

# STUDY OF THE KINETICS OF ROASTING OF ZINC AND COPPER CONCENTRATES IN A FLUIDIZED BED

*A Dissertation*  
*submitted in partial fulfilment*  
*of the requirements for the degree*

*of*

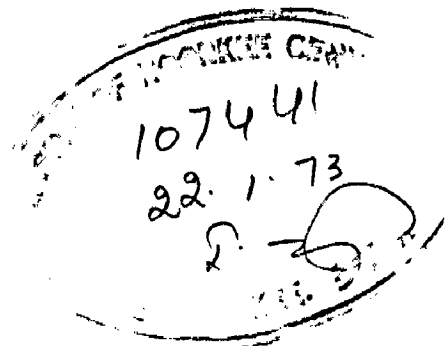
MASTER OF ENGINEERING

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METALLURGICAL ENGINEERING  
(EXTRACTIVE METALLURGY)

*By*

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C E R T I F I C A T E

Certified that the dissertation entitled "STUDY OF KINETICS OF ROASTING OF ZINC AND COPPER CONCENTRATES IN A FLUIDIZED BED" which is being submitted by Sri G.S.Agrawal in partial fulfilment of the requirement for the award of Degree of Master of Engineering in Extractive Metallurgy of University of Roorkee is a record of student's 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 is further to certify that he has worked for this dissertation for a period of about 9 months from January, 1971 to September, 1971.

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## P R E F A C E

The roasting of sphalerite and chalcopyrite concentrates is an important step in the production technology of zinc and copper. The recent development in the roasting is the use of fluidized bed technique in which the fine solids are transferred into a fluid like state through the contact of gas.

This technique was first developed in 1920's and the first large scale use of fluidized bed was made by Fritz and Winkler for the gassification of powdered coal. The patent for this process was awarded in 1922 and the first gas producer started its operation in 1926. A number of similar units were constructed in Germany and Japan to supply raw gas for the synthetic chemical industries. This type of gas producer was very inefficient therefore numerous developments were made by many individuals and organizations.

This technique was first developed by Chemical Engineers and later on its use was made in metallurgical field. In 1944 Dorr-Oliver Company acquired rights to use this technique in the roasting of sulphide ores. They soon developed the fluo-solid

system and first such unit was constructed in 1947 in Ontario, Canada to roast arsenopyrite and to obtain a cinder suitable for gold production by cyanidation.

In 1942 at Berlin, New Hampshire, Dorr-Oliver introduced this type of roaster for producing  $SO_2$  from sulphide ores.

As early as 1945 Badische Anilin and Soda-Fabrik (BASF) in Germany and Sumitomo Chemical Manufacturing Company in Japan independently developed a roaster similar to fluosolid system. Dorr-Oliver engineers pioneered two additional important uses of fluidized bed in the area of drying powdery materials and the calcination of lime stone.

Another application of fluidized bed in metallurgy is the reduction of Iron ore. This technique has been extensively used in the previous years particularly in the United States. The purpose of these studies is to develop a process for producing iron and steel from fines of high grade ores. Hydrocarbon Research Corporation and Bethlehem steel company jointly developed a process for direct reduction of iron ore called H-Iron process and the United States company

developed its Nu-Iron process for reduction with hydrogen of less than 10 mesh size ore. Further development made by ESSO Research engineers is the use of multi stage recorders.

In the present investigation an attempt has been made to study the effects of temperature and particle size on the rate of roasting of zinc sulphide and copper sulphide concentrates in fluidized bed by using chemical analysis method for sulphur determination.

i/ This thesis has been divided into four chapters. Chapter-I deals with the general introduction to the subject, advantages and disadvantages and industrial applications of fluidized bed.

Literature review is included in Chapter II and deals with fundamentals of fluidization, theory of oxidation of sulphide concentrates, and a brief review of the previous work done on the roasting of zinc and copper concentrates.

Chapter-III gives the description of the experimental set-up and procedure followed in the present investigation. Pellets of three various sizes (0.1435 cm, 0.184 cm, 0.219 cm.) of

spherical shapes were made with the help of pelletizer, they were then dried and roasted at various temperatures. The zinc concentrates were treated at temperature 700°C, 750° and 800°C and copper concentrates were treated at temperatures 500°, 550°, 600°, 650° and 700°C. The kinetic data were obtained by chemical analysis of roasted samples.

Results obtained from the experiments carried out and a discussion on them constitute the subject matter of Chapter-IV. The activation energies computed by the application of chemical reaction model are of the order of 29 K cal/mole <sup>and 14 K cal/mole</sup> for zinc and copper sulphide concentrates, respectively.

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# C O N T E N T S

PREFACE	(i)
ACKNOWLEDGEMENTS	(v)
LIST OF TABLES	(vi)
LIST OF FIGURES	(vii)
NOMENCLATURE	(ix)
<u>CHAPTER-I</u> INTRODUCTION	1-10
1.1.    Fluidization	3
1.2.    Advantages of fluidized bed	6
1.3.    Disadvantages of fluidized bed	6
1.4.    Industrial Applications of fluidized bed	8
<u>CHAPTER-II</u> LITERATURE REVIEW	11-31
2.1.    Solids in a fluidized bed	11
2.2.    Heat transfer in fluidized bed	18
2.3.    Theory of oxidation of sulphide concentrate	21
2.4.    Brief Review of previous work done	23
<u>CHAPTER-III</u> EXPERIMENTAL WORK	32-41
3.1.    Experimental set-up	32
3.2.    Material used	38
3.3.    Calculation of fluid mass velocity for minimum fluidization	38
3.4.    Calculation of mass flow rate of air through orifice meter.	39
3.5.    Experimental procedure	40



<b><u>CHAPTER-IV</u></b>	<b>RESULTS AND DISCUSSION</b>	42-74
<b>4.1.</b>	<b>Results</b>	42
<b>4.2.</b>	<b>Discussion</b>	65
<b>CONCLUSIONS</b>		75
<b>REFERENCES</b>		77
<b>APPENDIX</b>		81

LIST OF TABLES

1. Output of various roasting systems with pyrites containing 48% sulphur.
2. Ignition point of sulphides for 0.06 mm. fineness.
3. Mass flow rate of air ( $G_{mf}$  and  $G$ ).
4. Experimental Results for roasting of zinc concentrates at 700°C.
5. Experimental results for roasting of zinc concentrates at 750°C.
6. Experimental results for roasting of zinc concentrates at 800°C.
7. Experimental results for roasting of copper concentrates at 500°C.
8. Experimental results for roasting of copper concentrates at 550°C.
9. Experimental results for roasting of copper concentrates at 600°C.
10. Experimental results for roasting of copper concentrates at 650°C.
11. Experimental results for roasting of copper concentrates at 700°C.
12. Rate constant 'K' values at different temperatures for zinc concentrates.
13. Rate constant 'K' values at different temperatures for copper concentrates.
14. Activation energy required to roast samples of different sizes for zinc concentrates.
15. Activation energy required to roast samples of

LIST OF FIGURES

1. Pressure gradient in bed as function of fluid velocity.
2. Experimental set-up.
3. Cross section of partially roasted zinc concentrate pellet.
4. Cross section of partially roasted copper concentrate pellet.
5. A plot of fractional sulphur removal vs time for zinc concentrates of 0.1435 cm. particle size.
6. A plot of fractional sulphur removal vs time for zinc concentrates of 0.184 cm. particle size .
7. A plot of fractional sulphur removal vs time for zinc concentrates of 0.219 cm. particle size.
8. A plot of fractional sulphur removal vs time for zinc concentrates at temperature 700°C.
9. A plot of fractional sulphur removal vs time for zinc concentrates at temperature 750°C.
10. A plot of fractional sulphur removal vs time for zinc concentrates at temperature 800°C.
11. A plot of fractional sulphur removal vs time for copper concentrates of 0.1435 cm. particle size
12. A plot of fractional sulphur removal vs time for copper concentrates of 0.184 cm. particle size
13. A plot of fractional sulphur removal vs time for copper concentrates of 0.219 cm. particle size.

14. A plot of fractional sulphur removal vs time for copper concentrates at temperature 500°C.
15. A plot of fractional sulphur removal vs time for copper concentrates at temperature 550°C.
16. A plot of fractional sulphur removal vs time for copper concentrates at temperature 600°C.
17. A plot of fractional sulphur removal vs time for copper concentrates at temperature 650°C.
18. A plot of fractional sulphur removal vs time for copper concentrates at temperature 700°C.
19. Plot of  $(1-(1-R)^{\frac{1}{2}})$  vs. time for zinc concentrates of 0.1435 cm. particle size.
20. Plot of  $(1-(1-R)^{\frac{1}{2}})$  vs. time for zinc concentrates of 0.185 cm particle size.
21. Plot of  $(1-(1-R)^{\frac{1}{2}})$  vs time for zinc concentrates of 0.219 cm particle size.
22. Plot of  $(1-(1-R)^{\frac{1}{2}})$  vs time for copper concentrates of 0.1435 cm particle size.
23. Plot of  $(1-(1-R)^{\frac{1}{2}})$  vs time for copper concentrates of 0.184 cm particle size.
24. Plot of  $(1-(1-R)^{\frac{1}{2}})$  vs time for copper concentrates of 0.219 cm particle size.
25. Plot of  $\log K$  vs  $1/T \times 10^4$  for zinc concentrate .
26. Plot of  $\log K$  vs  $1/T \times 10^4$  for copper concentrate.

N O M E N C L A T U R E

- $A$  = Cross sectional area of bed  
 $A_2$  = Cross sectional area of throat, sq. ft.  
 $C$  = Coefficient of discharge, dimension less  
 $C_d$  = An experimentally determined drag coefficient  
 $C_p$  = Specific heat of gas at constant pressure  
 $C_s$  = Specific heat of solid  
 $D$  = Diameter of tube  
 $D_p$  = Particle size  
 $g_c$  = Dimensional constant,  $32.12(\text{lb})(\text{ft.})/(\text{lb force})(\text{Sec})^2$   
 $G$  = Fluid mass velocity  
 $G_{mf}$  = Minimum fluidization fluid mass velocity  
 $h$  = Heat transfer coefficient  
 $k$  = Thermal conductivity of the gas  
 $L$  = Length of bed  
 $P_1$  = Pressure at upstream static tap  
 $P_2$  = Pressure at downstream static tap  
 $q_1$  = Volumetric rate of discharge measured at upstream pressure and temperature  
 $u_t$  = Terminal velocity of a particle  
 $w$  = Weight rate of discharge, lb/sec.  
 $y$  = Expansion factor, dimension less  
 $\beta$  = Diameter ratio, dimension less  
 $\rho_1$  = Density at upstream pressure and temperature, lb/cuft.

$\rho_f$  = Density of fluid, lb/cuft.

$\rho_s$  = Density of solid, lb/cuft.

$\mu$  = Viscosity, poise

$\epsilon$  = Voidage of bed

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CHAPTER - I

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## I N T R O D U C T I O N

A fluid-bed reactor is a very versatile equipment for gas-solid reactions and, in particular, roasting reactions. A fluid-bed process has many advantages, namely, very good contact between reacting solids and gases, excellent temperature control, and uniformity throughout the mass of solids in fluid action. The primary objective of the present work was to study the kinetics of oxidation of zinc sulphide and copper sulphide concentrates in a fluidized-bed reactor as a step toward a better understanding of the effects on the reaction rate of different process variables, such as temperature and particle size.

Roasting of zinc sulphides in a fluidized column was studied by Anderson and Bolduc<sup>(1)</sup> with special attention to developing the reactor. They pointed out that roasting of zinc concentrate requires close control. There is a much danger of fusion with zinc concentrate than with pyrite. Neston Sedano Rivera<sup>(2)</sup> studied the theoretical and practical aspects of fluidized bed roasting of zinc concentrates. The operation was compared with wedge roaster. He found that fluid bed reactor requires less labour and no fuel as well as cost of



repairs is low, since it has no moving parts in the high temperature zone. Trojan and Vanecek<sup>(3)</sup> studied the kinetics of oxidation of zinc sulphide concentrates containing 47.8% zinc by weight in pilot plant scale reactors. They found that the removal of sulphur was a function of temperature, partial pressure of oxygen in the gas phase and residence time of zinc sulphide particles in the fluidized bed reactor. Natensan and Philbrook<sup>(4)</sup> studied the kinetics of roasting of zinc sulphide over a temperature range of 740°C to 1000°C with oxygen-nitrogen gas mixture of 20 to 40% oxygen. They found that the temperature dependence of kinetic constant corresponded to an activation energy of 40.25 K cal. per mole. Denbigh and Beveridge<sup>(5)</sup> also reported that oxidation of zinc sulphide concentrate is chemically controlled with an activation energy of 50 K cal. per mole.

James Blair<sup>(6)</sup> studied the fluosolid roasting of copper concentrates with special attention to developing the reactor. He found that the recovery of sulphur was increased from 63 to 85%. Sevebrennikova and Gultsena<sup>(7)</sup> studied the possibility of increasing the particle size of copper calcine and decreasing the dust carry out in fluidized bed roasting of copper concentrate. They found that by addition of 5 to 7% of  $\text{Na}_2\text{SO}_4$  &  $\text{FeSO}_4$  (60:40)

to ungranulated copper concentrate decreased the dust losses by 50 to 60%.

Oxidation of copper and zinc sulphides are heterogenous process involving transport and reaction steps. The reactions are exothermic and are irreversible.

### 1.1. FLUIDIZATION<sup>(8)</sup>

Fluidization is the operation by which fine solids are transformed into a fluid like state through contact with a gas or liquid. This method of contacting has a number of unusual characteristics, and fluidization engineering is concerned with efforts to take advantage of this behaviour and put it to good use. When a fluid is passed upward through a bed of fine particles, at a low flow rate, fluid merely percolates through the void spaces between stationary particles. This is a fixed bed. With an increase in flow rate, particles move apart and a few are seen to vibrate and move about in restricted regions. This is the expanded bed.

At a still higher velocity, a point is reached when the particles are just suspended in the upward flowing gas or liquid. At this point the frictional force between a particle and fluid counterbalances the

weight of the particle, the vertical component of the compressive force between adjacent particles disappears, and the pressure drop through any section of the bed nearly equals the weight of fluid and particles in the section. The bed is considered to be just fluidized and is referred to as an incipiently fluidized or a bed at minimum fluidization.

In liquid solid system an increase in flow rate above minimum fluidization usually results in a smooth, progressive expansion of the bed. Gross flow instabilities are damped and remain small, and large-scale bubbling or heterogeneity is not observed under normal conditions. A bed such as this is called a particularly fluidized bed, a homogeneously fluidized bed, a smoothly fluidized bed, or simply a liquid fluidized bed.

Gas-solid system generally behaves in a different manner. With an increase in flow rate beyond minimum fluidization large instabilities with bubbling and channeling of gas are observed. At higher flow rates agitation becomes more violent and the movement of solids becomes more vigorous. In addition, the bed does not expand much beyond its volume at minimum fluidization. Such a bed is called an aggregative fluidized bed, a heterogeneously fluidized bed, a bubbling fluidized bed or simply a gas fluidized bed.

Both gas and liquid fluidized beds are considered to be dense-phase fluidized bed as long as there is a fairly clearly defined upper limit or surface to the bed. However, at a sufficiently high fluid flow rate the terminal velocity of the solid exceeds, the upper surface of the bed disappears, and solids are carried out of the bed along with the fluid stream. In this state we have a disperse-dilute, or lean-phase fluidized bed with pneumatic transport of solids. Although the properties of solid and fluid alone will determine whether smooth or bubbling fluidization occurs, many factors influence the rate of solid mixing, the size of bubbles, and the extent of heterogeneity in the bed. These factors include bed geometry, gas flow rate, type of distributors, and vessel internals such as screens, baffles and heat exchangers.

Compared with other methods of gas-solid contact, gas fluidized beds have some rather unusual and useful properties. This is not shared to the same extent with liquid-solid system. Thus practically all the important industrial applications of fluidization are gas fluidized system.

### 1.2 Advantages of Fluidized Bed

The following are the advantages of fluidized bed.

1. Smooth, liquid like flow of particles allows continuously and automatically controlled operations with ease of handling.
2. The rapid mixing of solids leads to nearly isothermal conditions throughout the reactor, hence the operation can be controlled simply and reliably.
3. The circulation of solid between two fluidized beds makes it possible to transport the vast quantities of heat produced or needed in large reactors.
4. Heat and mass transfer rates between gas and particles are high when compared with other modes of contacting.
5. The rate of heat transfer between a fluidized bed and an immersed object is high, hence heat exchangers within fluidized bed requires relatively small surface area.

### 1.3 Disadvantages of fluidized bed

Apart from various advantages the fluidized beds

also have certain disadvantages. These are given below:

1. The difficult-to-describe flow of gas, with its large variations from plug flow and the by-passing of solids by bubbles, represents an inefficient contacting system. This becomes specially serious when high conversion of gaseous reactant is required.
2. The rapid mixing of solids in the bed leads to nonuniform residence time of solids in the reactor. For continuous treatment of solids this gives a nonuniform product and lower conversions especially at high conversion levels. On the other hand, for batch treatment of solids this mixing is helpful since it gives a uniform solid product.
3. Friable solids are pulverised and entrained by the gas; they then must be replaced.
4. Erosion of pipes and vessels from abrasion by particles can be serious.
5. For non-catalytic operations at high temperature the agglomeration and sintering of fine particles can necessitate a lowering in temperature of operation and hence reducing the reaction rate considerably.

#### 1.4 Industrial applications of fluidized beds

Any application of fluidization falls into one of the following two classes:

1. Physical and mechanical process or
2. Chemical reactions and catalysis

##### Physical and Mechanical Processes

- a) Transportation: The fluidity of fluidized solids is often as great as that of liquids and this property has effectively been used for the transportation of powdered solids.
- b) Mixing of Fine Powders: With conventional techniques it is difficult to mix intimately different kinds of powdery materials; however, fluidization of the mixture makes it possible to circulate solids in a storage bin giving comparatively good intermixing.
- c) Heat Exchange: Fluidized beds have been used extensively for heat exchange, in both physical operation and chemical process, because of their unique ability to rapidly transport heat and maintain a uniform temperature.

d) Drying and Sizing: Fluidized beds have been used for drying and sizing of powdery materials and one of the first commercial dryers is a Dorr-Oliver fluo-solid unit. Fluo-solid dryers have been widely used to dry materials such as limestone, dolomite, coal, blast furnace slag and plastics.

### Chemical reactions and catalysis

#### (a) Carbonisation and Gassification

- i) Carbonisation of oil and coal
- ii) Gassification of coal and coke
- iii) Activation of charcoal

#### (b) Calcining and Clinkering

- i) Calcination of limestone, dolomite and phosphate rock.
- ii) Cement Clinkering.

#### (c) Gas Solid Reactions

- i) Roasting of Sulphide Ores: These operations are all characterized by an exothermic oxidation, hence a simple-stage fluidized bed is usually satisfactory. No outside heating is necessary, and, some times cooling of the reactor may be needed. Compared to alternate designs, these



units have a higher capacity. They also require less excess air, thus giving off gas with high sulphur dioxide concentration.

Uniform temperature of fluidized beds also enables sulphides ores containing copper or cobalt to be roasted to the sulphate then separate the iron oxide cinder by heating with water or dilute sulphuric acid.

Fluidized beds can be used for roasting zinc concentrate and copper concentrate. A 1.5 meter diameter pilot fluo-solid reactor has been built by the Anaconda<sup>(1)</sup> copper mining company and has been operated successfully using a slurry of zinc concentrates as feed. Fluosolid roasting of copper<sup>(6)</sup> concentrates was begun at Copper Hill Tenn in June 1961 with an initial capacity of 250 Tons per day. Comparative analytical data on the roasting practice as obtained in commercial plants with pyrites containing 48% sulphur are given in table-1.

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CHAPTER - II

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## L I T E R A T U R E   R E V I E W

### 2.1 Solids in a Fluidized Bed

If a fluid is passed downwards through a bed of solids no relative movement between the particles takes place, unless the initial orientation is unstable. If the flow is stream like, the pressure drop across the bed will be directly proportional to the rate of flow but at higher rates it will rise more rapidly.

If the fluid passes upwards through the bed, the pressure drop will be the same as for downward flow at low rates, but when the fractional drag on the particles becomes equal to their apparent weight (actual weight + buoyancy), the particles become rearranged so that they offer less resistance to the flow of fluid and the bed starts to expand. This process continues as the velocity is increased with the total frictional force remaining equal to the weight of the particles, until the bed has assumed the loosest stable form of packing. If the velocity is increased still further, the individual particles separate from one another and become freely supported on the fluid and the bed is said to be fluidized.

Further increase in the velocity causes the particles to separate still further from one another and the pressure difference remains approximately equal to the weight per unit area of bed. With a gas uniform fluidization is obtained only at relatively low velocities and at high velocities two separate phases are formed, these are often referred to as dense phase and the lean phase and a condition of 'aggregative' fluidization is produced. Gas containing a relatively small proportion of suspended solids bubbles through a high density fluidized bed with the lean phase corresponding to the vapour and the dense or continuous phase to liquid. The bed is then often referred to as 'boiling bed'. Thus as the flow of gas is increased its velocity relative to the particles in the dense phase may not change appreciably, and it has been suggested that the flow relative to the particle can as a result remain streamline even at very high rates of flow. If the rate of passage of gas is high, and if the bed is deep, coalescence of the bubbles takes place and eventually slugs occupying the whole cross-section of the containing vessel are produced, these slugs of gas alternate with slugs of fluidized solids which are carried upwards and subsequently collapse causing the solids to fall back again. If the gas velocity is

now increased so that it exceeds the terminal falling velocity of the particles, in the absence of channelling, the slugs do not disintegrate but continue to rise indefinitely and transport of the solids takes place in the gas stream.

