

## INTRODUCTION

Zinc is one of the most important metals of the present age due to its high chemical activity as well as alloy forming property. Its main uses are in zinc base alloys (die-casting), brass, zinc powder, and in the form of various zinc salts. Of the various salts of zinc, zinc oxide and zinc sulfate are most important, and as a matter of fact zinc oxide constitutes about 80% of the total zinc compounds manufactured.

### 1.2. EXTRACTION OF ZINC AND ITS GRADES

Zinc is distributed in the earth's crust to the extent of about 120 gm. per ton, mostly in the form of sulfide, known as sphalerite or zinc blend depending on the crystalline structure. Generally it contains sulfide of some other metals also, viz. lead, cadmium, iron, copper etc.

In the metallurgy of zinc, the sulfide ore after crushing to proper size, is concentrated by using different methods like differential flotation, gravity concentration etc., depending on the nature of the ore.

In the next step, the sulfide concentrate is roasted at a very high temperature near about 1000°C, thereby converting it to a crude oxide with evolution of highly corrosive sulfur dioxide. This effluent gas is subsequently oxidized for the production of sulfuric acid. The oxide is subsequently subjected to distillation in retorts with coke or coal or leaching with sulfuric acid<sup>1</sup>. In both the cases additional treatments are necessary for obtaining zinc.

### 1.3. ZINC BASED INDUSTRIES IN INDIA

Upto 1971, Zawar Mine of Udaipur, Rajasthan was the only zinc mine in India. Hence most of the amount of zinc concentrate was being imported from different countries like Canada, Australia, Bolivia, Peru. In 1971 India imported 34,394 tons of zinc concentrate from these countries, at the cost of \$ 3.6 million. Imports of zinc metal, alloys, mostly zinc or spelter totalled 96,813 in 1971. This was imported from Australia, Canada, Japan, U.S.S.R. Zawar Mine produced 293,536 tons of ore containing 3.5% zinc in the respective year whereas zinc concentrate totalled 15,397 tons, compared to 15,888 tons in 1970.

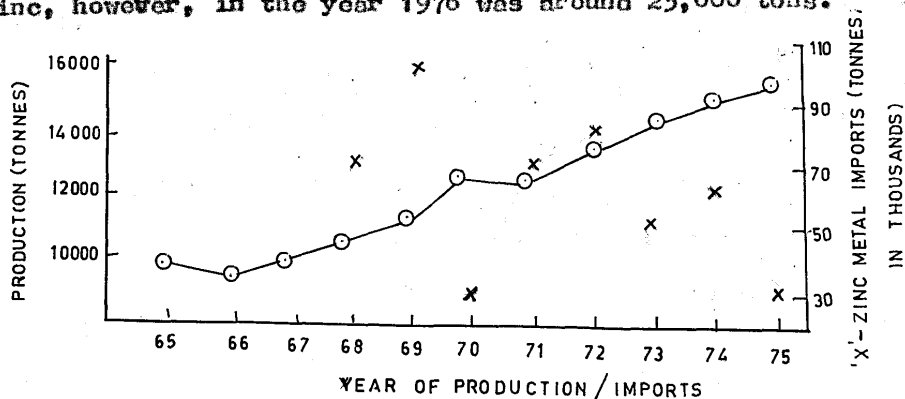
The second smelter at Alwaye, Kerala, i.e. the Caminco Biniani Zinc Limited smelter, produced only 10,267 tons of zinc

in 1971, though it was having a capacity of 20,000 tons per year. Production of zinc in Hindustan Zinc Limited, Debari (based on Zawar ore) was only 56% of its total capacity, i.e., it produced 11,000 tons instead of its capacity of producing 18,000 tons per year<sup>2</sup>.

Indian Government had approved in January 1971 the establishment of a new zinc smelter at Vishakhapatnam having a capacity of 30,000 tons per annum, based on zinc concentrates.

The expansion scheme of the Hindustan Zinc Ltd., and Caminco Biniani Zinc Ltd., together with a new smelter at Vishakhapatnam shows an expected total production of 106,000 tons per annum of zinc metal by 1978-79 against the established requirement of 200,000 tons of zinc by that year. They are also studying the feasibility of establishing a smelter, based on oreserves at Rajpura, Dariba with an annual capacity of 50,000 tons of metal.

The production of zinc concentrate in India has been given schematically in the following diagram, for different years, while the imports for the same along with the import data for the zinc metal is listed in the following graph. The annual production of zinc, however, in the year 1976 was around 25,000 tons.



#### 1.4. SULFUR AND ITS EXTRACTION

Sulfur is often considered along with salt, coal and limestone to be one of the four basic raw materials of chemical industry, due to its large applicability. 80% of the brimstone consumed in U.S. is burned to form sulfurdioxide and hence to convert it to sulfuric acid, consumption of which is estimated to be 69.3 million tons in 1980. The use of sulfur in various industries such as fertiliser, rubber, paper, textile and in various chemicals are quite well known<sup>1</sup>.

Though sulfur is one of the most important raw materials of the modern age, the acute shortage in the reserves of native sulfur has posed a great problem for the growth of various industries. To overcome this problem efforts are being made during the last few years throughout the world to utilise the sulfur bearing minerals and industrial waste gases either for the production of sulfur in the elemental form or to directly convert them to various other essential chemicals by modification of the existing processes or through discovery of new processes.

Generally the extraction of sulfur can be broadly categorised as (i) recovery in elemental form (ii) nonelemental form.

