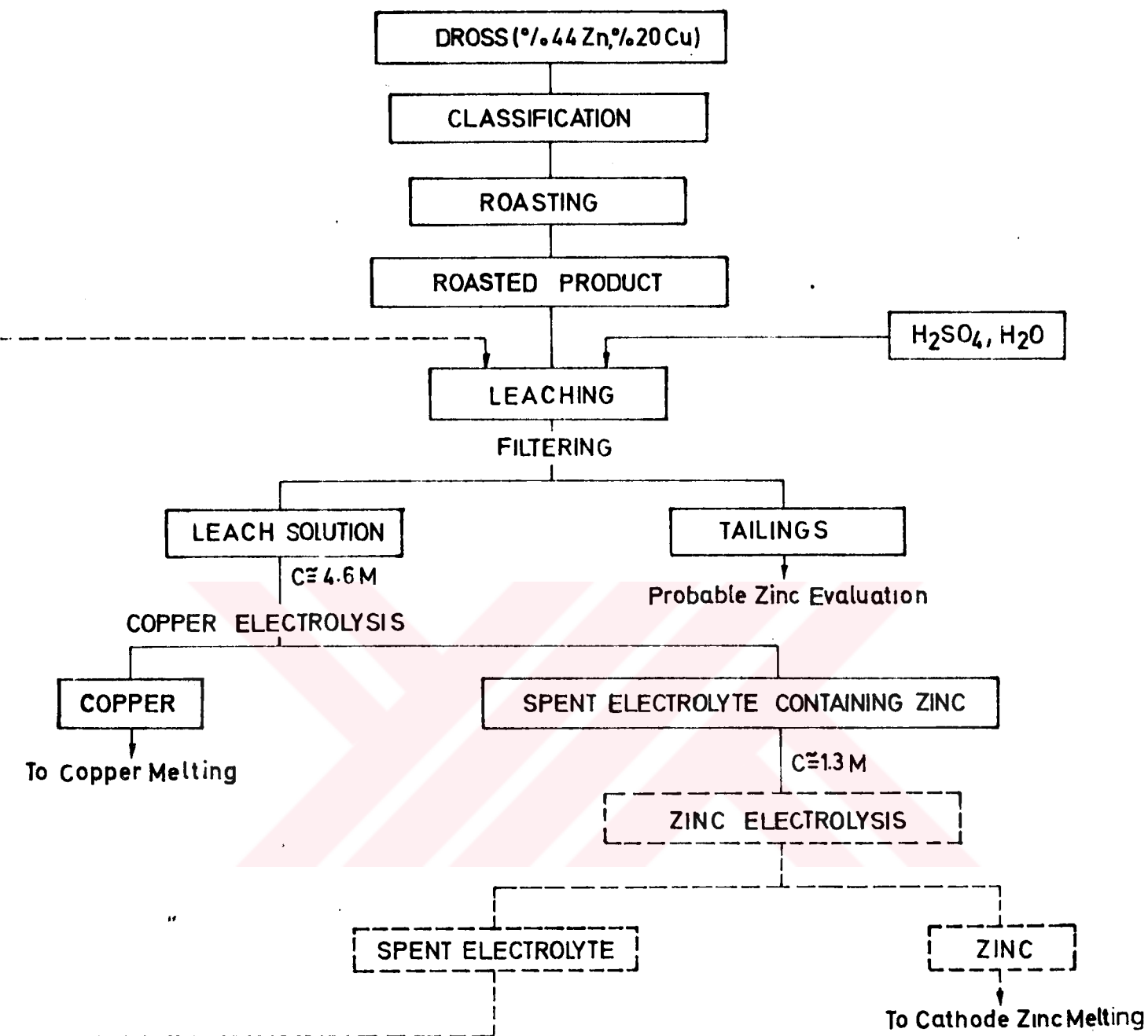
FIG. 21_ A SIMPLIFIED FLOW-SHEET SHOWING THE PROPOSED METHOD OF EXTRACTION.

decreases, the surface area of solids per unit weight increases, and the rate of solution is directly proportional to the surface area of the particles.

In Figures 11 and 12 an increase increase in the extraction of copper and zinc was shown as roasting time increases, because metals found more tendency to convert themselves into a more suitable form for the leaching.

When the extraction of copper and zinc as a function of leach solution acidity was considered, it was seen from Figures 13 and 14 that, the percent extraction for copper and zinc were decreased as the amount of sulphuric acid used was increased from 105 to 160 grams for 100 grams of dross, then the values obtained was increased as the concentration of the solution increased upto 180 grams of $H_2SO_4$ for the same amount of dross. Actually I expected an increase in the copper and zinc extraction as the leach solution acidity increases but the experiments gave different results for both particle sizes. In order to have an exact idea for the extraction values as a function of leach solution acidity, the experiments were made three times on each size group and in all cases the same results with an error of $\pm 2\%$ were obtained.

Figures 15 and 16 show an increase in the per cent extraction of copper and zinc as the leaching time increases. This is expected because the time of contact of metals with the leach solution increases.

Figures 17 and 18 show the extraction of copper and zinc as a function of liquid to solids ratio. When this ratio is small the particles have a tendency to stick together on each other and the per cent extraction obtained was very low, since the exposed surface area of the particles was thus decreased. As the ratio was increased the dross was effected with the solution more easily and better results were obtained.

Figures 19 and 20 show an increase in the amount of copper and zinc extraction as the leaching temperature was increased. This was again expected since an increase in the leaching temperature increases the rate of diffusion and the rate of chemical reactions between the dross and leaching solution.

In all leaching experiments the tailings obtained at the end of filtering process contain some amount of zinc that is insoluble in the leaching period if zinc ferrite formation occurs. A lot of time was spent to find a process to recover zinc from zinc ferrite, and some methods were found but majority of them were uneconomical. When the tailings that contain zinc ferrite were roasted at about $500-550^{\circ}C$ in the atmosphere of $SO_2$ gas, most of the zinc ferrite was converted into $ZnSO_4$ that is soluble in water[17]. As the temperature was increased up to $600^{\circ}C$, the iron was also converted to iron sulphate.

With considering the proposed method of extraction which is given in Figure 21, and the optimum

working conditions found, copper was extracted up to 98.10% whereas zinc was recovered up to 78.95%. These values are applicable under our conditions, and they are possibly suspectable to changes when the proper working condition were determined by considering all the effects of variables on each others.

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