### 2.1.1 Minimum Fluidization Velocity

The onset of fluidization occurs when

$$\begin{aligned} \text{(Drag force by upward moving gas)} &= \text{(Weight of particles)} \\ \text{or (Pressure drop across bed)} &\quad \times \text{(Cross-sectional area of tube)} \\ &= \text{(Volume of bed)} \times \text{(Fraction of Solid)} \times \text{(Specific weight of solids)}. \end{aligned}$$

Lava<sup>(9,10)</sup> gives a generalized equation derived from the fundamental consideration of pressure drop and velocity relationships at the onset of fluidization. He eliminates voidage, sphericity term by relating them with Reynolds number and is as given below:

$$G_{mf} = \frac{C D_p^2 g_c \rho_f (\rho_s - \rho_f)}{\mu} \text{-----(2.1)}$$

For  $Re$  less than 5

$$C \left( \text{a function of } \frac{D_p G}{\mu} \right) = 0.0007 \times Re^{-0.063}$$

and incorporating  $g_c$  in the experimental constant the above relationship yields

$$G_{mf} = \frac{688 D_p^{1.82} (\rho_s - \rho_f)^{0.94}}{\mu^{0.88}} \quad \text{-----} (2.2)$$

which gives  $G_{mf}$  in pound per hour per square foot if  $D_p$  is expressed in inches,  $\rho_f$ ,  $\rho_s$  in pounds per cubic foot and  $\mu$  in centipoise.

The above relation gives correlation only up to flow rates where  $R_o$  is less than 5. For this reason one must calculate  $\frac{D_p G_{mf}}{\mu}$  after  $G_{mf}$  has been calculated, in order to check on the range of validity in relation to the problem. If the resulting  $\frac{D_p G_{mf}}{\mu}$  is in excess of 5,  $G_{mf}$  must be corrected by means of standard graphs<sup>(10)</sup>.

### 2.1.2 Effect of Fluid Velocity on Expansion of Bed and Pressure Gradient

The relation between the superficial velocity number ( $u_o$ ) through bed of the fluid (calculated over the whole cross-section of containing vessel) and the pressure gradient is shown in figure 1. Here the flow is streamline and the curve is a straight line of slope unity. At the fluidization point, the pressure gradient begins to fall because the porosity of the bed increases, this continues until the velocity is high enough for transport of the material to take

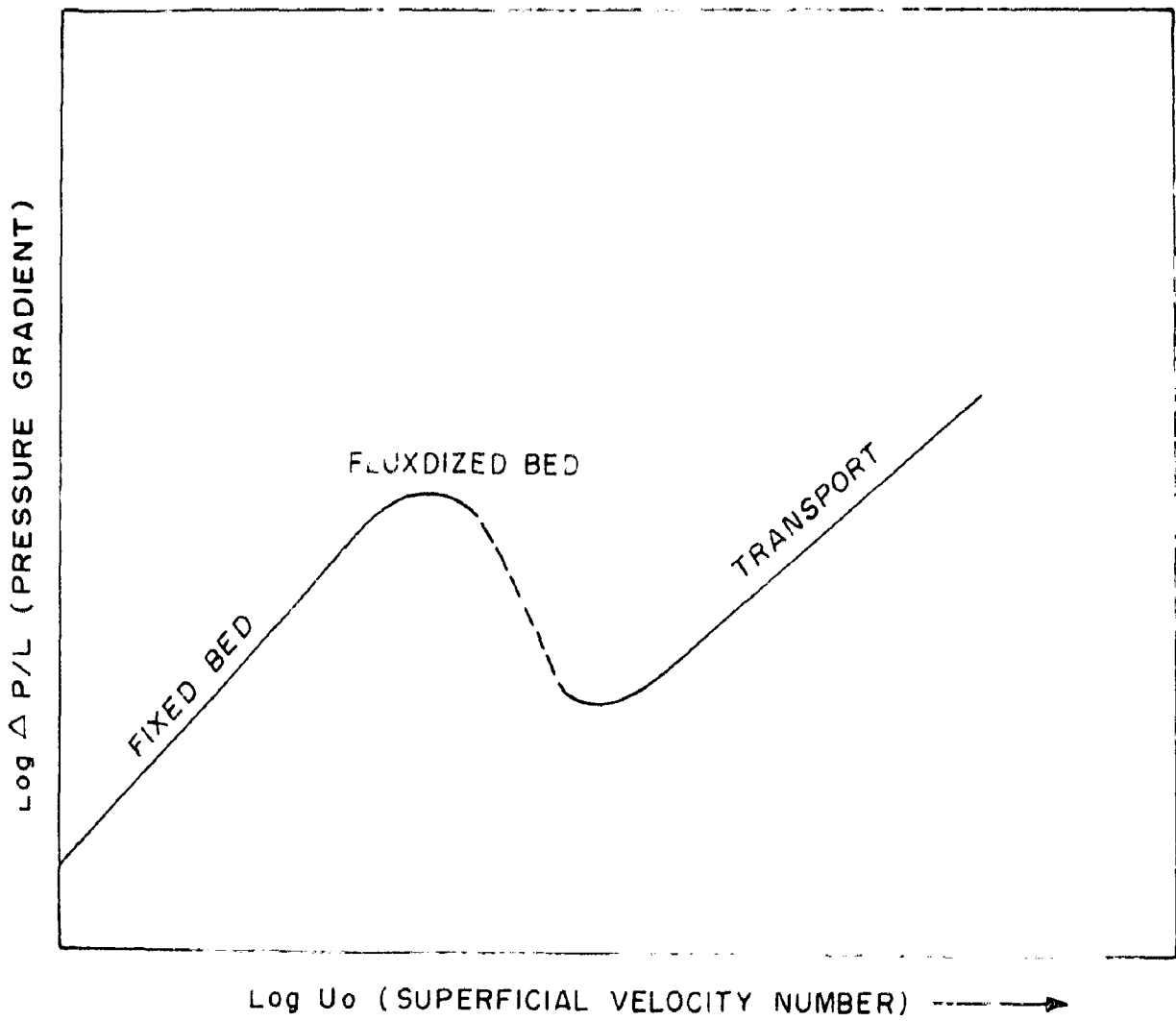


FIG. 1. PRESSURE GRADIENT IN BED AS FUNCTION OF FLUID VELOCITY.

place, the pressure gradient then starts to increase again because the fractional drag of the fluid at the walls of the tube starts becoming significant.

### 2.1.3 Pressure Drop in Fluidized Beds

For relatively low flow rates in a packed bed the pressure drop is approximately proportional to gas velocity, usually reaching to a maximum value slightly higher than the static pressure of the bed. With a further increase in gas velocity, the packed bed suddenly unlocks, in other words the voidage increases from  $\epsilon_m$  (over all bed-voidage fraction) to  $\epsilon_{mf}$  (bed-voidage fraction at point of minimum fluidization) resulting in a decrease in pressure drop to the static pressure of the bed. With gas velocities beyond minimum fluidization the bed expands, and gas bubbles are seen to rise with resulting non homogeneity in the bed. Despite this rise in gas flow, the pressure drop remains practically unchanged.

### 2.1.4 Terminal Velocity of Particles

The gas flow rate through a fluidized bed is limited on one hand by  $u_{mf}$  ( the average superficial



fluid velocity required for minimum fluidization) and on the other hand by entrainment of solids by the gas. When entrainment occurs these solids must be recycled or replaced by fresh material to maintain steady state operations. This upper limit to gas flow rate is approximately the terminal or free-fall velocity of the particles which can be estimated from fluid mechanics by

$$u_t = \left( \frac{4 g D_p (\rho_s - \rho_g)}{3 f_f C_d} \right)^{\frac{1}{2}} \text{-----(2.3)}$$

To avoid carry-over of solids <sup>from</sup> a bed, the gas velocity for fluidized bed operation should be kept between  $u_t$  and  $u_{mf}$ . The ratio of  $u_t$  to  $u_{mf}$  is usually between 10:1 and 90:1 and is an indication of the flexibility of possible operations. The ratio  $u_t/u_{mf}$  is smaller for large sized particles including less flexibility than for smaller particles. It is also an indication of the maximum possible height of fluidized bed. This is because the pressure drop through the bed results in an increase in gas velocity through the bed. Thus the maximum height of bed is where the bed is just fluidized at the bottom and where  $u_t$  is just reached at the top. Actually the range of satisfactory operations of a gas fluidized may be considerably narrowed by channeling and slugging. This is especially serious with large uniformly sized particles where it is often difficult to fluidize the

bed at all. With proper use of baffles or in tapered vessels this undesirable behaviour can be reduced.

It should be noted that violently bubbling gas fluidized beds can be made to operate at gas velocities in excess of the terminal velocity of practically all the solids, with some entrainment, which may not be severe. This is possible because the major portion of the gas flows through the beds as large, particularly solid free, gas bubbles while the bed solids are suspended by a relatively slow moving gas. In addition, by using cyclone separators to return the entrained solids, even higher gas velocities can be used.  $u_t/u_{mf}$  ratio upto 250 may be used with proper arrangement of dust separator.

## 2.2 Heat Transfer in Fluidized Bed

Fluidized systems are extensively used because the high rates of heat transfer and the uniform temperature within the bed, and the high coefficients to transfer heat from the bed to the walls of the containing vessel. Much experimental work (11,12,13) has been carried out but a completely satisfactory correlation of the data has not so far been evolved. Several expressions (14,15) of an empirical nature, in which the variables are arranged in the form of dimensionless groups, have been suggested for heat

transfer to a gas solid system but owing to the complexity of problem, no fundamental expression has been desired for the heat transfer coefficients, and agreement between the results of the various investigators<sup>(16, 17, 18)</sup> is generally poor.

Miller and Logwincik<sup>(15)</sup> obtained range of coefficients between 40 and 200 lb. cal/sq.ft. hr. °C for heat transfer between a fluidized bed and the walls of the container. They found that the coefficients were proportional approximately to the diameter of the particles raised to the power (- 0.6) and the velocity to the power 0.2. Van Heerden et. al.<sup>(16)</sup> have obtained an empirical expression for the heat transfer coefficients which was found to be independent of the thermal conductivity of the solid particles and to vary as the 0.5 power of the Prandtl Number of the gas.

Dow and Jakob<sup>(17)</sup> obtained heat transfer coefficients upto 170 lb.cal/sq.ft.hr.°C and these were about 100 times the value obtained for gases without suspended solids. The fluidized bed was formed in a vertical cylindrical container surrounded by jacket containing the heating medium. Accurate measurements of temperature were made at various points. The main body of the bed was found to be at a uniform temperature with a steep temperature gradient at the entry and near the walls.

The high heat transfer coefficient at the walls of the container cannot result from the heat exchange when the solid particles hit the wall, because this would account for only a small fraction of the heat actually transferred. It is suggested that the presence of the particles near the wall breaks up the laminar sub-layer which would otherwise exist. This is further supported by the fact that the transfer coefficient is not affected by the thermal conductivity of the solid material. The heat transfer coefficient is less than slugging occurs, presumably because there is then no longer a layer of particles near the wall throughout the whole depth of the bed.

The expression recommended by Dow and Jakob<sup>(17)</sup> for the calculation of heat transfer coefficient is

$$\frac{h D}{k} = 0.55 \left(\frac{D}{L}\right)^{0.65} \left(\frac{D}{D_p}\right)^{0.17} \left(\frac{(1-\epsilon) s C_s}{\epsilon \rho C_p}\right)^{0.25} \left(\frac{DG}{\mu k}\right)^{0.80} \quad (2)$$

Jakob<sup>(18)</sup> has attempted to explain differences between his results and those of Van Heerden in terms of the fact that in one case the fluidized bed was being heated and in the other it was being cooled. It is likely, however, that this is only a partial explanation because Molino and Hougen<sup>(19)</sup> found that the heat transfer is not affected by the type of process.

### 2.3 Theory of Oxidation of Sulphide Concentrate <sup>(8)</sup>

The oxidation of the sulphide particles by atmospheric oxygen produces more or less dense film oxide on its surface. For the oxidation to go on, a continuous exchange is essential between the solid and gaseous phase, i.e. free access for oxygen to the sulphide and withdrawal of sulphur dioxide. This is accomplished by the diffusion of the gases through pores and discontinuities in the oxide envelope over the sulphur grain.

As roasting progresses the oxide film grows in thickness and gases find it increasingly more difficult to penetrate it, the combustion of the sulphide slows down or stops altogether. Of course the latter alternative is less likely to occur with smaller than with larger particles which may have a thicker oxide film. Therefore, roasting may be speeded up by grinding, as this increases the ratio of surface area to unit weight of the sulphide.

The rate of gas diffusion through pores and discontinuities in the oxide film rises with temperature. Its rise, however, is usually kept within some limit to avoid fusion of the particles. The rate of diffusion is furthermore dependent on the difference in the partial pressure of the oxygen

and sulphur dioxide at the interface of the oxide film, rising with decreasing sulphur dioxide and with increasing oxygen in the gases surrounding sulphide particles, the rate of roasting is affected in a similar way. Therefore, the particles falling down or floating in the gas are roasted quicker than those lying in the bed. The roasting of the latter may be accelerated by stirring.

The heat given up by sulphide combustion goes to raise the temperature of the burning grains, although the bulk of heat is given to surroundings. At high rate of roasting, which is true of falling or floating of particles, the rate of heat input per unit time appreciably rises, while the rate of heat exchange with the surroundings remains nearly unchanged. Therefore, heat is accumulated in the grains, rising their temperature and that of roasting.

Sulphide minerals widely differ in ignition temperature which is also affected by grain size, being higher for bigger than for smaller particles. This is shown in table-2.

Ignition temperature, besides other things, depends on the mineralogical composition. The rate of

combustion increases with temperature and decreases as more sulphur is burnt out, for the reason that oxide film formed on the surface of each grain shuts out oxygen. Too high temperature of roasting may cause fusion of particles, which will hamper the inflow of air and thus the rate of reaction will slow down.

#### 2.4 A Brief Review of Previous Work Done

Very few attempts have been made to study analytically the nature of the kinetics involved in oxidation of zinc and copper sulphide concentrates in fluidized bed. Anderson and Raymond Bolduc<sup>(1)</sup> studied fluo-solid roasting of zinc concentrates. They reported that the roasting of zinc concentrate required close control. There is a much greater danger of fusion with zinc concentrates than with pyrite, the melting points of  $ZnS$  and  $FeS_2$  being  $1020^\circ C$  and  $1193^\circ C$ , respectively. Lead and other impurities in the concentrates further complicate the problem.

Roasting of sphalerite concentrates from Zawar mines had been investigated by Murelimohan Rao and Abraham<sup>(20)</sup> with the object of determining the operational controls which could be exercised during roasting to encourage the formation of desired products, like zinc oxide and sulphate and to

minimise the formation of undesirable zinc ferrite silicate. They reported that no sulphate was found in the roast above 850°C when zinc sulphide concentrate was roasted in air or in oxygen. At lower temperatures, oxygen enrichment ~~increased~~ the percentage of zinc sulphate formed. Though oxygen enrichment shortened the time for the completion of roasting, there was no appreciable decrease in the amount of zinc ferrite formed at the end of roasting. Practically all the iron in the roast was present as ferrite. The amount of silicate formed was minimum when oxygen-enriched air was employed. This was due to the short time of roasting. Maximum amount of zinc oxide was formed when roasting was done in air or oxygen at 850°C.

Snurikov, Larin and Magulis<sup>(21)</sup> studied the roasting of zinc concentrates in fluidized bed at high  $\text{SO}_2$  concentration in the gas phase. The concentrates containing zinc 58.2%, Fe 3.5%, Cu 0.8%, Pb 2.2% and S 33.1% were roasted with a  $\text{SO}_2$  (50 to 90% by volume) and oxygen mixture for 25 to 300 minutes at 600-900°C. When roasted for 25 minutes with a gas mixture containing  $\text{SO}_2$  60% and 80%, the zinc sulphide content of the calcine was decreased to about 5% at 800°C, but the zinc sulphate concentration remained about 30% even at 900°C, though 96% of Zn was acid soluble. At 900°C and 25 min. roasting period when  $\text{SO}_2$  content of the gas mixture was increased



from 50 to 90% by volume, the water soluble zinc concentrate decreased from 31.5 to 26.4% where as on roasting with air, only 0.5% of Zn was found to be water soluble. When roasted with 60% SO<sub>2</sub> and 40% oxygen at 900°C, increasing the time by more than one hour had little effect on zinc sulphide oxidation and zinc sulphate formation. These experiments showed that fluidized bed roasting of zinc concentrate with oxygen and gas recirculation may produce gas containing about 80% SO<sub>2</sub> but will yield a calcine unsuitable for hydrometallurgical treatment by existing commercial methods.

Besser and Babina<sup>(22)</sup> studied the simultaneous roasting of zinc concentrate and lime stone in a fluidized furnace. They reported that it was possible to roast zinc concentrates without any fuel at temperatures of 1120 to 1180°C, rate of air flow being 23 to 24 cm/sec., and with addition of 6-10% lime stone. But production experiments were not successful because the fluidized bed could not be heated to about 1120°C and the extraction of lead and cadmium was not satisfactory.

A series of roasting<sup>(23)</sup> of zinc concentrate

was carried out at different temperatures on a constant flow of air. The results showed that an increase in temperature of roasting of concentrate from 800 to 1000°C had no influence on the extraction of zinc in the sulphuric acid leach solution which was in the range of 94.2 to 95.7%. Roasting of concentrate at a temperature of 700°C and under similar leaching conditions gave a still lower extraction of zinc in the solution which was only 92.8%.

Denbigh and Beveridge<sup>(14)</sup>, in an extensive investigation on the oxidation of sulphide from 500 to 1400°C, have noted some unusual features. The reaction was observed to start at temperature between 500 and 600°C, the exact value depending on surface area available. With pellets which were preinterred the rate exhibits an Arrhenius-type relationship with temperature until about 900°C, and for this reason it is believed to be chemically controlled with an activation energy of 50 K Cal./g mole. Additional evidence for chemical control was provided by Canon and Denbigh<sup>(23)</sup>, who noted that crystals of sphalerite oxidized at all temperatures below 830°C, the shrinking core of zinc sulphide maintained a similar geometry to that of original crystal.

At low temperatures the initial rate with unsintered pellets, owing to larger surface area available, is appreciably higher than with pre-sintered pellets. However, the rate increases less rapidly with temperature than would be expected from a chemically controlled reaction, and this is attributed to the reduction in surface area caused by the sintering of the pellet prior to or during oxidation.

Above 830°C, or some what higher, if no oxide layer is present transport control becomes significant. The corners of the sulphide core in sphalerite crystals become rounded. It has also been shown that at temperatures of 850 to 880°C an increase in the oxygen partial pressure causes a proportional increase in the reaction rate, where as below 850°C a limiting oxygen reaction rate remains constant<sup>(24)</sup>. The oxidation of zinc sulphide may be considered irreversible over the whole of the temperature range examined. Consequently, with the exception noted below, the reaction rate in the transport controlled regions is relatively insensitive to temperature. The exception occurs at higher temperature in the region of 1250°C when the rate becomes appreciably higher than would be expected from the transport of oxygen and sulphur dioxide between the reacting

interface and the bulk gas. This acceleration in the rate is believed to be due to the vaporization of zinc sulphide which reacts with the oxygen in the boundary layer surrounding the solid. In this range a complete shell of oxide may be formed outside and separated from the original sulphide pellets. The vapour pressure increases exponentially with temperature and at still higher temperatures (1400°C) the rate of vaporization is so rapid that the reaction occurs entirely in the vapour phase and no coherent oxide skin is formed.

Denbigh and Beveridge<sup>(5)</sup> have shown that on the intermediate range 1050-1200°C there is a rapid fall of the reaction rate. It is believed some vaporization of zinc sulphide occurs and reacts with oxygen in the porous oxide layer, depositing zinc oxide, which eventually blocks the pores, confirmatory evidence was provided by the density of the product layer, which rose from 2.0 g/c.c. for reaction at 950°C to 4.8 g/c.c. at 1150°C.

Kinetic studies of the oxidation of zinc sulphide were carried out by Natesan and Philbrook<sup>(4,25)</sup> in a fluidized bed reactor over a temperature range

of 740 to 1000°C with oxygen-nitrogen gas mixture of 20 to 40% O<sub>2</sub>. A mathematical model was developed to describe the overall conversion of the solids. Application of the model to the experimental data indicated that the chemical reaction at the outer boundary of the unreacted sulphide core was the rate-limiting step for the process. The temperature dependence of the kinetic constant corresponded to an activation energy of 42.25 K cal per mole. Oxygen starvation in the bed was not limiting in any of the experimental runs, but an increase in the inlet-oxygen mole fraction resulted in a substantial increase in reaction rate.

Most of the published literatures deal with the possibility of selective sulphating individual components in the ore. Frank M Steplens<sup>(27)</sup> conducted a series of tests on oxidation of copper concentrate with a fluidized-bed reactor. He reported that the fluidized bed reactor can be used successfully for treating copper and cobalt ores to produce water soluble copper and cobalt sulphates while retaining the iron in insoluble-oxide form.

Krishanmurthi<sup>(37)</sup> studied calcination of Indian chalcopyrite concentrates for recovery of copper

sulphate in a fluidized bed. He found that at 550°C the recovery of copper was about 80% by treating the calcine with boiling water containing 5% sulphuric acid and 5% ferric sulphate under the minimum fluidization velocity and twice the theoretical requirement of air supply.

Razouk, Kolta and Mikhail<sup>(41)</sup> found that in case of chalcopyrite, sulphatation of iron took place more rapidly than that of copper, but above 450°C interaction between the formed ferric sulphate and copper oxide led to the production of copper sulphate in increasing quantities. At about 600°C both sulphates decompose to yield the corresponding oxides which react together at 900°C forming cupric ferrite.

Ramakrishna Rao and Abraham<sup>(56)</sup> studied the oxidation of cuprous sulphide pellet in the temperature range of 750 to 950°C. The apparent activation energy from the experimental data was found to be different for the initial and subsequent periods. Rate controlling mechanism for these two intervals have

been proposed based on interface chemical reaction, mass transfer resistance and heat transfer concepts. The activation energies were found to be of the order of 25.0 K cal/ g. mole and 6.0 K cal/g. mole, for the initial and subsequent periods respectively.

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CHAPTER - III

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## EXPERIMENTAL WORK

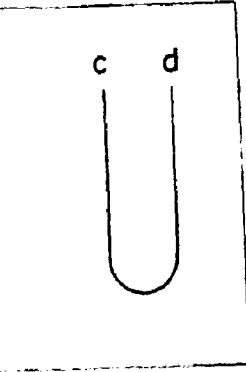
### 3.1 Experimental Set-up

The experimental set-up is shown in figure - 2 and consists primarily of the following major components:

- (a) Air compressor
- (b) Orifice meter with 1/16" orifice plate
- (c) Air preheater
- (d) Air distributor
- (e) Fluidizer (Reactor)
- (f) Crucible with perforated bottom
- (g) Heating furnace
- (h) Control panel board
- (i) Thermo couples
- (j) Cyclone dust catcher
- (k) Manometer

3.1(a) Air Compressor: Air required for roasting of sulphide concentrates was supplied by an air compressor . The rating of the compressor was:  
H.P. 1; R.P.M. 750; Max. Pressur 75 psi

ETE  
ETE  
ER  
ICO  
ICO  
ICO  
UTO  
EHEA  
FU  
ME  
MPR  
PLA  
RE  
VA  
L V  
A. G  
E D  
F TA  
E W  
E V



2

TO MONOMETER ←

9

19

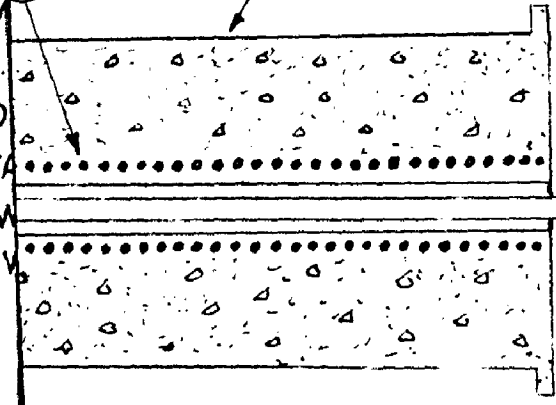
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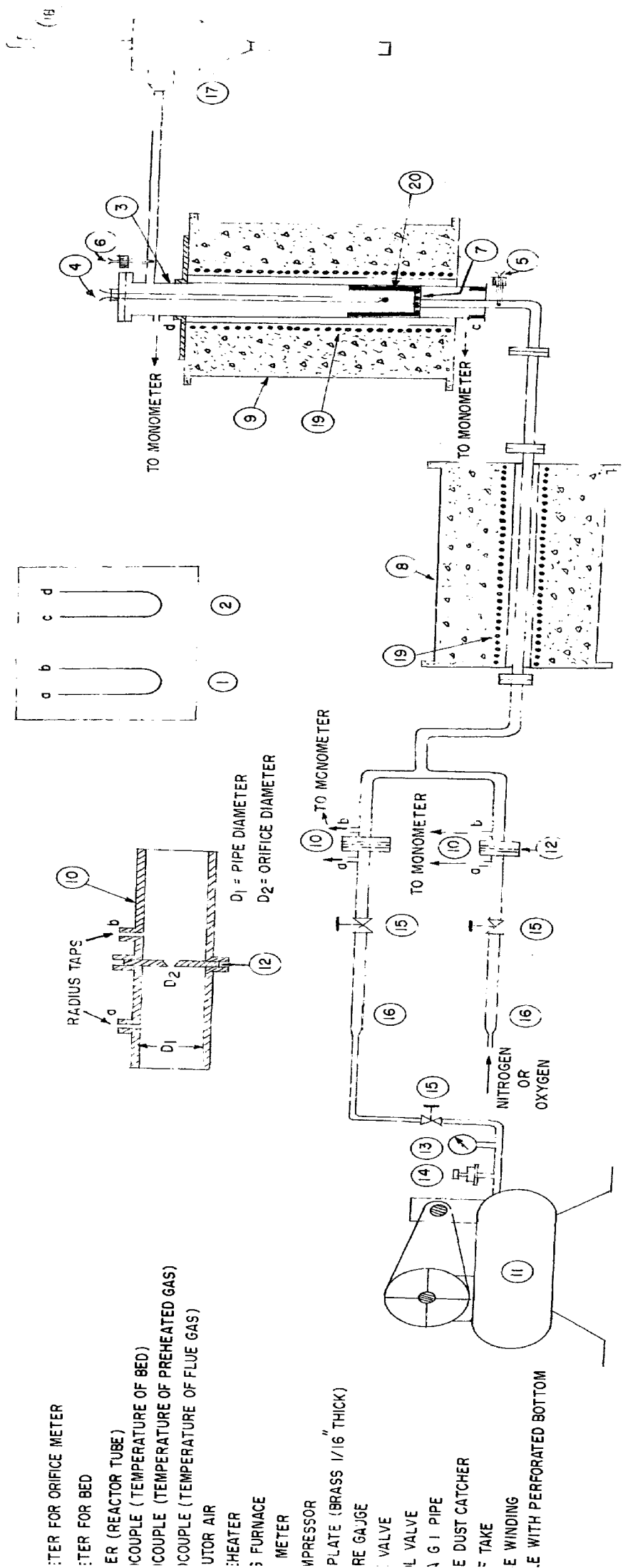
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TO MONOMETER ←

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8





- 1. METER FOR ORIFICE METER
- 2. METER FOR BED
- 3. REACTOR TUBE
- 4. COUPLE (TEMPERATURE OF BED)
- 5. COUPLE (TEMPERATURE OF PREHEATED GAS)
- 6. COUPLE (TEMPERATURE OF FLUE GAS)
- 7. TAP FOR FLUE GAS
- 8. HEATER
- 9. FURNACE
- 10. METER
- 11. COMPRESSOR
- 12. PLATE (BRASS 1/16" THICK)
- 13. PRESSURE GAUGE
- 14. VALVE
- 15. VALVE
- 16. GAS PIPE
- 17. DUST CATCHER
- 18. TAKE
- 19. WINDING
- 20. PERFORATED BOTTOM

FIG. 2 EXPERIMENTAL SET UP.

3.1(b) Orifice meter: Orifice meter is a device for measurement of quantity of gas flowing per unit time. It can also measure the velocity of flow. It must be calibrated in order to obtain the correct flow rate by some standard flow meter.

The practical working equation for weight rate of discharge, adopted by A.S.M.E. Research Committee on fluid meter for use with either gases or liquids is:

$$w = q_1 d_1 = c y A_2 \sqrt{\frac{2g_c (P_1 - P_2) d_1}{1 - \beta^4}} \quad \text{-----}(3.1)$$

The value of 'y' can be taken for liquid as unity but in the case of gases its value can be obtained from standard curves for square-edged or sharp edged concentric circular orifice, the value of coefficient of discharge 'c' falls between 0.595 and 0.629.

The orifice meter was made out of two flanges of 10 cm. outer dia each fitted with four bolts of 8 mm. diameter. Between the two flanges there was an 0.159 cm. thick orifice plate of brass having a hole 0.636cm dia at the centre. The pressure tapping static holes were located at a place nearest to orifice plate in the down stream side and about 1½" from orifice plate in up stream side.

3.1(c) Air Preheater: A tube furnace was designed and fabricated to preheat the air up to 500°C within an accuracy of  $\pm 5^\circ\text{C}$ . Inside the tube furnace a stainless steel tube was placed with flange coupling arrangement. Other particulars are:

Maximum temperature of the furnace	- 1000°C
Voltage	- 220 V
Length of the tube	- 61 cm.
Diameter of the tube	- 10 cm.
Heating element	- Kanthal wire (18 SWG)
Refractory tube	- Silliminite
Length of Wire	- 29 meter
Current	- 8.7 amps.

3.1(d) Air Distributor: For uniform distribution of air a distributor was used which consists of a mild steel plate of 0.317 cm. thickness with 5 holes per sq. cm. of 3/32" diameter.

3.1(e) Fluidizer (Reactor): This is the most important part of the whole set-up. The fluidized bed reactor was constructed from type 304 stainless steel seamless tube. The inside diameter of the tube was 5.588 cm. and it was 74 cm. long. At a distance of 5.1 cm. from the top of this stainless steel tube a mild steel tube

of 1.9 cm. inside diameter was welded to the cyclone dust catcher with the help of a socket to allow the escape of flue gas to the atmosphere through cyclone dust catcher.

3.1(f) Crucible with perforated bottom: A crucible with a perforated bottom having 5 holes per sq. cm. of  $3/32''$  diameter was used which was 15 cm. in height and 4.445 cm. in diameter.

3.1(g) Heating furnace: The fluidizer was heated upto the desired temperature of roasting with the help of a vertical tube furnace with the following specifications:

Maximum temperature	- 1000°C
Voltage	- 220 V
Length of tube(Silliminite)-	46.25 cm.
Tube Diameter (outer)	- 15.25 cm.
Shell Diameter	- 48.5 cm.
Heating element	- Kanthal wire(18 SWG)
Length of wire	- Upper winding 21 meter lower winding 18.5 meter
Total current	- 13.9 amps.

3.1(h) Control Panel Board: A control panel board to control the temperature of the furnace was made.

Separate temperature indicators were provided to indicate the temperature of furnace, reactor tube and the temperature of preheated air and flue gas.

3.1(i) Thermocouples: Chromel-Alumel thermocouples were used for temperature measurement. This thermocouple can satisfactorily measure the temperature upto 1300°C. Two Chromel-Alumel thermocouples were provided to measure the temperature of preheated air and that of flue gas. At the control panel the temperature indicators were mounted.

3.1(j) Cyclone dust catcher: This unit was designed to trap any solid particle being carried over by the gas. The cyclone dust catcher was made of mild steel sheet (1/16" thick). The diameter and height of the cylindrical portion were 15.25 cm. each while the height and diameter of the cone were 22.5 cm. and 2.5 cm., respectively. The diameter of the opening at the entrance was 5 cm. while at the exit it was 2.5 cm. The cyclone dust catcher was supported on a tripod-stand made out of M.S. rod. The height of the stand was 1.75 meter. A lid was provided at the bottom to facilitate the removal of solid particles.

3.1(k) Manometer: Three manometers of 1.2 meter height were made of glass tube (1 cm. outer diameter). Water was used as manometric liquid.

### 3.2 Material Used

The following materials were used:

- i) Zinc concentrate : The analysis of concentrate is given below:

Zinc	-	50.72 %
Sulphur	-	31.7 %
Iron	-	6.47%
SiO <sub>2</sub>	}	- Rest
Al <sub>2</sub> O <sub>3</sub>		
Copper		
Lead		

- ii) Copper concentrate: The analysis of concentrate is given below:

Copper	-	25.23%
Sulphur	-	29.51%
Iron	-	30.32%
Silica	}	- Rest
Alumina		

### 3.3 Calculation of Fluid Mass Velocity for Minimum Fluidizat

The fluid mass velocity for minimum fluidization,  $G_{mf}$ , of a bed of solids was calculated as a function of



particle size using Leva's correlation<sup>(8,9)</sup>.

$$G_{mf} = 0.702 \frac{D_p^{1.82} (\rho_f (\rho_s - \rho_f))^{0.94}}{(u_f)^{.88}} \text{-----(3.2)}$$

The above correlation is valid only if the Reynolds number ( $R_e = (D_p G_{mf} / \mu_f)$ ) is less than 5.0, otherwise the  $G_{mf}$  values should be corrected by a factor determined experimentally<sup>(9)</sup>.

### 3.4 Calculation of Mass Flow Rate of Air Through Orifice Met

The fluid mass velocity in  $\text{g/cm}^2 \text{ sec.}$  was calculated using correlation as given below<sup>(21)</sup>:

$$W = cy A_2 \sqrt{\frac{2g_c (P_1 - P_2) \rho_1}{1 - \beta^4}} \text{-----(3.3)}$$

Taking  $y = 1$

$$c = 0.61$$

and  $\Delta p = P_1 - P_2 = 40 \text{ cm. of water}$

Gauge pressure of compressor = 2 kg/sq.cm.

Orifice diameter - 2/8"

Pipe diameter - 1.5 cm.

The calculated values are given in Table-3.

### 3.5 Experimental Procedure

The various steps involved are discussed below:

Pelletizing: Fine ore concentrate was converted into small pellets by means of pelletizer. The pellets thus formed were dried.

Sieve Analysis: The copper sulphide and zinc sulphide pellets were classified into various sizes by means of sieve shaker.

Roasting : The empty reactor was first heated to the required temperature and after that the crucibles with perforated bottom containing 50 gms. of pellets was introduced. A slow stream of preheated air (3000°C) was passed through the reactor. The flow of air was adjusted gradually to the required rate of  $0.2097 \text{ gm/cm}^2 \text{ sec}$ . In the initial stages of roasting the temperature was increased and it was controlled by controlling power input. The temperature of inlet and outlet gases and that of bed were noted periodically. Samples of bed were

taken from the top of the reactor at various time intervals. The samples were then analysed for sulphur. The method for analysing these samples is given in Appendix.

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CHAPTER - IV

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## RESULTS AND DISCUSSION

### 4.1 Results

In the present investigation oxidation tests were made in fluidized bed reactor on both zinc and copper concentrate pellets. The effect of temperature and particle size on the rate of roasting were studied. The temperature was varied in the range of 700° to 800°C in case of zinc concentrate and 500° to 700°C in case of copper concentrate pellets. The various sizes of the particles were 0.1435 cm. (-10 + 14 mesh size), 0.184 cm. (-9 + 10 mesh size) and 0.219 cm. (-8 + 9 mesh size). The samples were analysed chemically for sulphur to obtain fraction of reaction completed.

The experimental results from different runs in a fluidized bed for zinc concentrates are presented in Tables 4 to 6 and for copper concentrates in Tables 7 to 11. These data provided a measure of the extent of oxidation with time. Plots of fractional sulphur removal vs time at various temperatures and for various particle sizes for zinc and copper concentrates are plotted in Fig. 5 to 10 and Fig. 11 to 18, respectively.

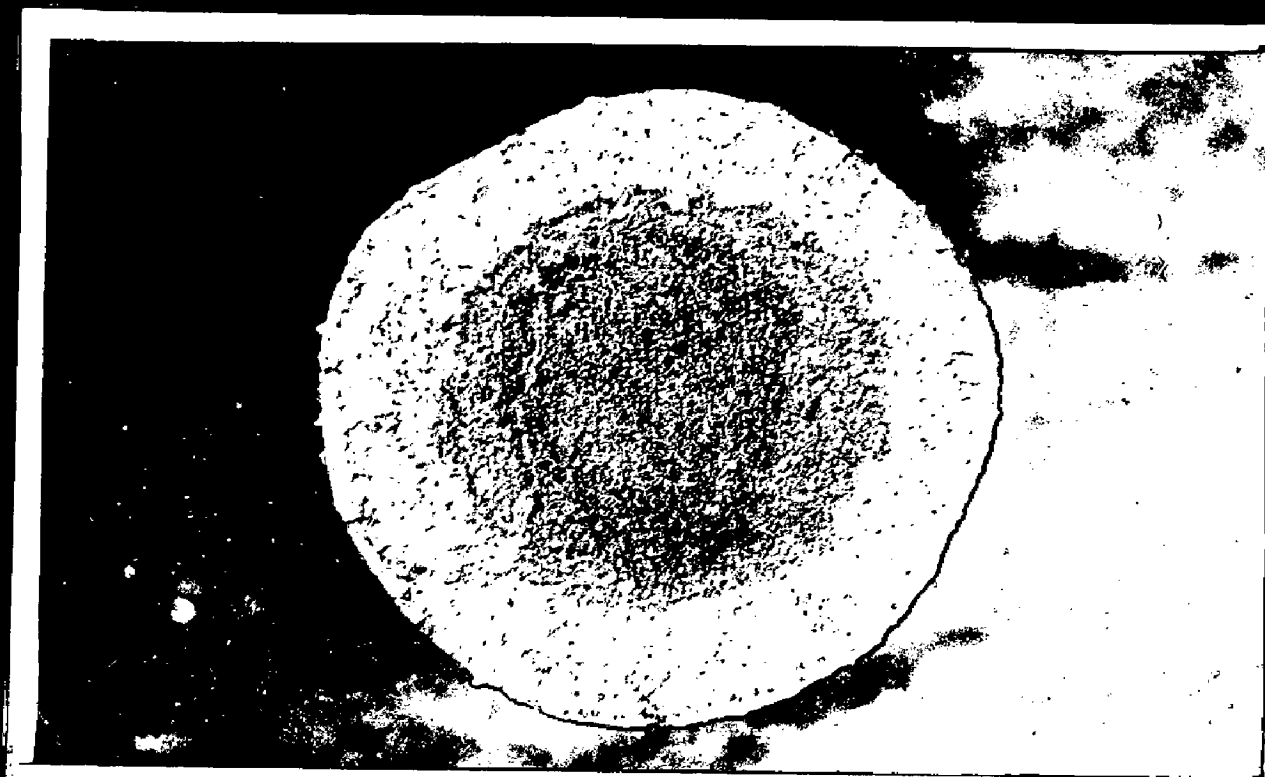


Fig. 3 - Cross section of partially roasted zinc concentrate pellet.

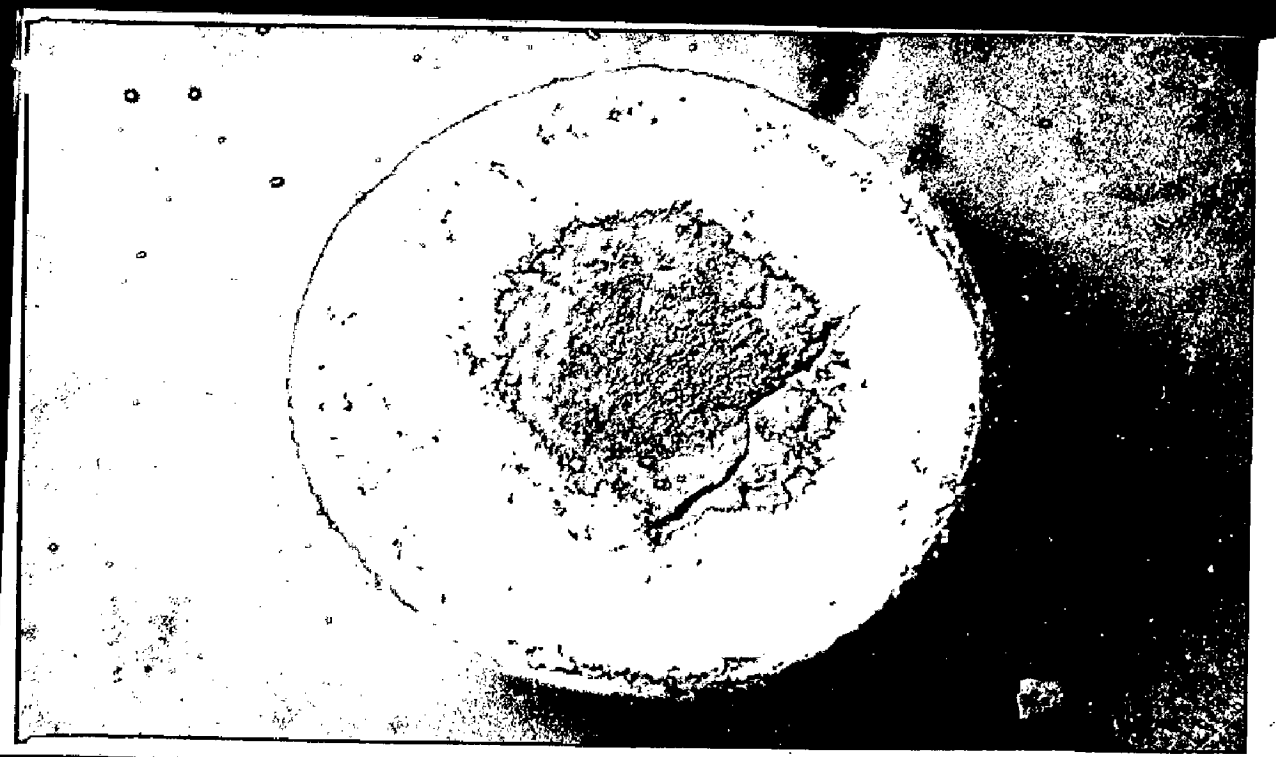


Fig. 4 - Cross section of partially roasted

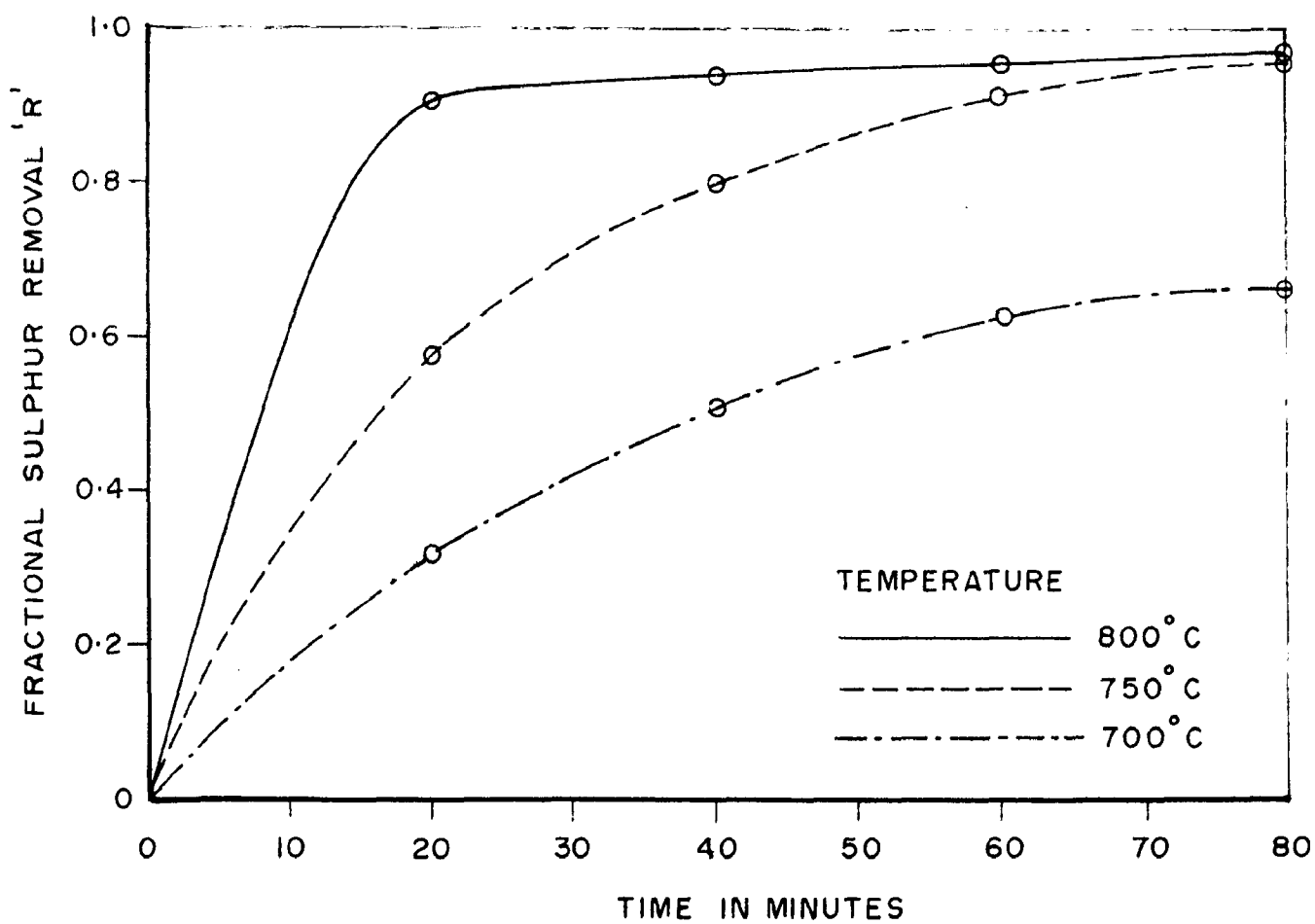


FIG. 5. A PLOT OF FRACTIONAL SULPHUR REMOVAL VS. TIME FOR ZINC CONCENTRATES OF 0.1435 cm. PARTICLE SIZE.

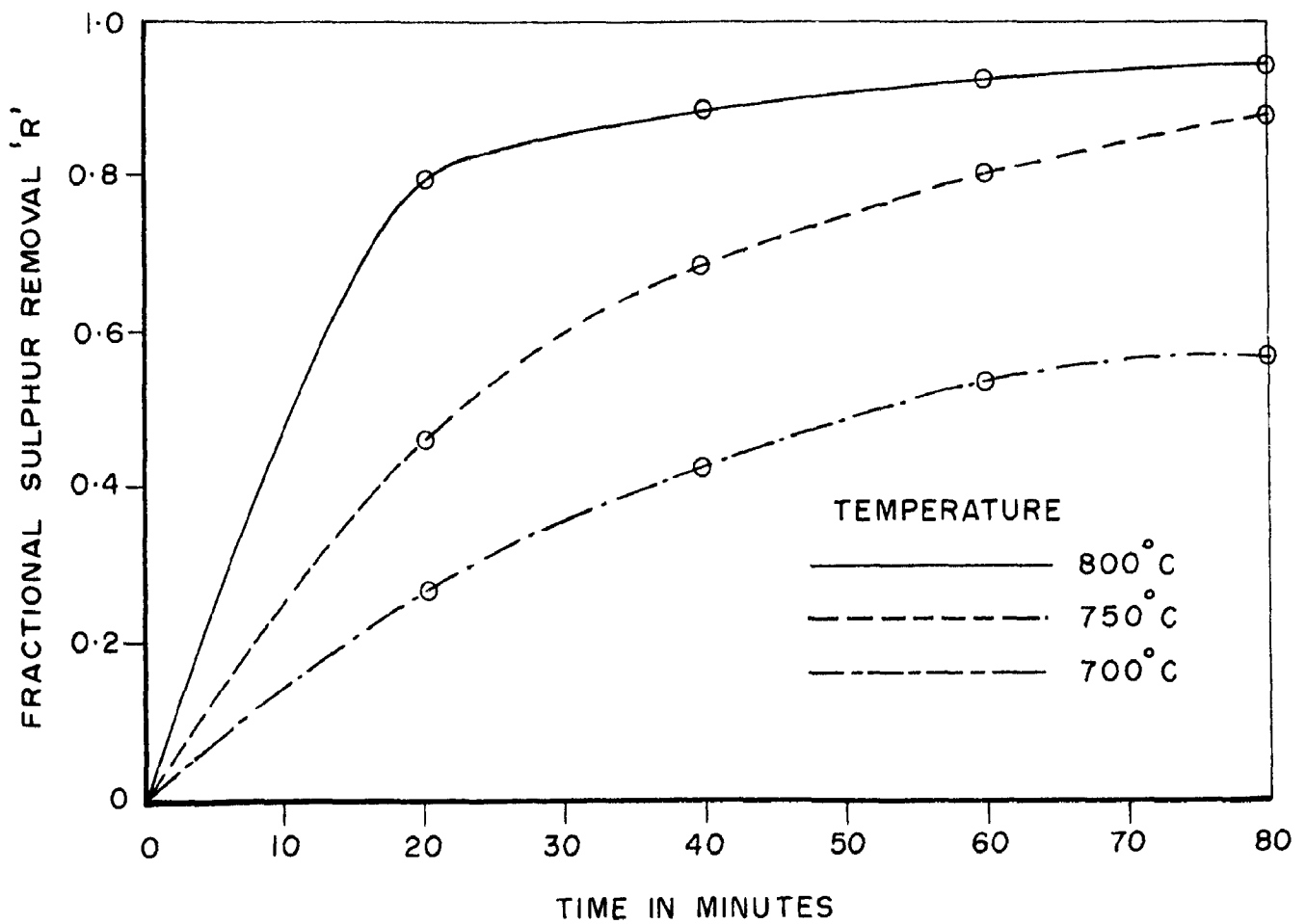


FIG. 6. A PLOT OF FRACTIONAL SULPHUR REMOVAL VS. TIME FOR ZINC CONCENTRATES OF 0.184 Cm. PARTICLE SIZE.



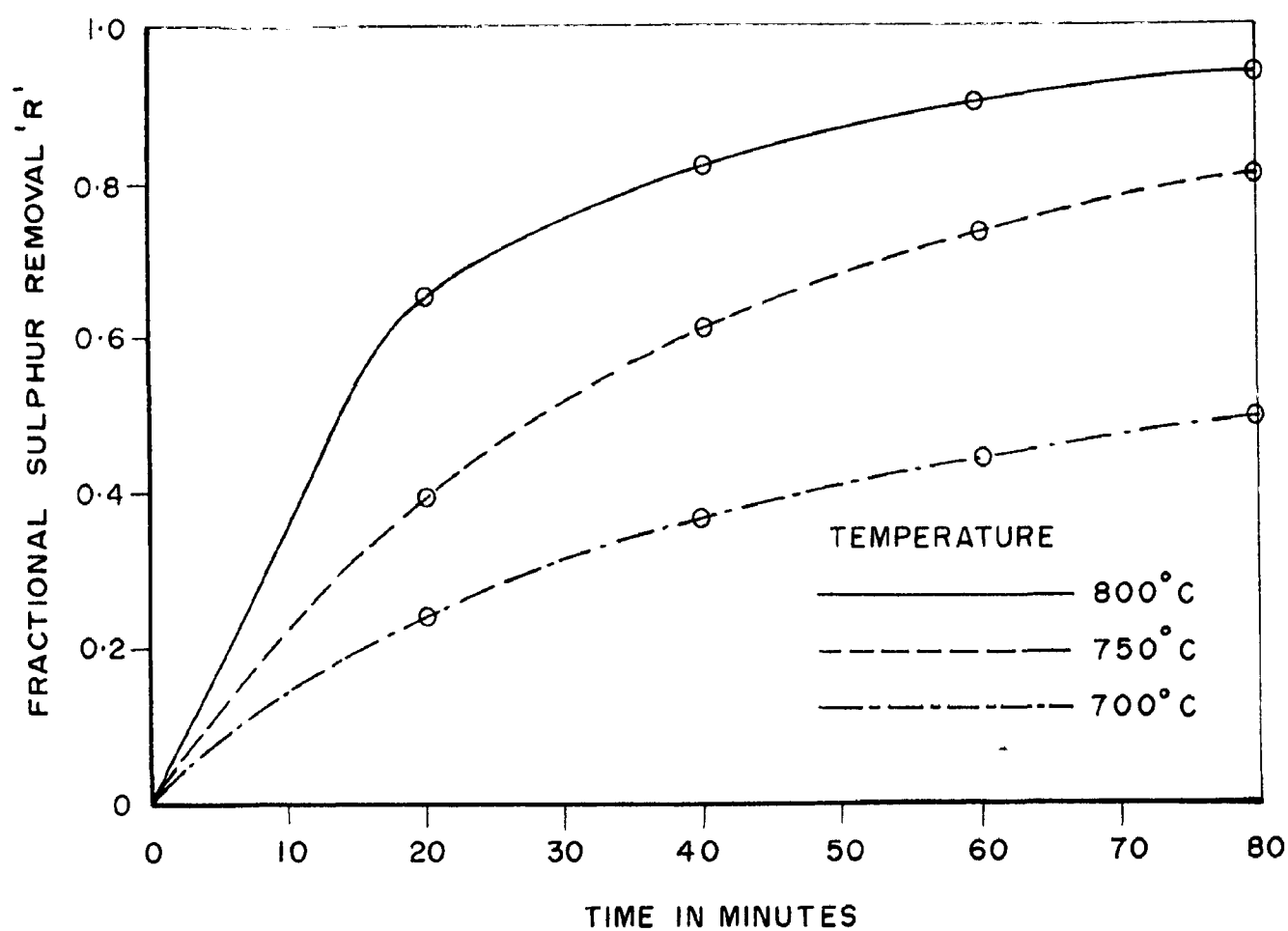


FIG. 7. A PLOT OF FRACTIONAL SULPHUR REMOVAL VS. TIME FOR ZINC CONCENTRATES OF 0.219 Cm. PARTICLE SIZE.

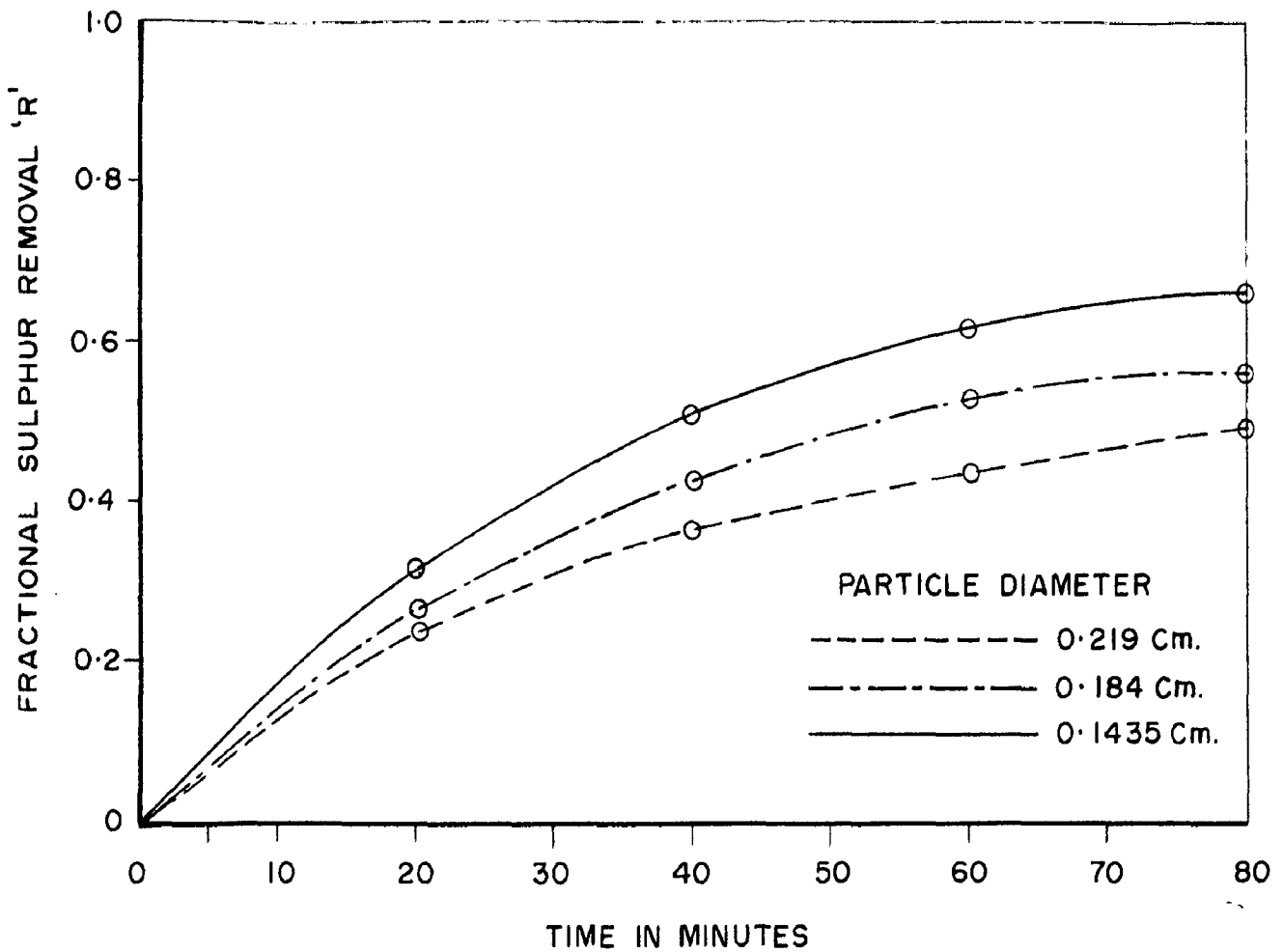


FIG. 8. A PLOT OF FRACTIONAL SULPHUR REMOVAL VS. TIME FOR ZINC CONCENTRATES AT TEMPERATURE 700°C.

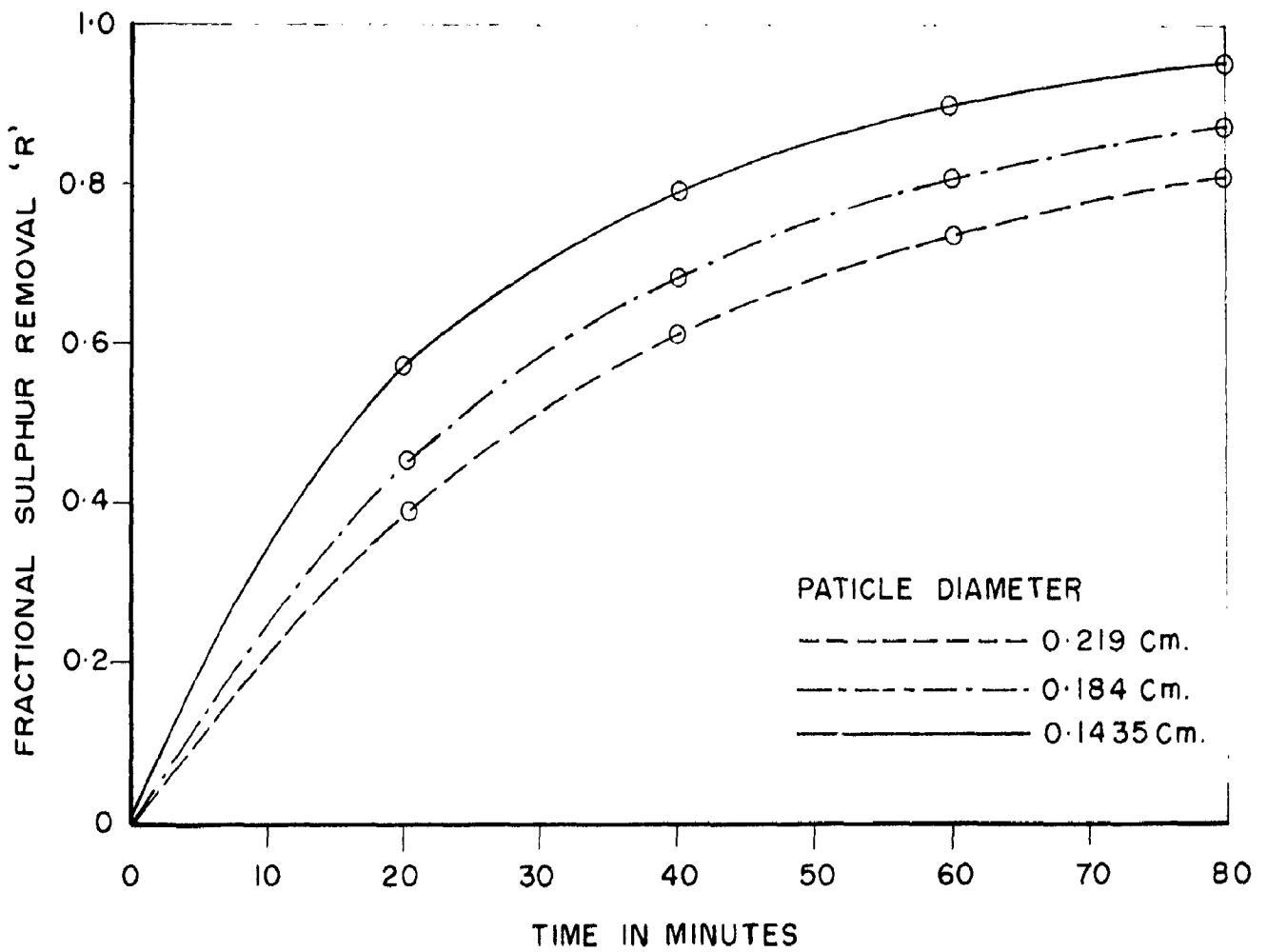


FIG. 9. A PLOT OF FRACTIONAL SULPHUR REMOVAL VS. TIME FOR ZINC CONCENTRATES AT TEMPERATURE 750°C.

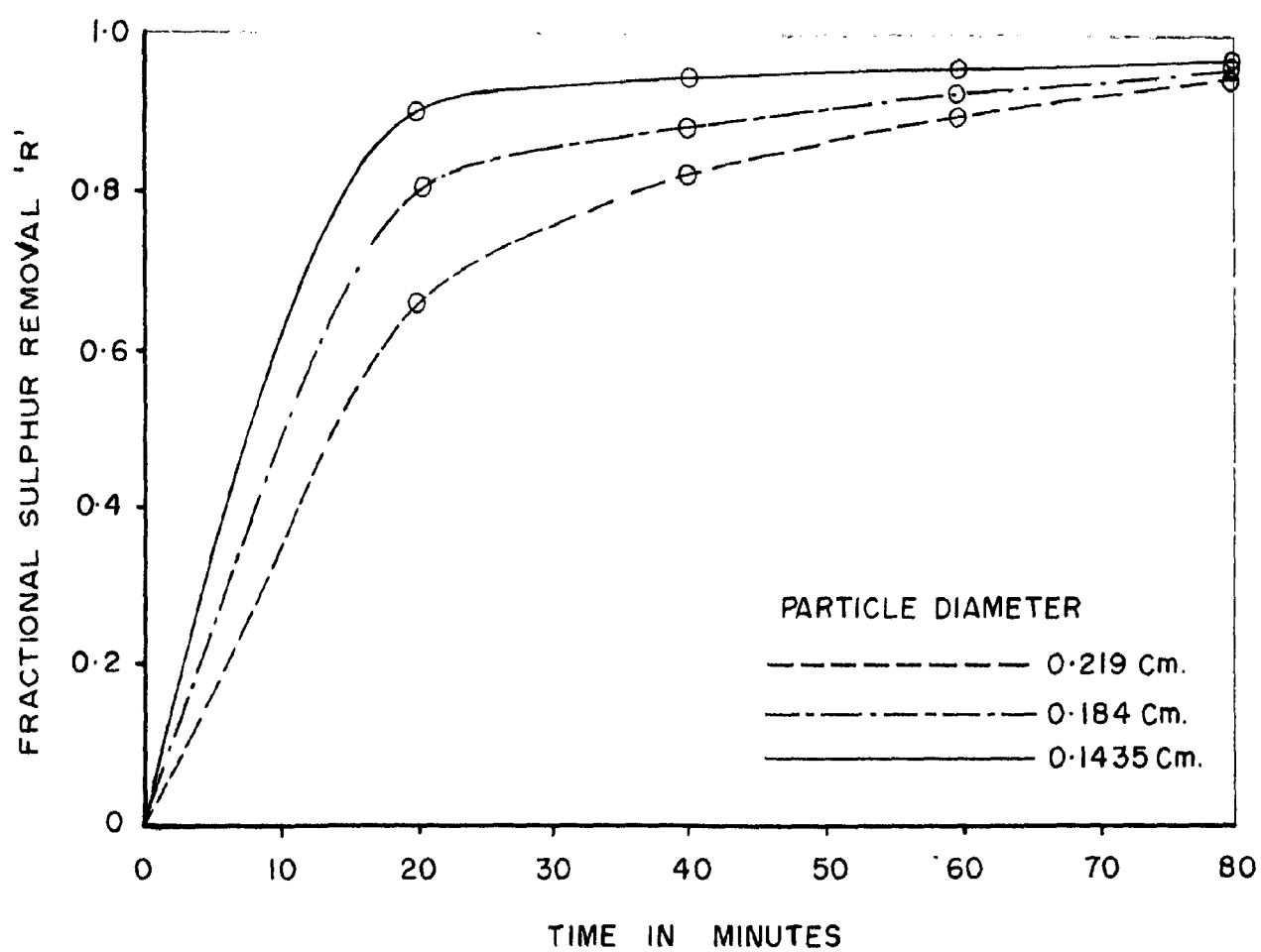


FIG.10. A PLOT OF FRACTIONAL SULPHUR REMOVAL VS. TIME FOR ZINC CONCENTRATES AT TEMPERATURE  $800^{\circ}\text{C}$ .

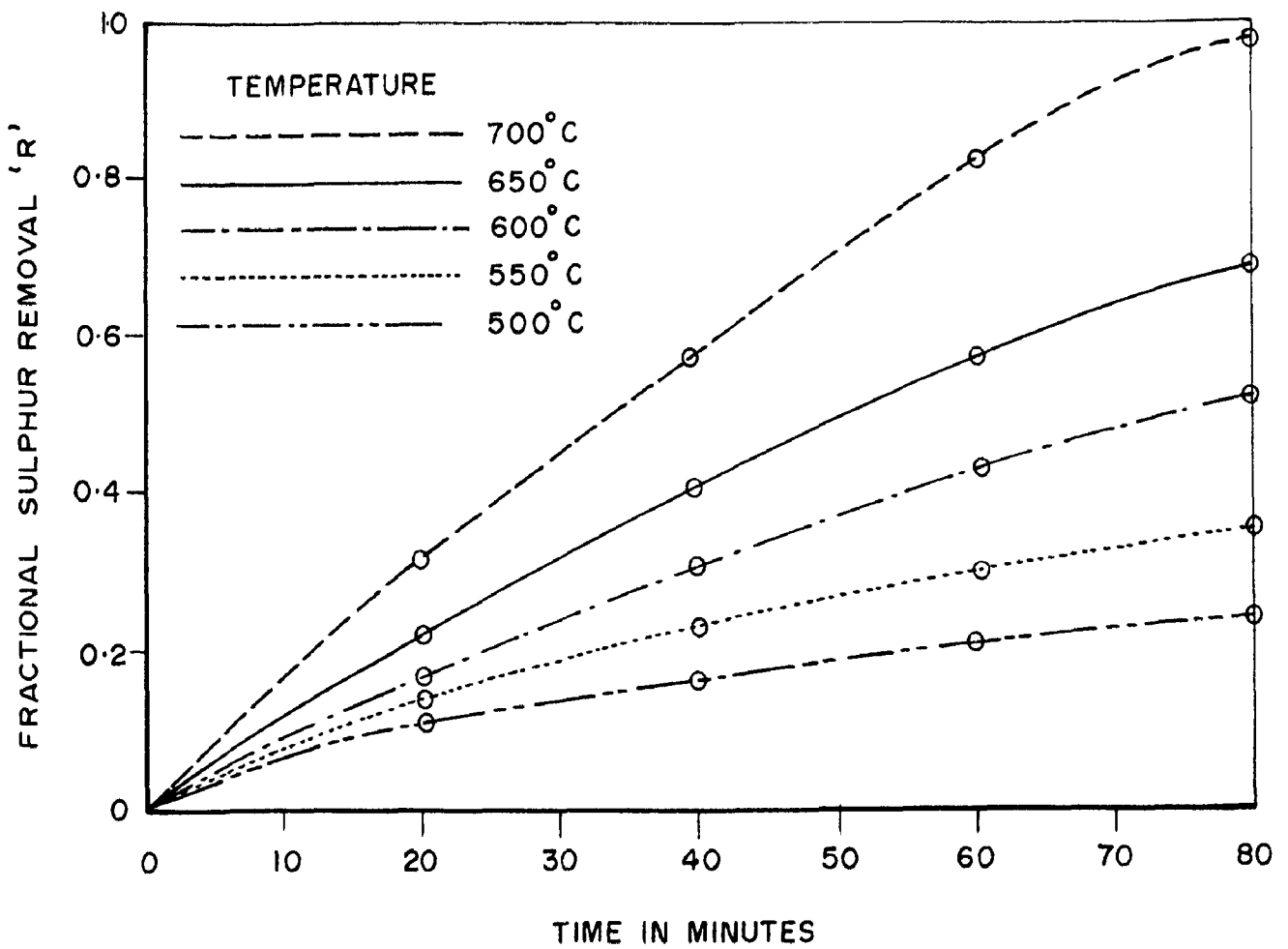


FIG. II. A PLOT OF FRACTIONAL SULPHUR REMOVAL VS. TIME FOR COPPER CONCENTRATES OF 0.1435 cm. PARTICLE SIZE.

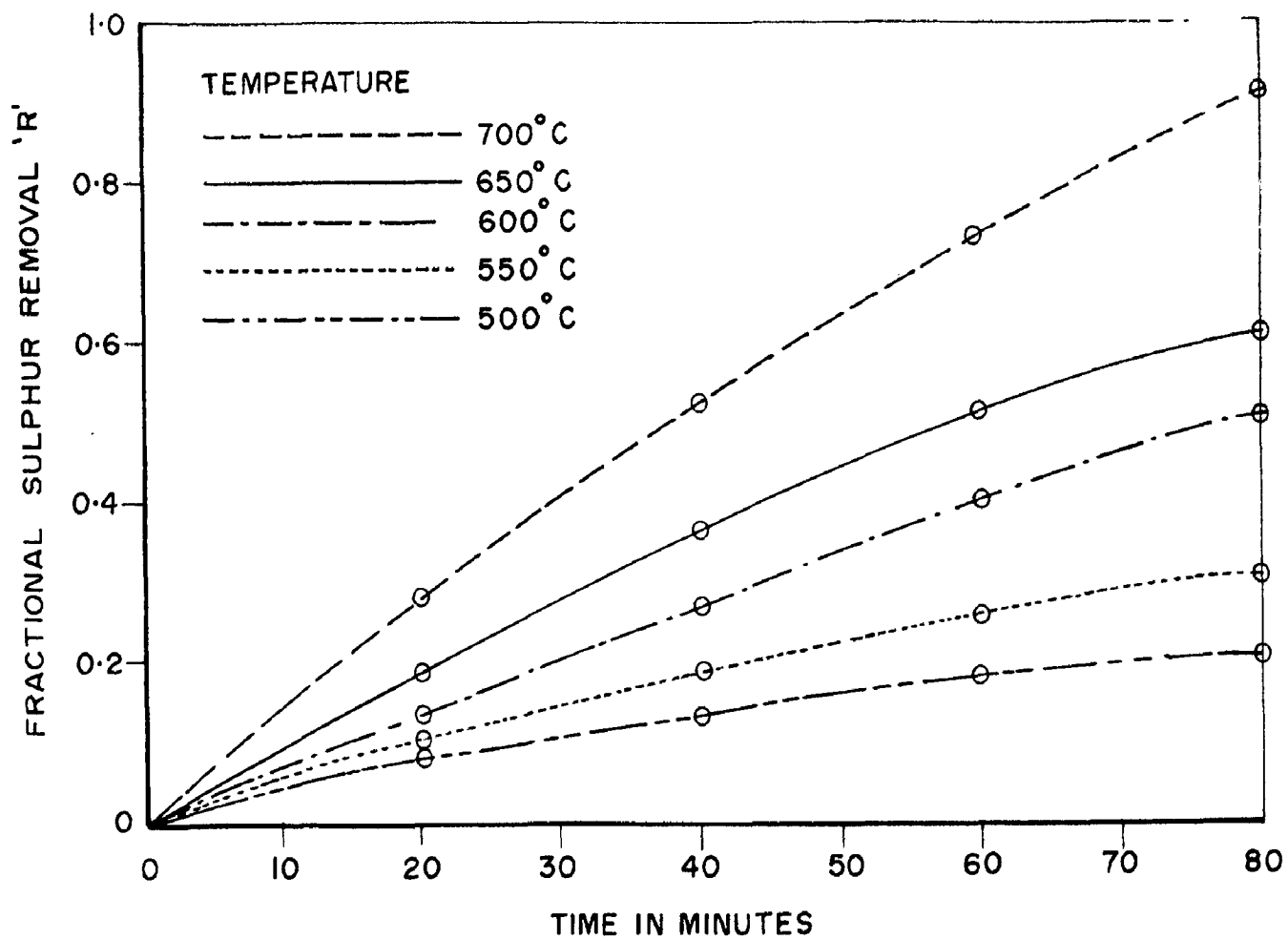


FIG.12. A PLOT OF FRACTIONAL SULPHUR REMOVAL VS. TIME FOR COPPER CONCENTRATES OF 0.184 cm. PARTICLE SIZE.

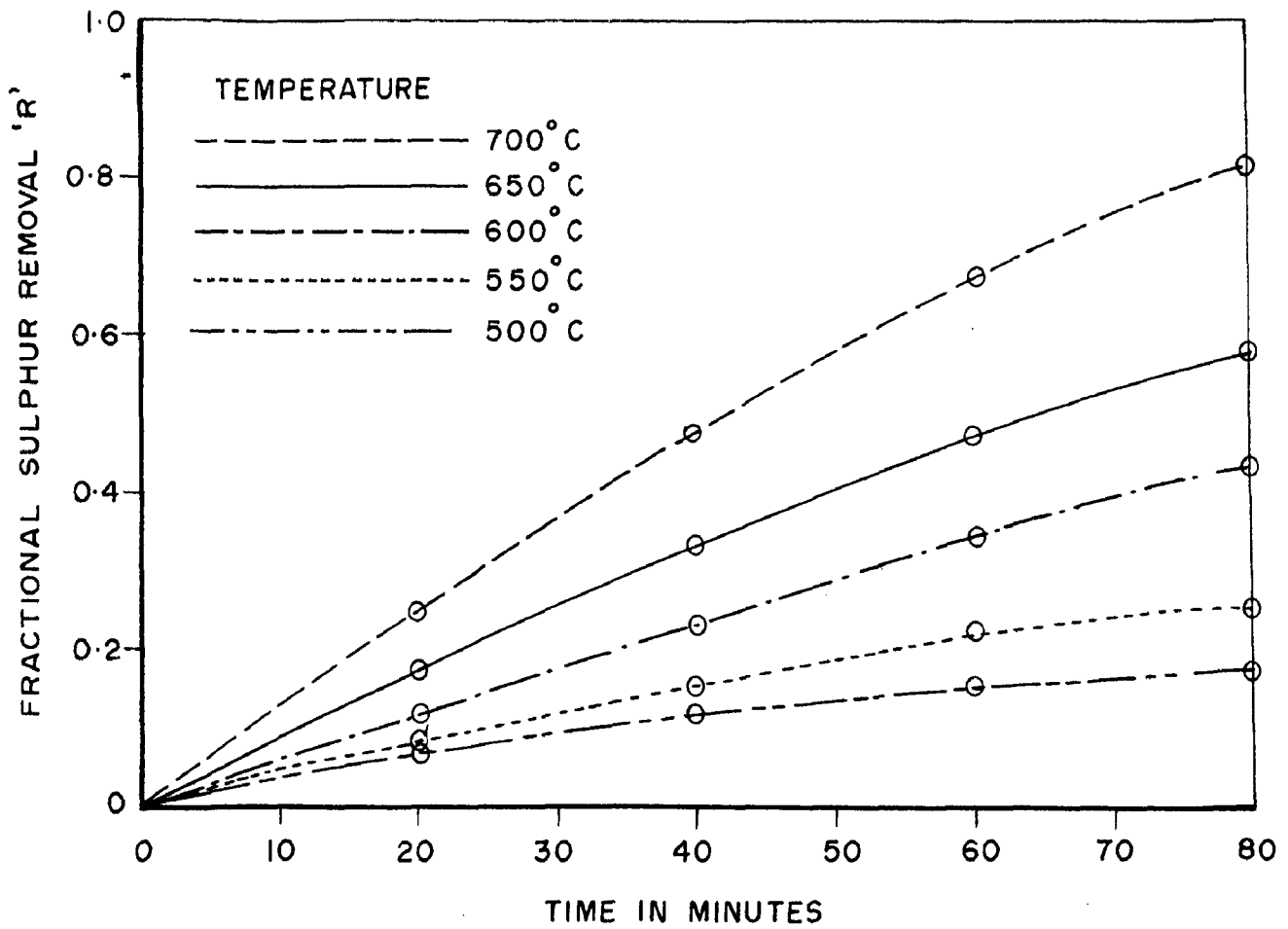


FIG. 13. A PLOT OF FRACTIONAL SULPHUR REMOVAL VS. TIME FOR COPPER CONCENTRATES OF 0.219 Cm. PARTICLE SIZE.

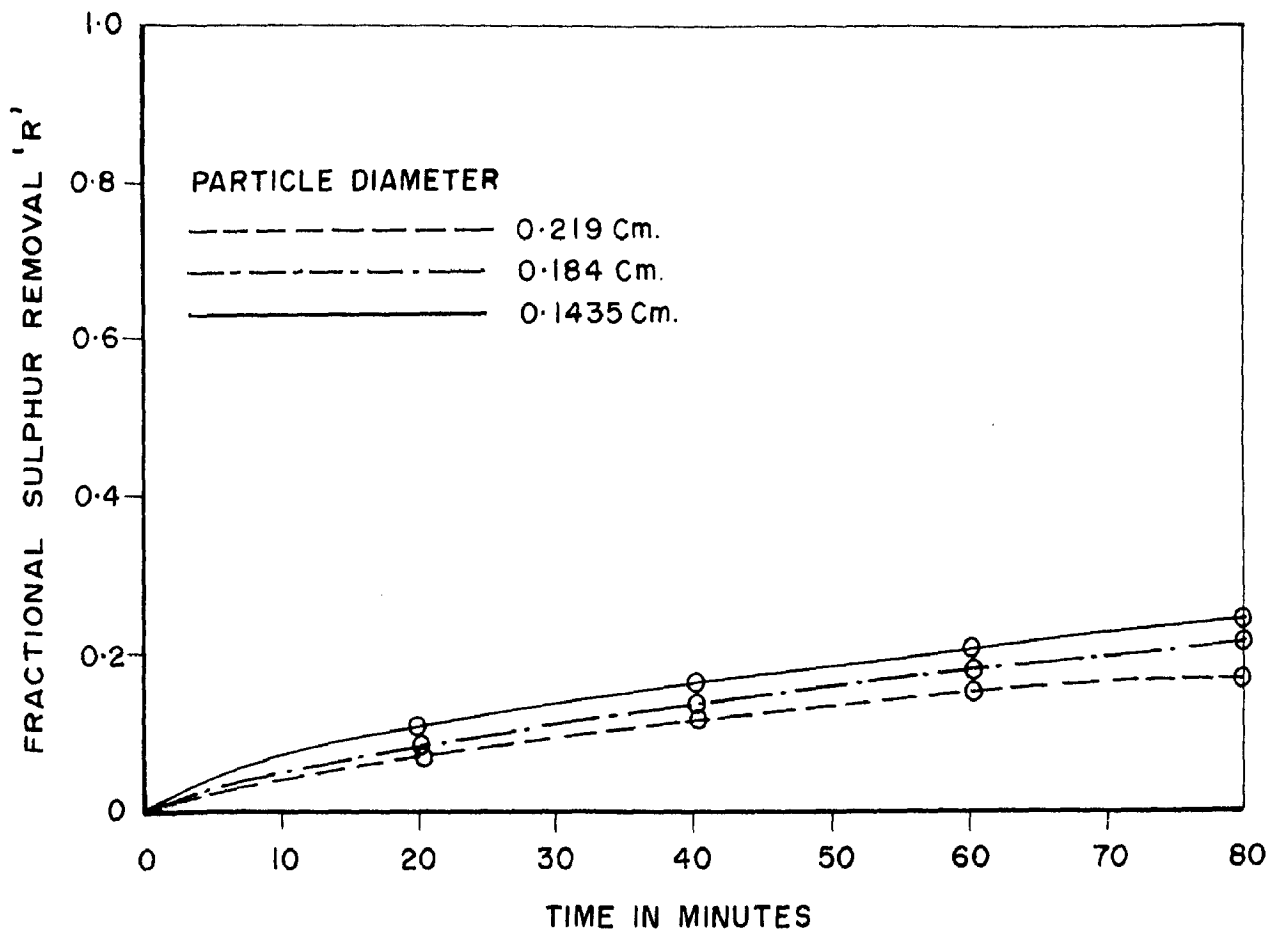


FIG.14. A PLOT OF FRACTIONAL SULPHUR REMOVAL VS. TIME FOR COPPER CONCENTRATES AT TEMPERATURE  $500^{\circ}$  C.



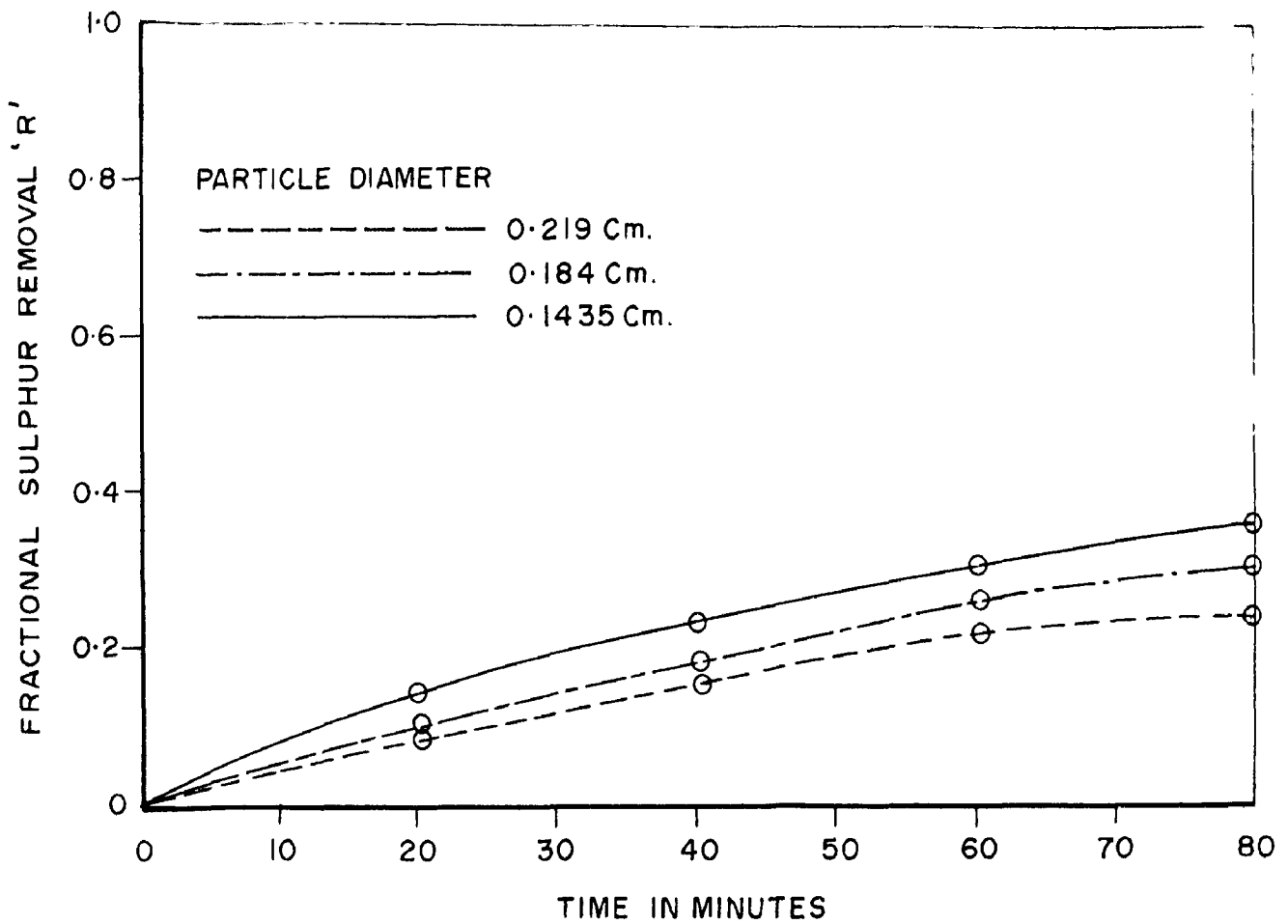


FIG. 15. A PLOT OF FRACTIONAL SULPHUR REMOVAL VS. TIME FOR COPPER CONCENTRATES AT TEMPERATURE  $550^{\circ}\text{C}$ .

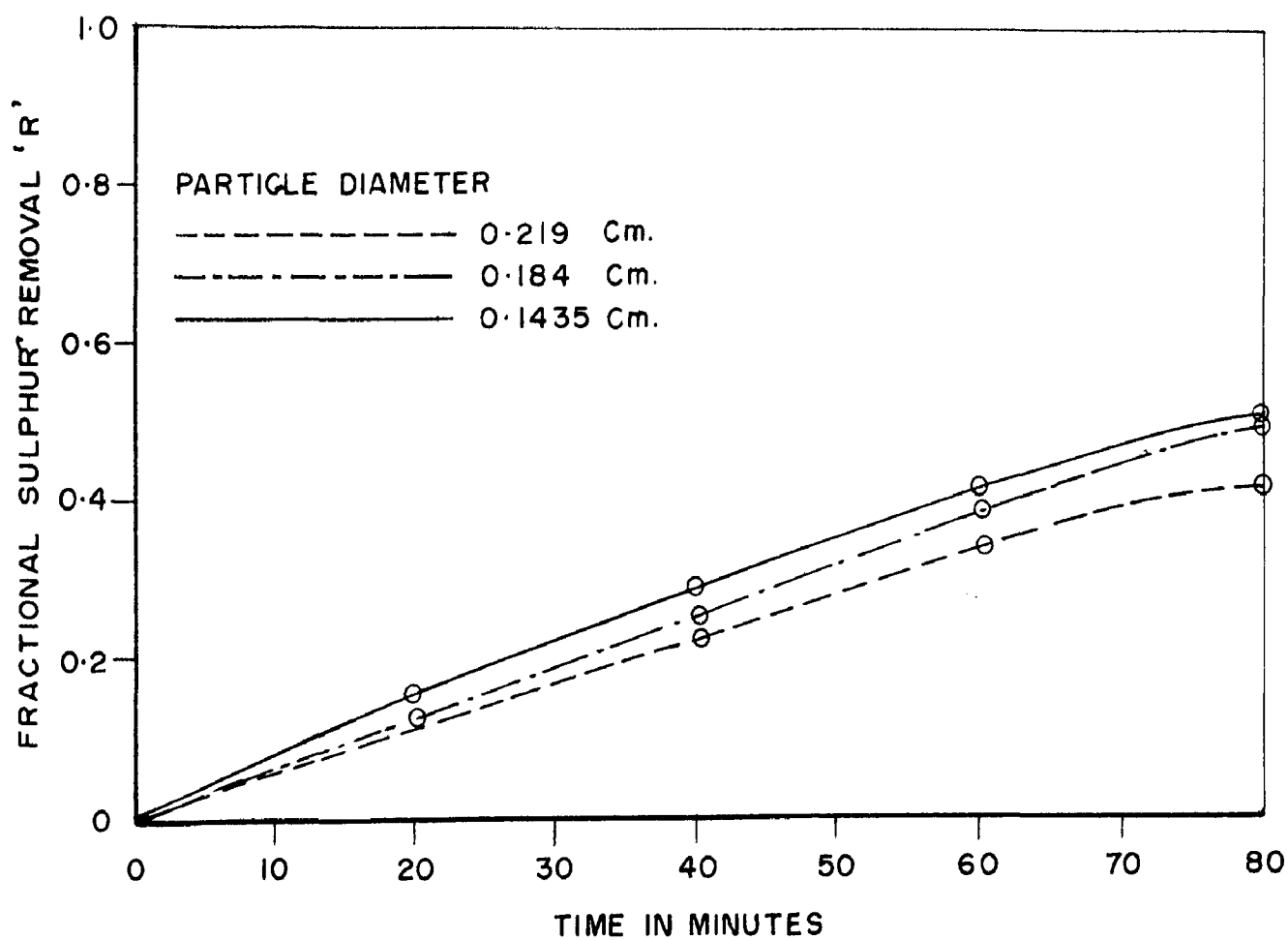


FIG.16. A PLOT OF FRACTIONAL SULPHUR REMOVAL VS. TIME FOR COPPER CONCENTRATES AT TEMPERATURE  $600^{\circ}\text{C}$ .

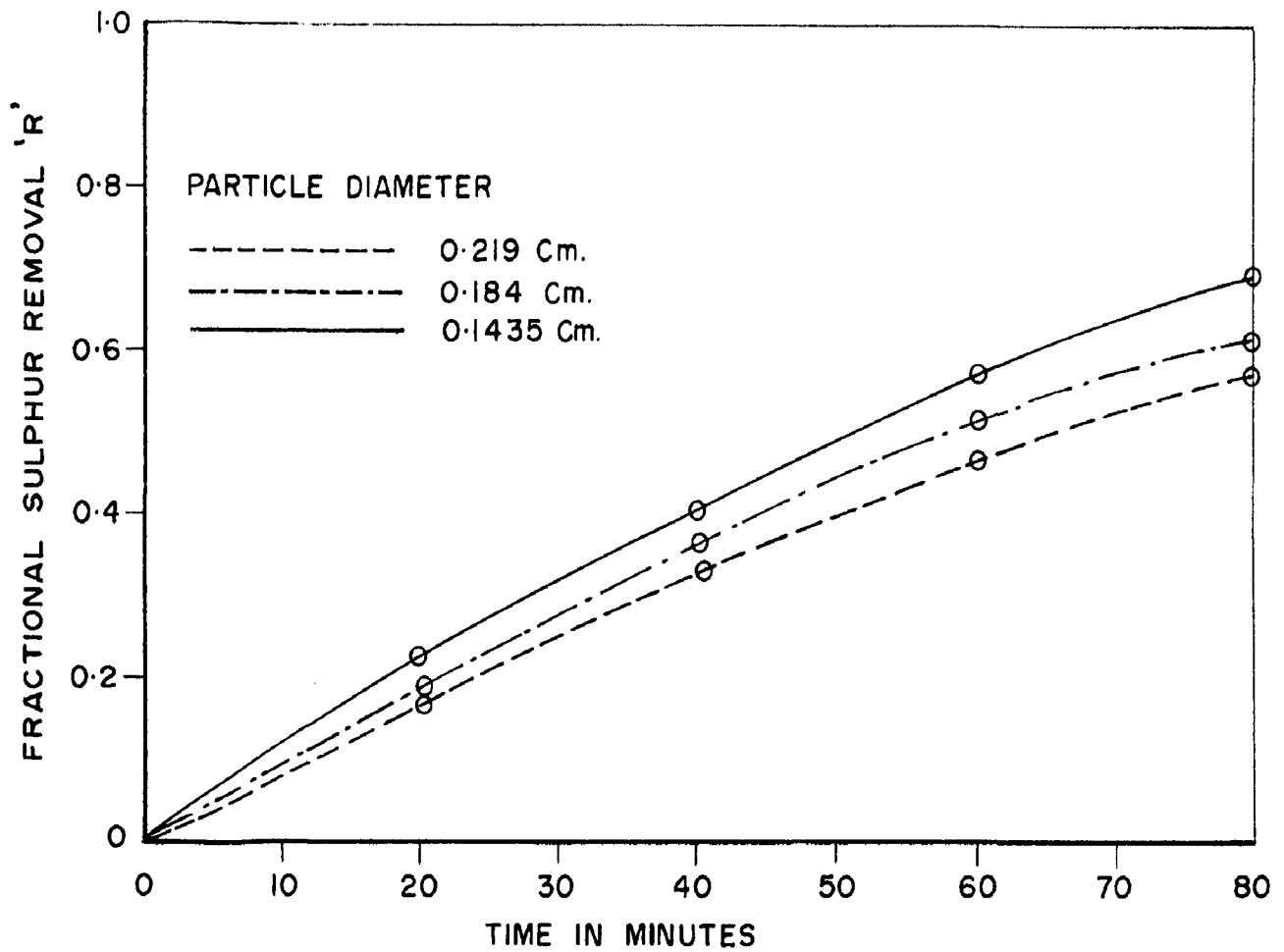


FIG. 17. A PLOT OF FRACTIONAL SULPHUR REMOVAL VS. TIME FOR COPPER CONCENTRATES AT TEMPERATURE  $650^{\circ}\text{C}$ .

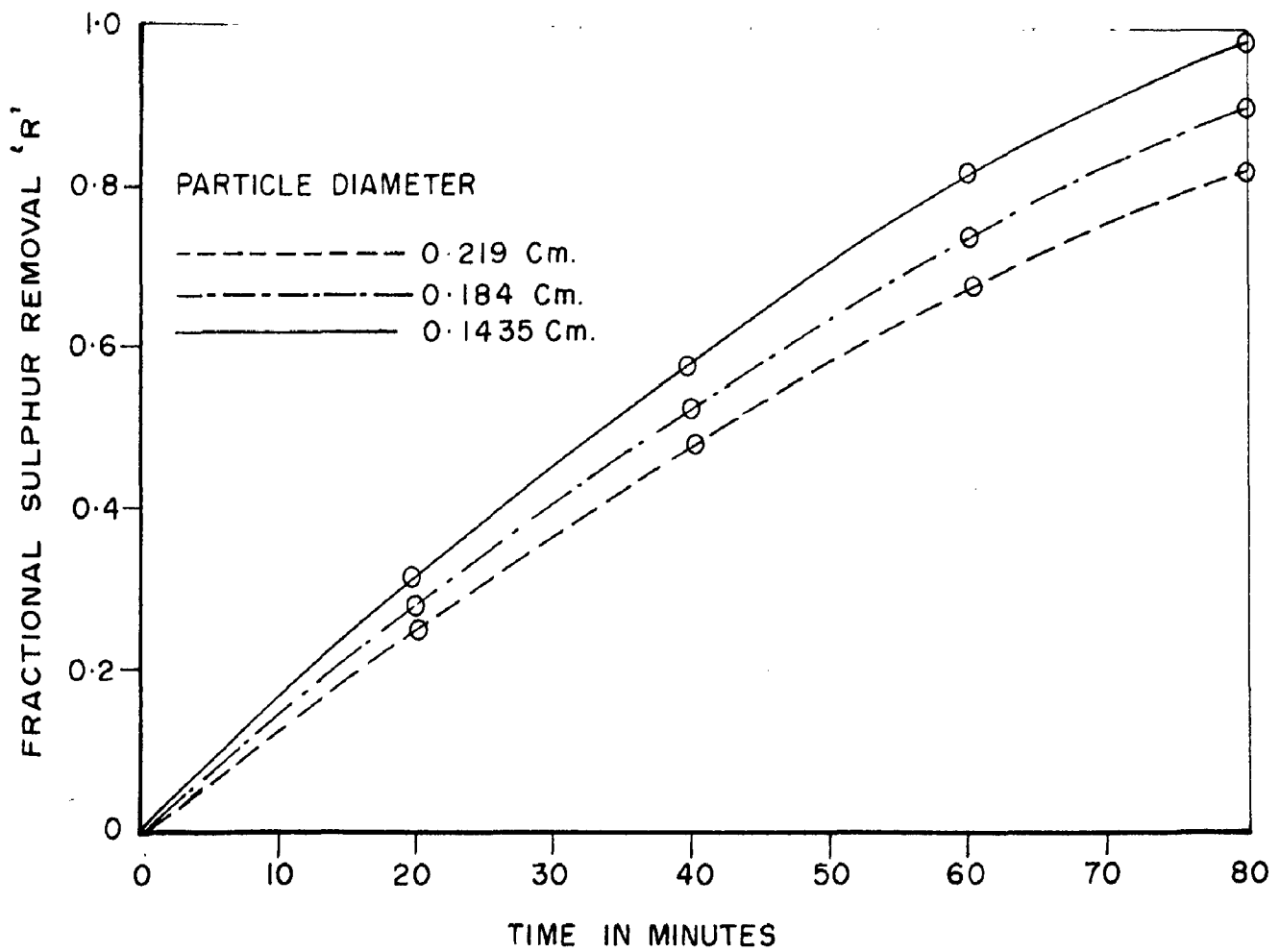


FIG.18. A PLOT OF FRACTIONAL SULPHUR REMOVAL VS. TIME FOR COPPER CONCENTRATES AT TEMPERATURE  $700^{\circ}\text{C}$ .

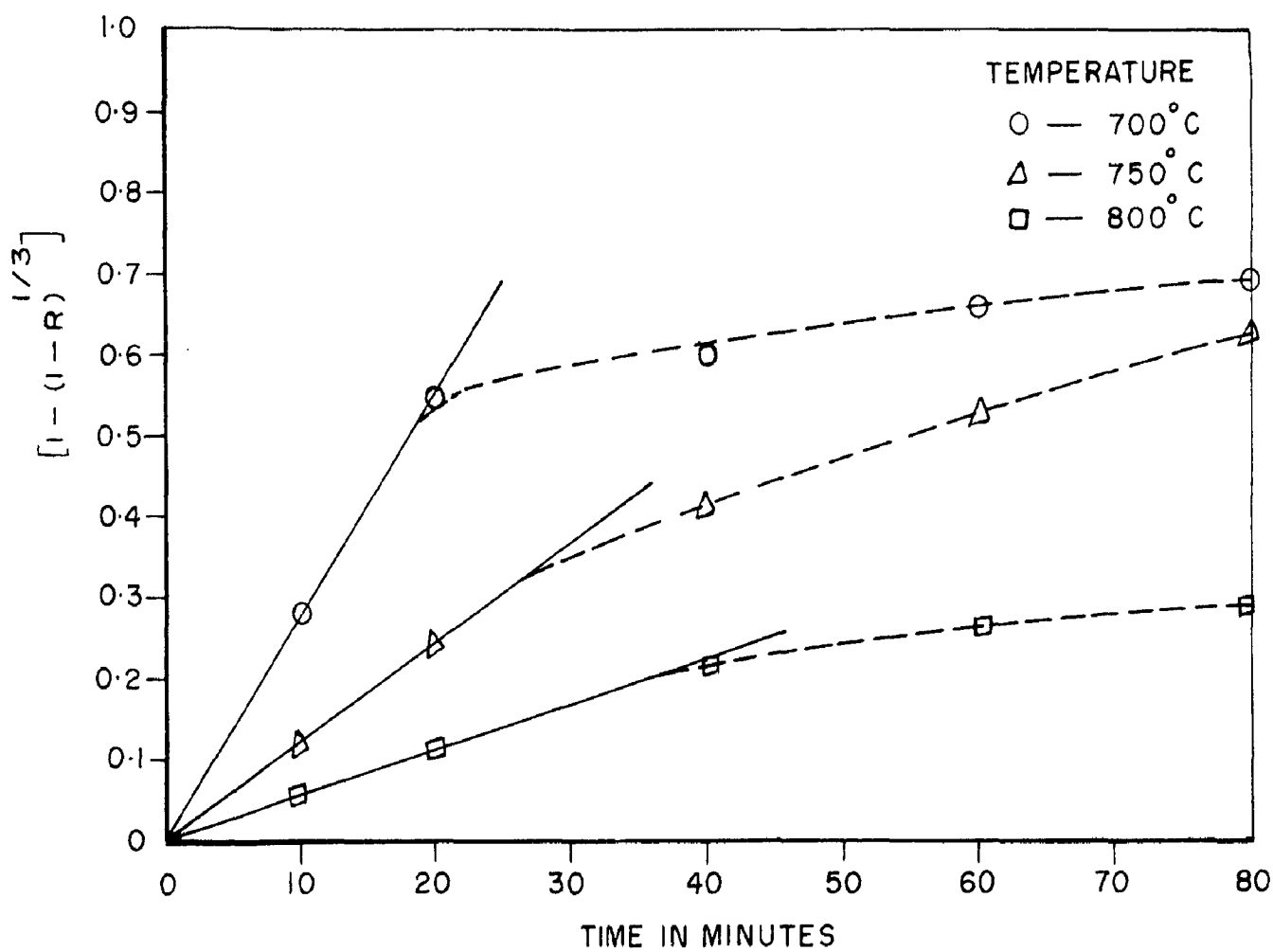


FIG.19. PLOT OF  $[1 - (1 - R)]^{1/3}$  VS. TIME FOR ZINC CONCENTRATES OF 0.1435 Cm. PARTICLE SIZE.

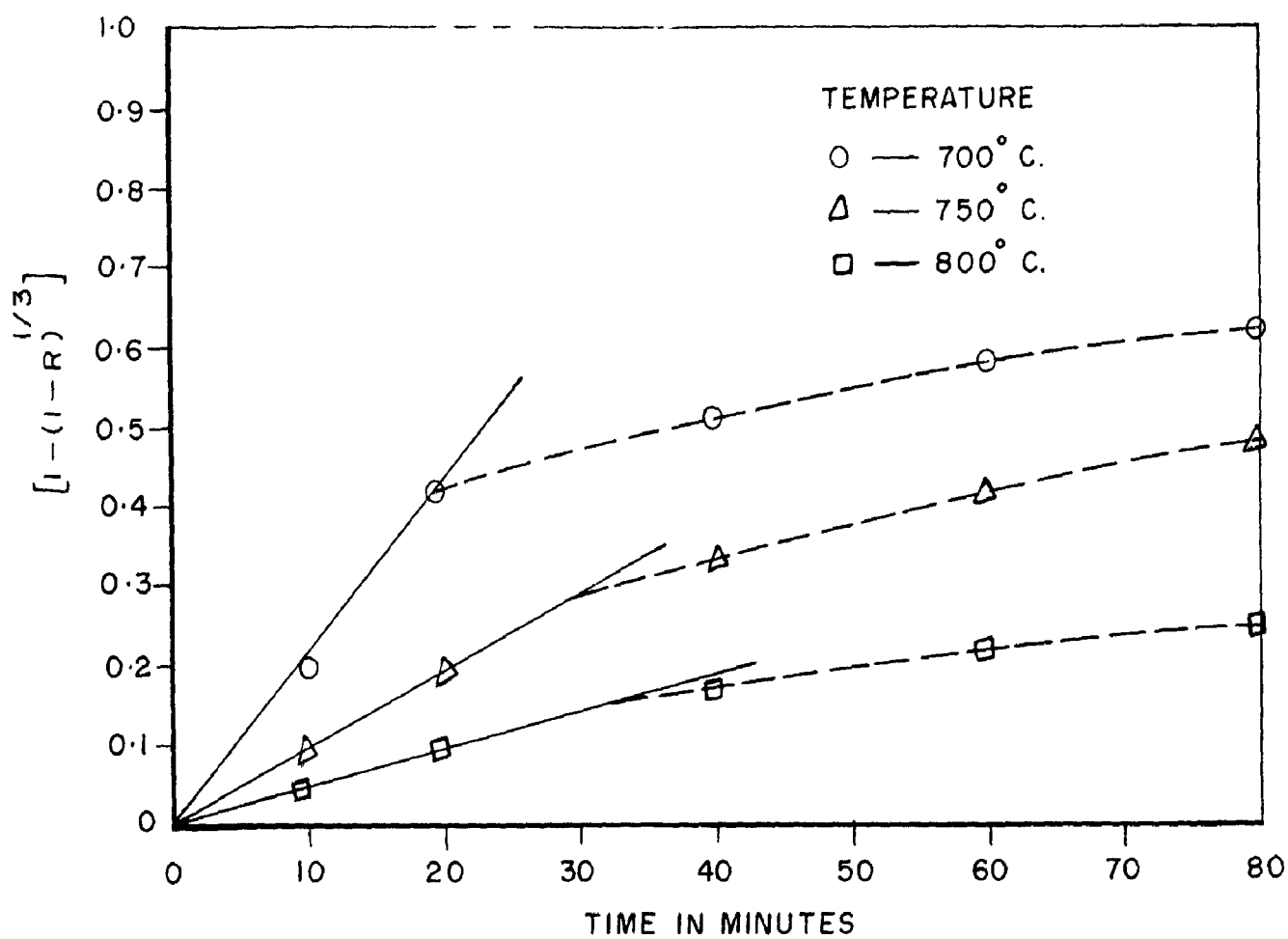


FIG. 20. PLOT OF  $[1 - (1 - R)]^{1/3}$  VS. TIME FOR ZINC CONCENTRATES OF 0.184 Cm. PARTICLE SIZE.

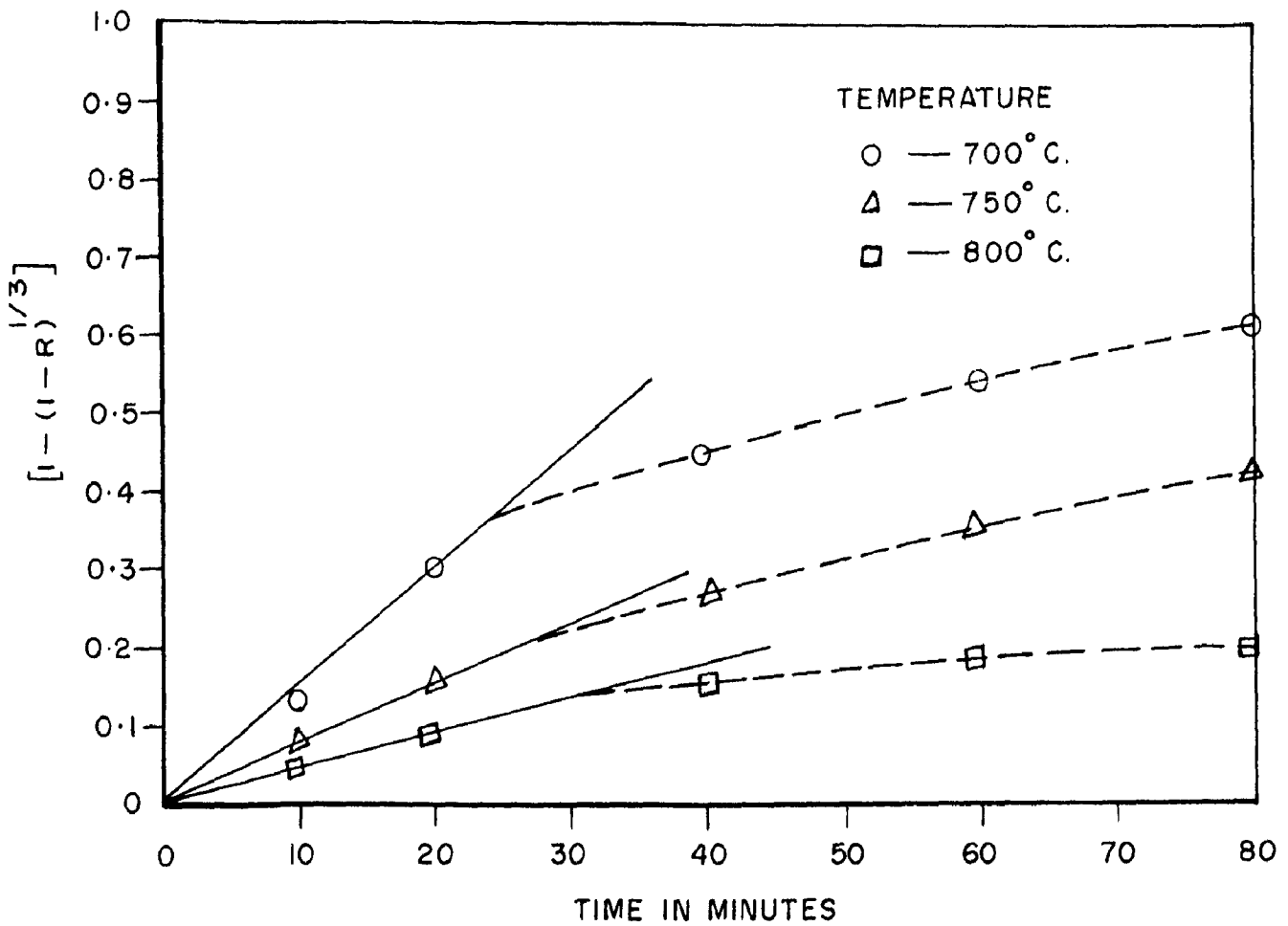


FIG. 21. PLOT OF  $[1 - (1 - R)]^{1/3}$  VS. TIME FOR ZINC CONCENTRATES OF 0.219 Cm. PARTICLE SIZE.

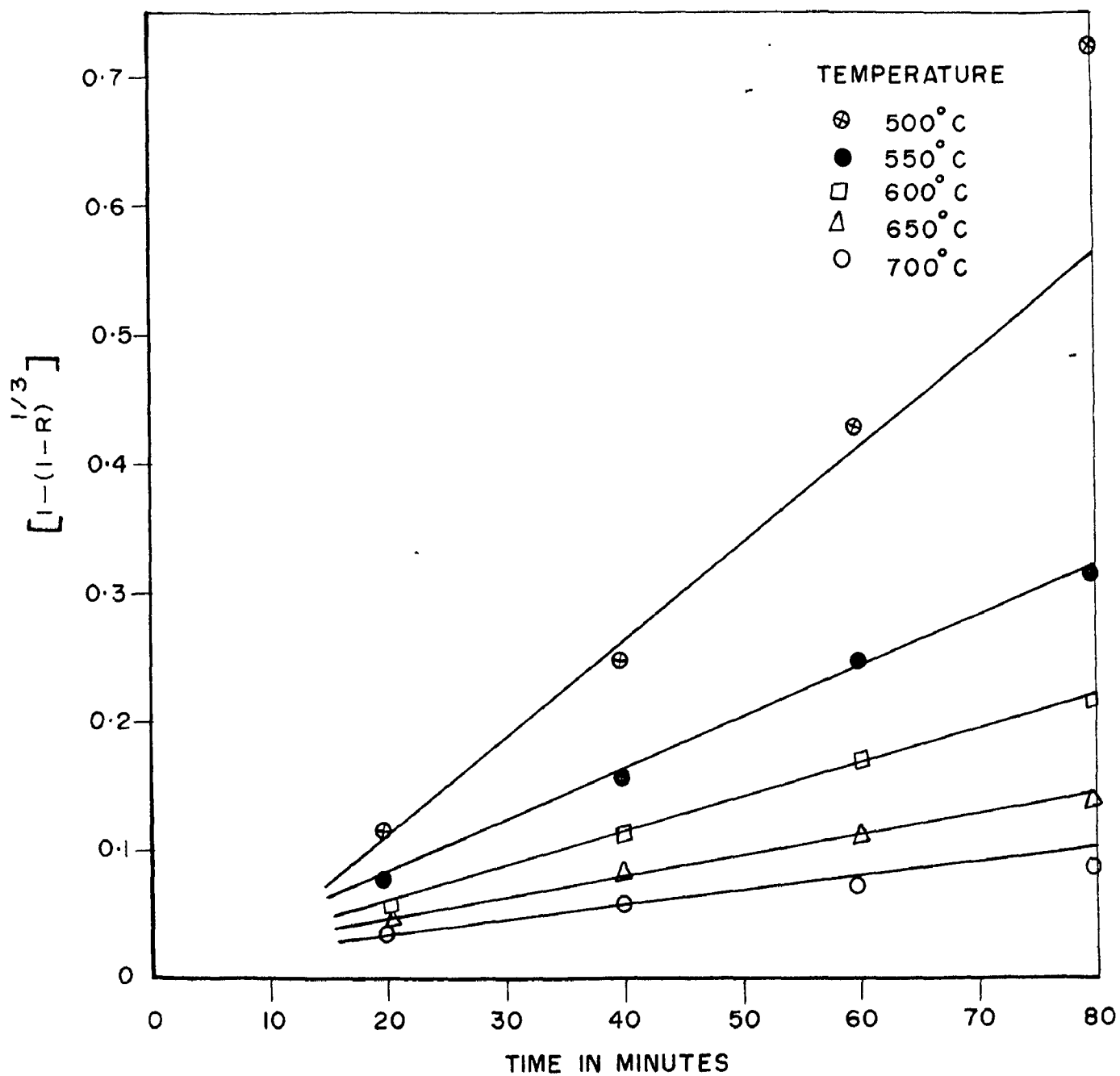


FIG.22. PLOT OF  $[1-(1-R)]^{1/3}$  VS. TIME FOR COPPER CONCENTRATES OF  $\phi 1435$  cm. PARTICLE SIZE.



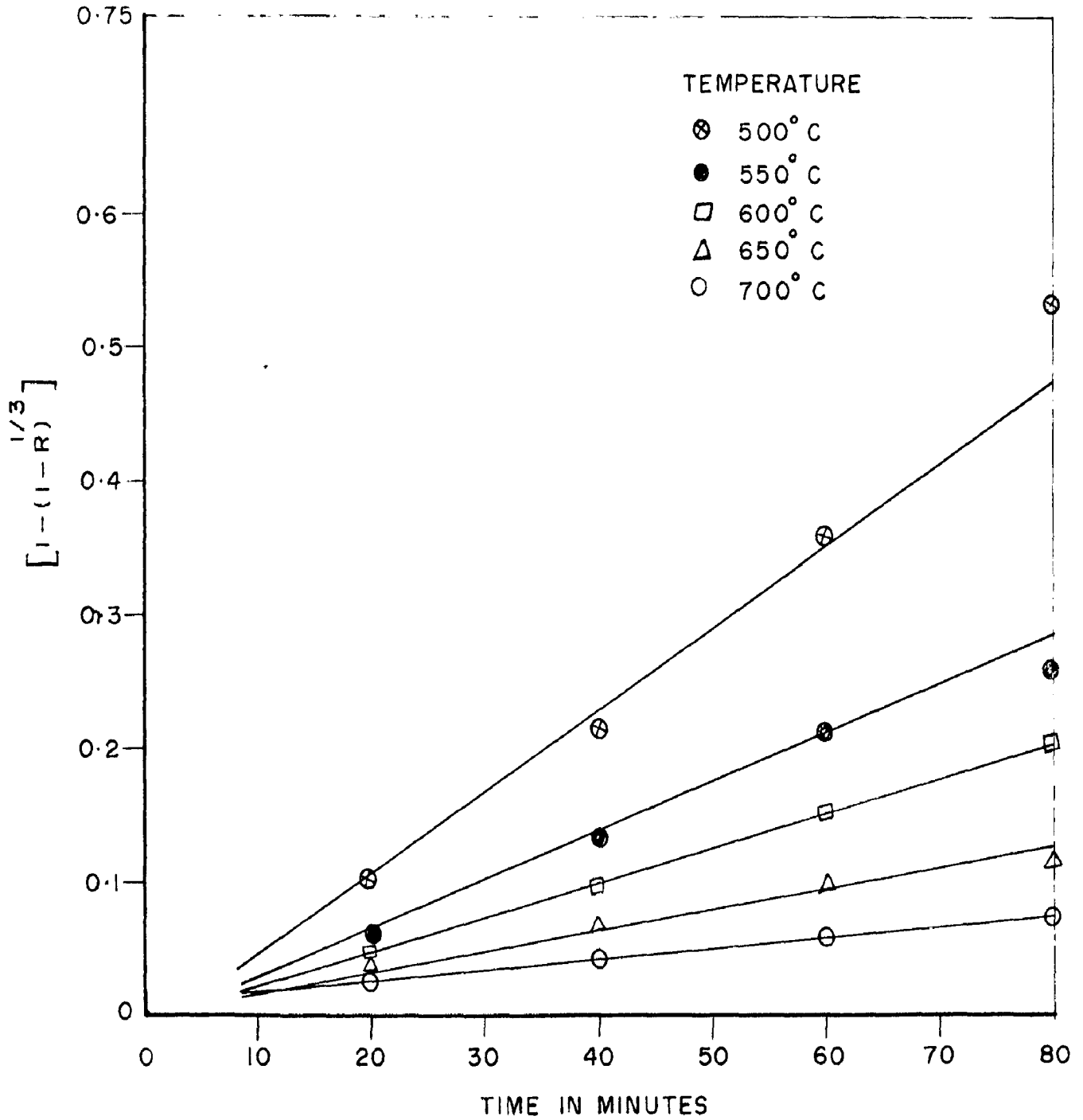


FIG. 23. PLOT OF  $[1 - (1 - R)]^{1/3}$  VS. TIME FOR COPPER CONCENTRATES OF 0.184 Cm. PARTICLE SIZE.

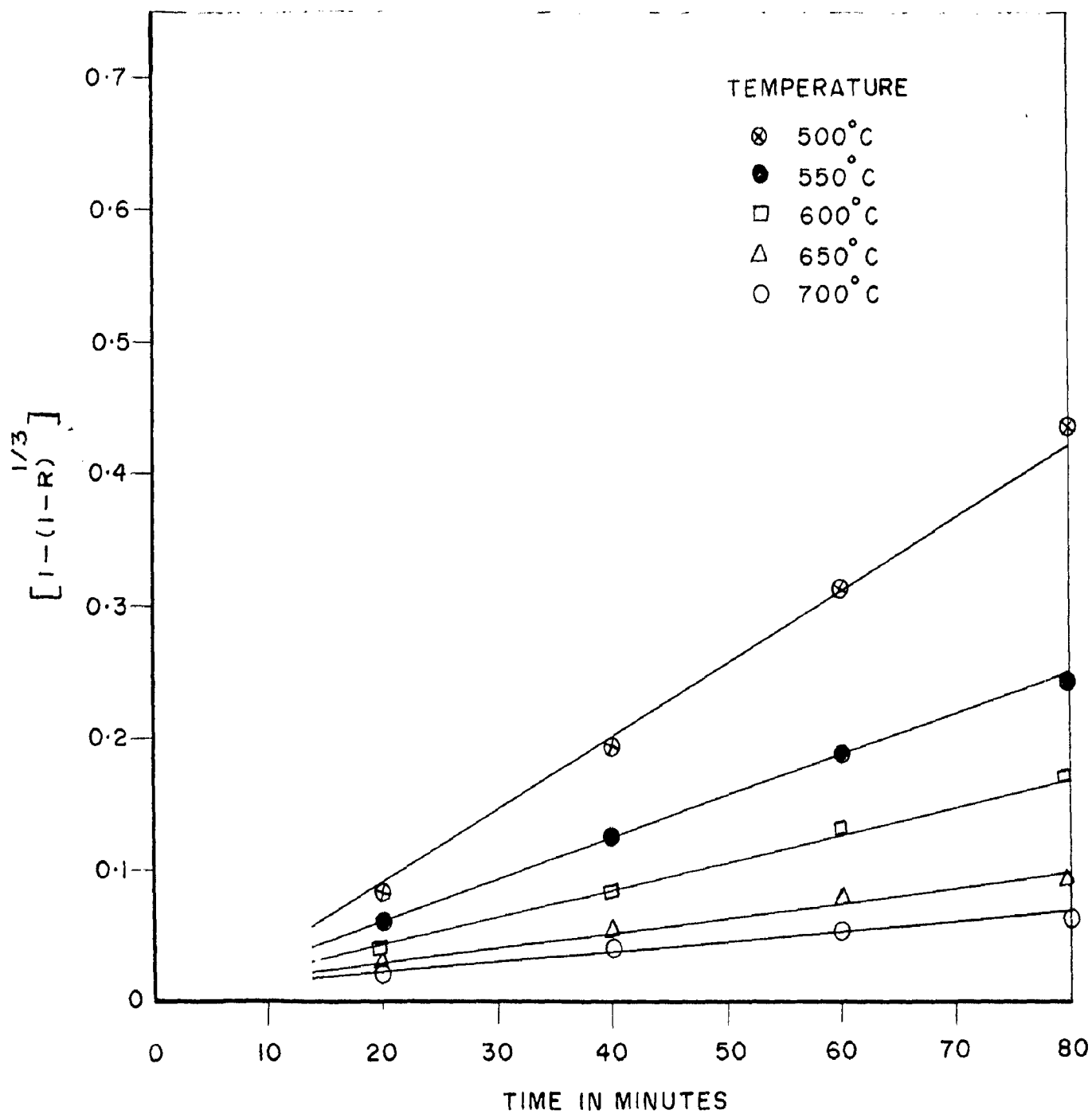


FIG.24. PLOT OF  $[1-(1-R)]^{1/3}$  VS. TIME FOR COPPER CONCENTRATES OF 0.219 cm. PARTICLE SIZE.

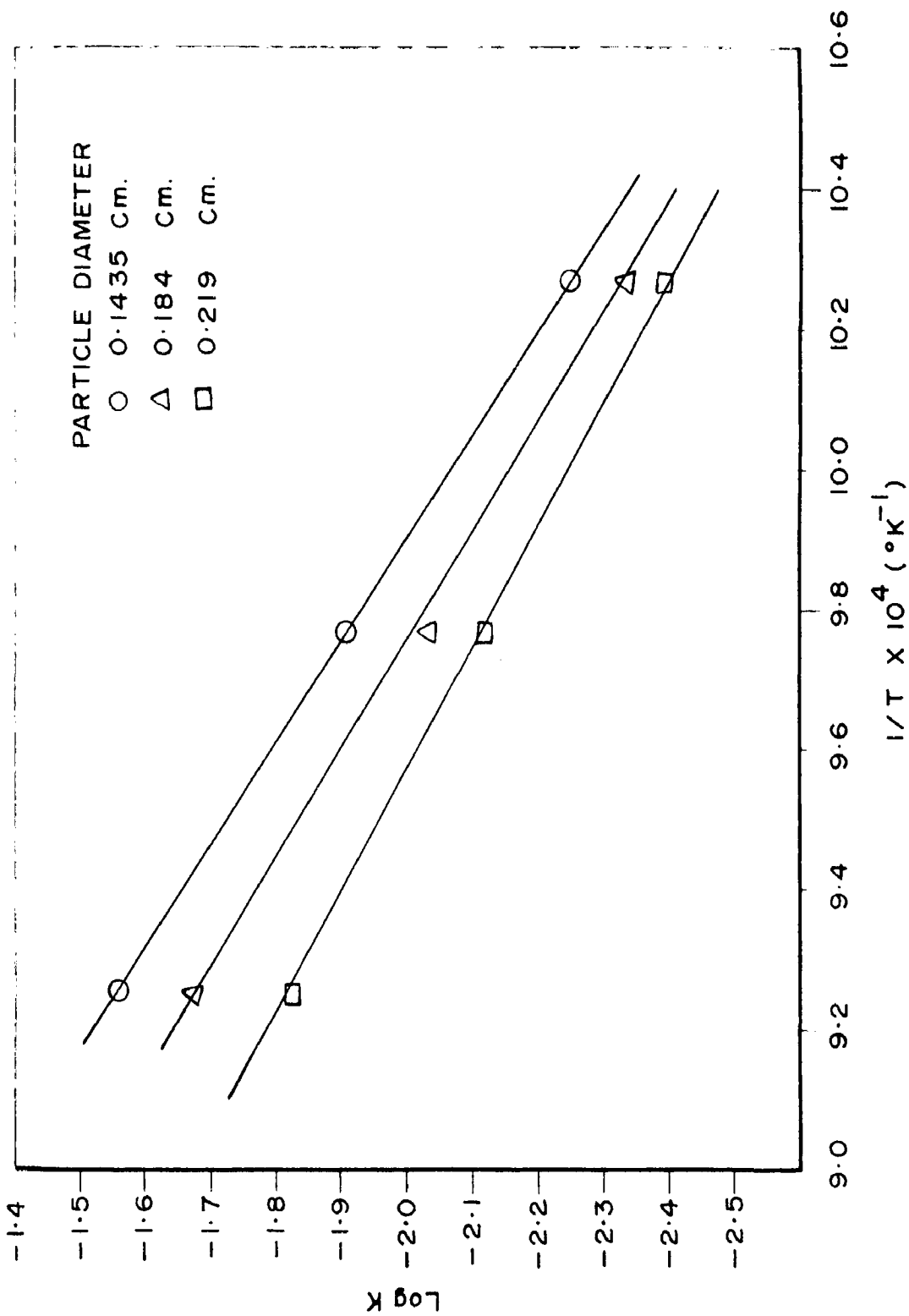


FIG.25. PLOT OF Log K VS.  $1/T \times 10^4$  FOR ZINC CONCENTRATES.

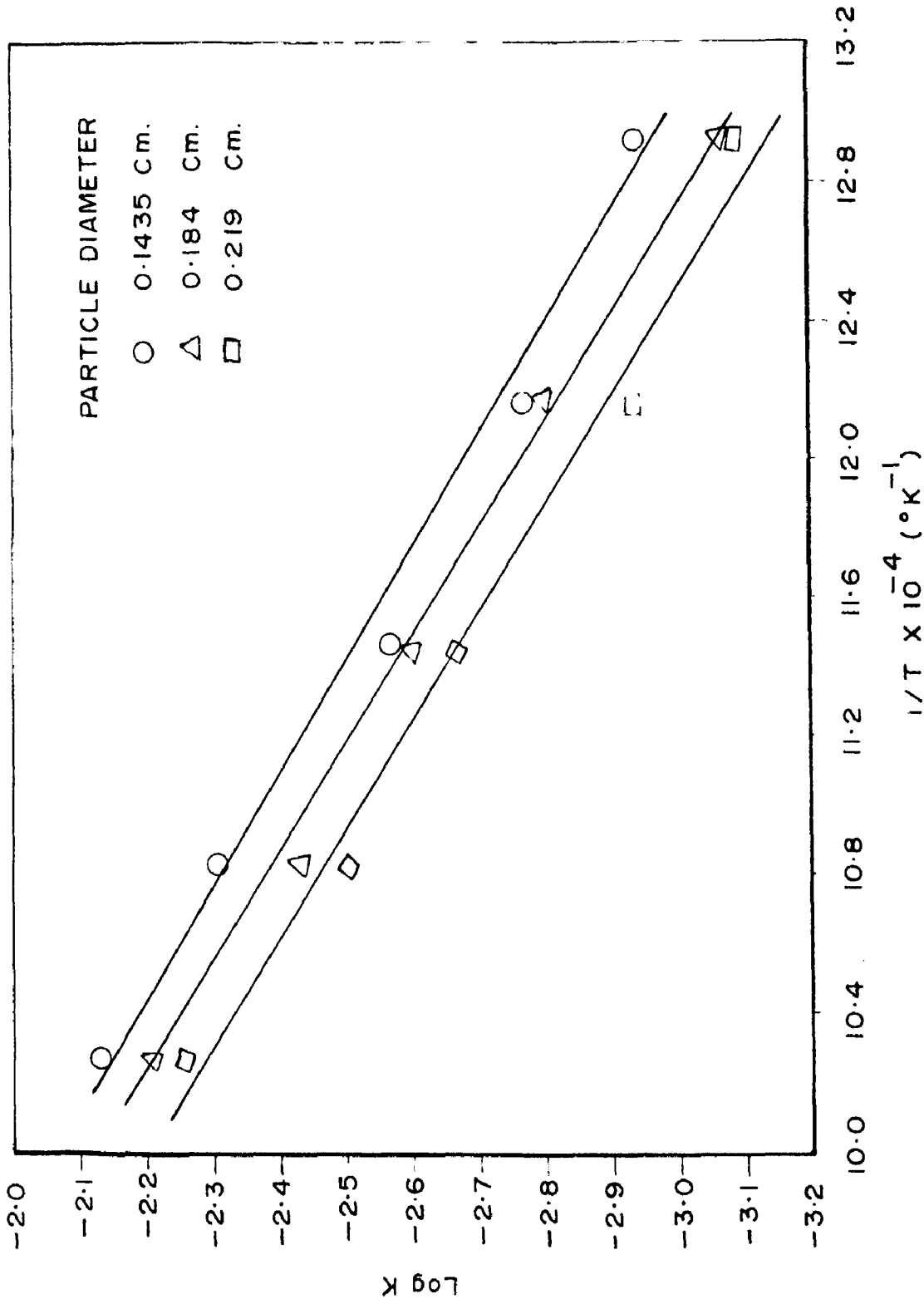


FIG.26. PLOT OF Log K VS.  $1/T \times 10^4$  FOR COPPER CONCENTRATES.

The specific rate values were calculated with the help of plots of  $(1-(1-R)^{\frac{1}{2}})$  vs time. These plots are shown in Fig. 19 to 21 and Fig. 22 to 24 for zinc and copper concentrates, respectively. The values of log of specific reaction rate constant (K) were then plotted against the reciprocal of the absolute temperature which are shown in Fig. 25 for zinc concentrate and in Fig. 26 for copper concentrate, respectively.

The values of activation energies found for zinc concentrate<sup>one</sup> listed in Table 14 and for copper concentrate in Table 15.

The physical examination of sample after roasting revealed the presence of an inner core where the pellet was remained undecomposed. Cross section of partially roasted samples of zinc and copper concentrates are shown in Fig. 3 and 4, respectively.

#### 4.2 Discussion

The rate of oxidation of zinc and copper sulphide concentrate were found to be extremely

temperature sensitive and hence from the results of some preliminary runs, kinetics studies were confirmed to a small temperature range of 700° to 800°C and 500° to 700°C for zinc and copper concentrates, respectively. The results are shown in Fig. 5 to 18.

4.2.1 Study on Zinc Sulphide Concentrate: The effects of following parameters were studied on zinc sulphide concentrates.

a) Effect of Temperature: The zinc concentrate pellets were roasted in a fluidized bed at temperatures 700°, 750° and 800°C. The results are shown in Fig. 5 to 7.

Pronounced effect of temperature and time on the amount reacted at any period of roasting is self evident from these figures. In general at all temperatures the reaction is rapid in the initial stage and slows down considerably in later stage. An analysis of fraction sulphur removal vs time for particle size of 0.1435 cm. (Fig. 5), 0.184 cm (Fig. 6) and 0.219 cm. (Fig. 7) at various temperatures reveals that the sulphur is increasingly removed with increasing temperature. For example in 20

minutes for particle size of 0.1435 cm., 91.5% sulphur is removed at 800°C as compared to only 57% at 750°C and 31.5% at 700°C. Similarly for 60% removal of sulphur from pellet of same size nearly nine minutes were required at 800°C, 20 minutes at 750°C and 55 minutes at 700°C (Fig. 5).

Referring to Fig. 7, a plot of percentage sulphur removal vs time for 0.219 cm particle size at various temperatures, it is noticed that in about 40 minutes 81.5% sulphur is removed at 800°C where as only 61% and 37% sulphur are removed at 750°C and 700°C, respectively. Similar results were obtained for particle size 0.184 cm. at various temperatures (Fig. 7).

b) Effect of Particle Size: The plots of percentage sulphur removal vs time for different particles sizes at various temperatures from experimental data are shown in Fig. 8 to 10.

An analysis of the fraction of sulphur removal vs time at 700°C, 750°C and 800°C are shown in Fig. 8, 9 & 10 respectively. These figures show that the recovery of sulphur goes down with increase in particle size for any period and temperature of

roasting. For example at 800°C, in 20 minutes, 90.5% sulphur can be removed from a pellet of 0.1435 cm. diameter as compared to only 81% and 66% sulphur from pellets of diameter 0.184 and 0.219 cm., respectively. Also for removal of 80% sulphur from pellet of 0.1435 cm. diameter takes only 14.5 minutes as compared to 19.5 and 38 minutes for particle diameters 0.184 and 0.219 cm., respectively (Fig. 10).

From Fig. 9 it is evident that 80% sulphur is removed from particles of sizes 0.1435, 0.184 and 0.219 cm. diameter in 41, 60 and 76 minutes, respectively at 750°C. At 700°C (Fig. 8) 36% sulphur is removed in 40 minutes from pellets having diameter of 0.219 cm. as compared to 43% and 51% from pellets having diameter 0.184 and 0.1435 cm., respectively.

Study of Kinetics and Mechanism of Roasting : The experimental results are plotted in terms of chemical reaction rate control model, i.e.  $(1-(1-R)^{\frac{1}{3}}) = Kt$ . With the help of experimental data the values of  $(1-(1-R)^{\frac{1}{3}})$  for different particle sizes at various temperatures are calculated and summarised in Tables 4 to 6. Plot of  $(1-(1-R)^{\frac{1}{3}})$  vs time of the sulphur removal at various temperatures and particle



sizes have been found to yield straight line relationship in the initial period of roasting. These are shown in Fig. 19 to 21. The slope of these curves will give the reaction rate constant 'K'. The values of 'K' at various temperatures and particle sizes are listed in Table-12.

With the help of these 'K' values  $\log K$  vs  $1/T$  plots were made in terms of Arrhenius equation ( $K = Ae^{-Q/RT}$ ). These plots for various particle sizes are shown in Fig. 25. The slope of these lines will give the value of  $(-Q/2.302 R)$  and hence the activation energy can be found out. These are listed in Table 14. In the present investigation the activation energy comes out of the order of 29.0 K.cal/mole. The value obtained by Philbrook (4, 25) is 40.25 K cal/mole. The difference in the activation energy obtained in present investigation and by Natesan and Philbrook may be due to different chemical composition of the concentrates and of some other reasons, for example, the presence of various other impurities etc.

The Fig. 3 is a photograph of partially roasted pellet. The various layers of reacted product, partially reacted and unreacted core are quite evident. This figure shows that as the time increases the core

of the pellet is to be consumed. In this way oxidation of zinc sulphide proceeds in a topo chemical manner and the various reaction steps can be listed as follows:

1. Transfer of reactant gas (oxygen from the bulk gas stream) across the gas boundary layer to the exterior surface of the pellet and the reverse transfer of the product gas ( $\text{SO}_2$ ).
2. Diffusion and bulk flow of oxygen from the pellet surface through the product shell ( $\text{ZnO}$ ) on to the  $\text{ZnS}/\text{ZnO}$  interface and the reverse transfer of sulphur dioxide.
3. Chemical reaction at the interface, which results in the consumption of oxygen gas and generation of  $\text{SO}_2$  gas and heat, at the same time the  $\text{ZnS}$  core is consumed and  $\text{ZnO}$  shell thickens.

On the basis of the above mentioned steps the rate of roasting is either diffusion controlled or chemical reaction or mixed controlled. The rate based on step 1. depends on the flow characteristics of the system, such as the mass velocity of the fluid stream, the size of the pellet, the diffusional

characteristics of the fluid involved. The rate based on step 2 depends on the degree of porosity of the product shell, and the diffusional characteristics of the system. The rate based on step 3, depends on the interface area available for the reaction.

Natesan and Philbrook found that oxygen starvation in the fluidized bed was not rate limiting in any of experimental runs. Therefore step 1 can not be the rate controlling. If diffusion through the roasted shell is considered to be the rate limiting step the activation energy required for the process should have a value much less than experimentally determined value of the order of 29.0 K cal/mole. This value is sufficiently high for diffusion to be accounted as a rate controlling step and therefore it can be concluded that the surface reaction should be the probable rate controlling step. This is further supported by the fact that a plot of  $(1-(1-R)^{\frac{1}{3}})$  vs time has yielded straight line relationship in the initial stages of roasting. Where as in the final stages of roasting when the product layer is very thick then the rate might be controlled by diffusion. It is also evident from the plots of  $(1-(1-R)^{\frac{1}{3}})$  vs time as this relationship is not obeyed throughout the roasting period. Hence it can be concluded that the kinetics of roasting of zinc concentrate is mixed controlled.

4.2.2 Study on Copper Sulphide Concentrate: The effect of the following parameters were studied on kinetics of roasting of copper sulphide concentrate.

a) Effect of Temperature: The copper concentrates pellets were roasted in a fluidized bed at temperatures 500°, 550°, 600°, 650° and 700°C. The results are shown in Fig. 11 to 18. From these plots the pronounced effect of temperature and time on the amount reacted at any definite period is self evident. The fraction of sulphur removed vs time for particle size of 0.1435 cm (Fig. 11), 0.184 cm (Fig. 12) and 0.219 cm. (Fig. 13) at various temperatures (500°C -700°C) reveals that the sulphur is increasingly removed with increasing temperature. For example from a pellet of size 0.1439 cm., 57.5% sulphur is removed at 700°C as compared to only 16.5% sulphur removed at 500°C in 40 minutes of roasting period.

b) Effect of Particle Size: Effect of particle size on removal of sulphur from pellets at various temperatures are shown in Fig. 14 to 18. The recovery of sulphur is seen to fall with increase in the particle size at any period and temperature of roasting.

For example at 700°C (Fig. 18) 60% of the total sulphur is removed in 42 minutes from pellet of 0.1435 cm. diameter as compared to 47 minutes and 52 minutes from pellets of 0.184 and 0.219 cm. diameter, respectively and at the end of 60 minutes of roasting period about 67% , 73% and 82% sulphur are removed from the pellets of 0.219, 0.184 and 0.1435 cm. diameter, respectively.

Study of Kinetics and Mechanism of Roasting: To test the validity of chemical reaction rate controlled model the values of  $(1-(1-R)^{\frac{1}{3}})$  were calculated at various temperatures and particle sizes from the experimental results in the similar fashion as in case of zinc sulphide concentrate. These values are listed in Tables 7 to 11. The plots of  $(1-(1-R)^{\frac{1}{3}})$  vs time at various temperatures and particle sizes were made and is found to yield straight line. These plots are shown in Fig. 22 to 24. Slope of the lines will give the values of apparent specific reaction rate constant 'K'. The log K vs 1/T are plotted to find out activation energy as is described in 4.2.1. The values of activation energies are listed in Table 15 and these are of the order of 14 K cal/mole.

In this case also the photograph (Fig. 4) of partially reduced pellet shows the various layers of reacted product, partially reacted and unreacted core. The various steps during roasting may be either transport of the gaseous reactants and products through the diffusion boundary layer and porous shell formed on the surface; and chemical reaction at the interface of  $\text{Cu}_2\text{O}/\text{Cu}_2\text{S}$  similar to the roasting of zinc sulphide concentrates. The diffusion through the gas boundary layer can not be the rate controlling step as has been shown by Natsan and Philbrook. The diffusion through the reacted shell may be the rate controlling step. The activation energy data show that it can not be the rate controlling step. For this to be rate controlling step the activation energy should have much less value than the value obtained in this investigation. Moreover, the chemical reaction rate model fits the experimental data well as can be seen in Fig. 22 to 24. Therefore the rate controlling step should be chemical reaction at the interface.

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C O N C L U S I O N S

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## C O N C L U S I O N S

On the basis of the results and discussion the following conclusions can be drawn:

1. Oxidation of copper and zinc sulphide concentrate proceeds in a topochemical manner.
2. Removal of sulphur increases with the increase in time and temperature of roasting.
3. Removal of sulphur falls with increase in particle size at any period and temperature of roasting.
4. In general at all temperatures the reaction is rapid in the initial stage and shows down considerably in later stage of roasting.
5. The values of reaction rate constant increase with increase in temperature for a particular particle size, thereby showing the temperature dependence of the reaction.
6. A plot of  $(1-(1-R)^{1/n})$  vs time has yielded a straight line relationship in case of copper concentrate whereas in case of zinc concentrate it is followed in the initial stage only and then the curves deviate from linearity.
7. Activation energies for the zinc and copper sulphide concentrates were found to be of the order of 29.0 K cal/mole and 14.0 K cal/mole, respectively.



8. On the basis of the above two observations it is inferred that the oxidation of copper sulphide concentrates are surface reaction controlled in the temperature range of 500 to 700°C whereas oxidation of zinc sulphide concentrates are mixed controlled in the temperature range of 700° to 800°C.

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R E F E R E N C E S

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A P P E N D I X

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TABLE-1<sup>(28)</sup>: OUTPUT OF VARIOUS ROASTING SYSTEMS WITH  
PYRITES CONTAINING 48% SULPHUR.

Type of Roaster	Capacity in tons (per 24 hrs.)	Sulphur roasted in 24 hrs/sq. meter of roasting surface,kg.
Mechanical Roaster	25	80
Rotary Kilns	70	100
Flash Roaster	20	1100
Fludized Roaster	30	9600

TABLE-2<sup>(8)</sup>: IGNITION POINT OF SULPHIDES FOR 0.06 mm. FINENESS.

Mineral	Chemical Formula	Ignition point°C
Pyrite	$\text{FeS}_2$	360
Chalcocite	$\text{Cu}_2\text{S}$	435
Sphalerite	$\text{ZnS}$	615
Galenite	$\text{PbS}$	755



TABLE-3: MASS FLOW RATE OF AIR ( $G_{mf}$  and  $G$ ).

Sulphide ore concentrate	Density gm/cc.	Particle diameter (cm.)	$G_{mf}$ calcu- lator g/cm <sup>2</sup> sec	$R_{emf}$	Correct- ion factor	$G_{mf}$ g/cm <sup>2</sup> sec	$G$ g/cm <sup>2</sup> sec.
Zinc	3.94	0.1435	0.214	170.5	0.42	0.0894	0.2097
Zinc	3.94	0.184	0.411	419.0	0.32	0.134	0.2097
Zinc	3.94	0.219	0.5645	686.0	0.28	0.158	0.2097
Copper	2.86	0.1435	0.195	155.5	0.44	0.0857	0.2097
Copper	2.86	0.184	0.307	314.0	0.25	0.1075	0.2097
Copper	2.86	0.219	0.421	512.0	0.29	0.122	0.2097

**TABLE-4: EXPERIMENTAL RESULTS FOR ROASTING OF ZINC CONCENTRATE  
AT 700°C.**

Particle size	Time in min.	Sulphur in pellet percentage	Fraction sulphur removal 'R'	$(1-(1-R)^{1/3})$
0.1435 cm.	10**	26.15	0.1750	0.062
(-10 + 14)*	20	21.93	0.3082	0.117
	40	15.83	0.5006	0.210
	60	12.12	0.6165	0.276
	80	10.98	0.6543	0.298
	0.1840cm.	10**	27.51	0.1320
(-9 + 10)*	20	23.24	0.2676	0.098
	40	18.28	0.4241	0.168
	60	14.92	0.5296	0.222
	80	13.12	0.555	0.240
	0.2190cm.	10**	27.86	0.1210
(-8 + 9)*	20	24.24	0.2350	0.085
	40	20.12	0.3656	0.140
	60	17.56	0.4149	0.173
	80	15.92	0.4978	0.204

\* Tayler Sieve Number.

\*\* Data taken from plots.

**TABLE-5: EXPERIMENTAL RESULTS FOR ROASTING OF ZINC CONCENTRATES  
AT 750°C.**

Particle size	Time in min.	Sulphur in pellet, %age	Fraction sulphur removal 'R'	$(1-(1-R)^3)$
0.1435 cm.	10**	20.29	0.3570	0.136
(-10 + 14)*	20	13.49	0.5721	0.246
	40	6.521	0.7942	0.408
	60	3.242	0.8999	0.536
	80	1.889	0.9426	0.622
0.1840 cm.	10**	23.99	0.2430	0.088
(-9 + 10)*	20	17.12	0.4596	0.184
	40	9.983	0.6842	0.321
	60	6.032	0.8120	0.416
	80	4.008	0.8743	0.4980
0.2190 cm.	10**	25.23	0.2040	0.073
(-8 + 9)*	20	19.09	0.3982	0.155
	40	12.31	0.6123	0.269
	60	8.563	0.7310	0.354
	80	5.752	0.8193	0.433

\* Tayler Sieve Number

\*\* Data taken from plots

**TABLE-6: EXPERIMENTAL RESULTS FOR ROASTING OF ZINC CONCENTRATES  
AT 800°C.**

Particle size	Time in min.	Sulphur in pellet, percentage	Fraction sulphur removal 'R'	$(1-(1-R)^2)$
0.1435 cm.	10**	12.114	0.6182	0.274
(-10 + 14)*	20	3.021	0.9070	0.546
	40	2.103	0.9342	0.596
	60	1.963	0.9393	0.656
	80	0.9131	0.9698	0.689
0.1840 cm.	10**	17.64	0.4750	0.194
(-9 + 10)*	20	6.210	0.8077	0.423
	40	3.513	0.8878	0.517
	60	2.003	0.9381	0.604
	80	1.421	0.9452	0.622
0.2190 cm.	10**	20.61	0.350	0.134
(-3 + 9)*	20	11.12	0.6648	0.304
	40	5.492	0.8272	0.443
	60	2.963	0.9062	0.536
	80	1.821	0.9429	0.615

\* Tayler Sieve Number

\*\*Data taken from plots.

**TABLE-7: EXPERIMENTAL RESULTS FOR ROASTING OF COPPER CONCENTRATES  
AT 500°C.**

Particle size	Time in min.	Sulphur in Pellet, percentage	Fraction Sulphur removal 'R'	$(1-(1-R)^3)$
0.1435 cm. (-10 + 14)*	20	26.41	0.105	0.036
	40	24.76	0.161	0.057
	60	23.37	0.203	0.074
	80	22.43	0.24	0.087
0.1840 cm. (-9 + 10)*	20	27.15	0.08	0.027
	40	25.44	0.138	0.047
	60	24.23	0.179	0.063
	80	23.21	0.21	0.075
0.219 cm. (-8 + 9)*	20	27.50	0.063	0.022
	40	26.06	0.117	0.041
	60	25.08	0.15	0.053
	80	24.46	0.171	0.060

\* Tayler sieve number.

TABLE-8: EXPERIMENTAL RESULTS FOR ROASTING OF COPPER CONCENTRATES AT 550°C.

Particle Size	Time in Min.	Sulphur in Pellet, Percentage.	Fraction Sulphur Removal 'R'	$(1-(1-R)^2)$
0.1435 cm. (-10 + 14)*	20	25.23	0.135	0.041
	40	22.66	0.232	0.084
	60	20.57	0.303	0.114
	80	18.90	0.368	0.141
0.184 cm. (-9 + 10)*	20	26.59	0.099	0.034
	40	24.08	0.184	0.065
	60	21.75	0.263	0.096
	80	20.33	0.311	0.116
0.219 cm. (-8 + 9)*	20	27.18	0.079	0.026
	40	26.97	0.154	0.054
	60	22.99	0.221	0.08
	80	22.13	0.251	0.092

\* Tayler Sieve Number.

**TABLE-9: EXPERIMENTAL RESULTS FOR ROASTING OF COPPER  
CONCENTRATES AT 600°C.**

Particle Size	Time in Min.	Sulphur in Pellet, Percentage	Fraction Sulphur Removal 'R'	$(1-(1-R)^3)$
0.1435 cm. (-10 + 14)*	20	24.76	0.161	0.056
	40	20.68	0.30	0.112
	60	16.76	0.432	0.173
	80	14.13	0.521	0.217
0.184 cm. (-9 + 10)*	20	25.68	0.13	0.046
	40	21.81	0.261	0.096
	60	17.25	0.392	0.152
	80	14.76	0.50	0.206
0.219 cm. (-8 + 9)*	20	26.38	0.1062	0.039
	40	23.88	0.23	0.083
	60	19.21	0.349	0.133
	80	16.17	0.428	0.170

\* Tayler Sieve Number.

**TABLE-10: EXPERIMENTAL RESULTS FOR ROASTING OF COPPER CONCENTRATES  
AT 650°C.**

Particle Size	Time in Min.	Sulphur in Pellet, Percentage	Fraction sulphur removal 'R'	$(1-(1-R)^3)$
0.1435 cm. (-10 + 14)*	20	23.17	0.215	0.077
	40	17.56	0.405	0.158
	60	12.63	0.572	0.246
	80	9.33	0.684	0.318
0.184 cm. (-9 + 10)*	20	24.14	0.182	0.064
	40	18.83	0.362	0.138
	60	14.40	0.512	0.212
	80	11.48	0.611	0.270
0.219 cm. (-8 + 9)*	20	24.76	0.161	0.056
	40	19.63	0.335	0.126
	60	15.84	0.463	0.187
	80	12.62	0.572	0.242

\* Tayler Sieve Number.



**TABLE-11: EXPERIMENTAL RESULTS FOR ROASTING OF COPPER  
CONCENTRATES AT 700°C.**

Particle Size	Time in Min.	Sulphur in Pellet, Percentage	Fraction Sulphur Removal 'R'	$(1-(1-R)^2)$
0.1435 cm. (-10 + 14)*	20	20.80	0.3152	0.116
	40	12.55	0.575	0.248
	60	4.98	0.831	0.426
	80	0.66	0.978	0.728
0.184 cm. (-9 + 10)*	20	21.42	0.2743	0.104
	40	13.93	0.528	0.218
	60	7.81	0.7353	0.361
	80	2.95	0.9002	0.536
0.219 cm. (-8 + 9)*	20	22.34	0.2431	0.081
	40	15.48	0.4753	0.194
	60	9.64	0.6735	0.312
	80	5.36	0.8182	0.435

\* Tayler Sieve Number

TABLE-12: RATE CONSTANT 'K' VALUE AT DIFFERENT TEMPERATURES FOR ZINC CONCENTRATES.

Particle Size	Temperature °C	1/T X 10 <sup>4</sup> (°K <sup>-1</sup> )	Rate Constant 'K'	log K
0.1435 cm.	700	10.27	0.0057	-2.2441
	750	9.76	0.0123	-1.9101
	800	9.32	0.0275	-1.5607
0.184 cm.	700	10.27	0.02135	-2.3420
	750	9.76	0.00925	-2.0339
	800	9.32	0.2135	-1.6706
0.219 cm.	700	10.27	0.00405	-2.3925
	750	9.76	0.0075	-2.1249
	800	9.32	0.015	-1.8239

TABLE 13: RATE CONSTANT (K) VALUE AT DIFFERENT TEMPERATURES FOR COPPER CONCENTRATES.

Particle Size	Temperature °C	$1/T \times 10^4$ ( $^{\circ}K^{-1}$ )	Rate Constant 'K'	log K
0.1435 cm.	500	12.92	0.00116	-2.9355
	550	12.15	0.00166	-2.7799
	600	11.45	0.00266	-2.5751
	650	10.82	0.00393	-2.3956
	700	10.72	0.00758	-2.1203
0.184 cm.	500	12.92	0.000833	-3.0794
	550	12.15	0.00158	-2.8013
	600	11.45	0.00258	-2.5884
	650	10.82	0.00363	-2.4401
	700	10.72	0.00616	-2.2104
0.219 cm.	500	12.92	0.000830	-3.0809
	550	12.15	0.00113	-2.9469
	600	11.45	0.00217	-2.6635
	650	10.82	0.00315	-2.5017
	700	10.72	0.00554	-2.2564

TABLE-14: ACTIVATION ENERGY REQUIRED TO ROAST SAMPLES OF  
DIFFERENT SIZES FOR ZINC CONCENTRATES.

Particle Size	Activation Energy K cal per mole.
1.435 mm.	30.549
1.84 mm.	29.029
2.19 mm.	27.312

TABLE-15: ACTIVATION ENERGY REQUIRED TO ROAST SAMPLES OF  
DIFFERENT SIZES FOR COPPER CONCENTRATES.

Particle Size	Activation Energy K cal per mole
1.435 mm.	14.105
1.84 mm.	14.787
2.19 mm.	14.409

### Method for Analysis of Roasted Samples

The sulphur content of the pellet was estimated before and after roasting as barium sulphate. One gram of sample was dissolved in a mixture of concentrated nitric acid and  $KClO_3$  (small amount). All the sulphur was converted into sulphuric acid which was fixed up as  $BaSO_4$  by the addition of barium chloride. The precipitate was filtered off, ignited and weighed. Sulphur was finally estimated from known weight of  $BaSO_4$  thus formed.