The elemental sulfur is either obtained from nature as such, recovered by the well-known Frasch Process<sup>3</sup> or from minerals. The minerals are generally subjected to oxidation utilising suitable oxidising agent by various well-known methods<sup>4-10</sup>.

Sometimes reduction of some sulfates under hydrogen pressure has been utilised to obtain elemental sulfur from these.

The recovery of sulfur in the non-elemental form from the sulfide ore is mainly based on oxidising them. Besides the effluent gases coming out of such processes, the gaseous products from other treatment plants also contain either  $\text{SO}_2$  or  $\text{H}_2\text{S}$ . Recovery of sulfur from these gases are generally achieved through oxidation or reduction of the gases. Thus quite a few processes are in vogue<sup>11-18</sup> for recovering sulfur from gases containing either  $\text{SO}_2$  or  $\text{H}_2\text{S}$ .

#### 1.5. SULFUR BASED INDUSTRIES IN INDIA

In 1971, the total consumption of sulfur in India was 314,126 tons whereas in 1970 it was less than this by 3%. Sulfuric acid registered an increase by 4% in 1971 compared to 1970, while in paper and paint industry the same was 2% and 8% respectively. The various patterns of consumption has been presented in adjacent Table 1.

Unfortunately India is having a very poor deposit of elemental sulfur near Puga Valley of Kashmir. An inferred reserve of 20,000 tons of elemental sulfur has been estimated from Puga, Ladakh, Jammu and in Kashmir.

Hence the sulfur recovery in India is mainly made from sulfur bearing ores such as pyrites and pyrrohotite, reserves of which are placed at about 108 million tons, of which 82.6 million tons are in Saladipura Sirkar District, Rajasthan.

Table 1 : Consumption of sulfur in various industries in the different years (in tonnes).

Industry	1967	1968	1969	1970	1971
Sulfuric Acid	282,840	354,741	409,115	419,475	435,530
Chemicals and CS <sub>2</sub>	25,319	42,428	38,296	44,805	48,925
Sugar	6,635	6,937	15,200	17,290	14,240
Paint	11	16	9	7,400	8,083
Textile				4,753	4,975
Paper	172	410	305	4,041	4,140
Rubber	1,734	2,003	2,139	2,445	2,718
Battery	117	191	177	227	240
Hydrogenation of edible oils	91	69	71	85	123
<b>Total</b>	<b>326,919</b>	<b>406,605</b>	<b>465,512</b>	<b>500,616</b>	<b>514,126</b>

Table 2 : Import Data for Sulfur.

Year	Total sulfur import		Elemental sulfur		Sulfur (colloidal, pptd. sublime, dyes, etc.)	
	Qty. (ton)	Cost (Rs. thousands)	Qty. (ton)	Cost (Rs. thousands)	Qty. (ton)	Cost (Rs. thousands)
1967	592,978	325,637	592,641	324,163	337	1,474
1968	390,390	214,818	389,547	212,539	843	2,287
1969	305,010	119,930	304,517	117,647	493	2,283
1970	521,423	137,316	521,081	135,435	342	1,881
1971	420,607	98,004	420,075	95,482	532	2,522

The imports of sulfur and its indigenous production (from Madras refineries) for the years 1975 and 1976 were respectively 617,115 , 588,763 and 6,200 and 7.348 tonnes.

But this is not enough to face the sulfur consumption in India, which as a result necessitates the import of sulfur from countries as Canada, Poland and Iran.

The value of the imported sulfur in 1971 decreased to Rs. 98.0 million from Rs. 137.3 million in 1970, which in terms of quantity means a decrease by 19%. The average annual rate of increase in imports of sulfur in India was 19% during 1967 to 1971. However the import of sulfur in the year 1973-74 was around 589,000 tonnes which was estimated to rise to 1775,000 tonnes in the year 1978-79, of which 83% was to be utilised for sulfuric acid manufacture. The chart of the imports of sulfur is given in the following Table 2.

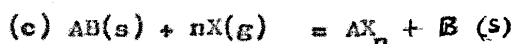
An approximate percentage of sulfur present in different sulfide ore is given below :

<u>Nature of ore</u>	<u>Approximate percentage of sulfur in the ore</u>
Iron pyrites	40 - 45% of S
Pyrrhotite	38 - 39% of S
Sphalerite	28 - 32% of S
Galena	13% of S
Copper Sulfides	30% of S
Gypsum	46.6% of SO <sub>3</sub> radical
Anhydrite	58.8% of SO <sub>3</sub> radical

#### 1.6. GENERAL THEORY OF GAS SOLID REACTIONS

The roasting reaction system involving the metal sulfide is obviously heterogeneous in nature. The possible reactions

which generally occur in these type of reactions are those involving formations of the metal oxide and sulfur dioxide (b) the metal oxide and elemental sulfur and (c) the sulfate of the metal.



The present investigation is mainly based on the type 'c' reaction.

These reactions can either be diffusion controlled or chemically controlled.

The diffusion controlled reactions are characterised by low energy of activation and generally of first order kinetics. These are subdivided into two groups i.e. (a) diffusion through the boundary layer surrounding the solid particle may control the overall rate and or (b) diffusion of gaseous reactants or reaction products through the pores of the solid and the product layer may control the overall rate. The rates of these reactions are generally dependant on the flow rate of the gaseous constituents of the reaction/product and on the size of the particles involved in the reaction.

The resistances offered by these processes can be minimised to negligible extent by either increasing the flow rate of the gases and/or reducing the size of the solid particles<sup>20</sup>.

The other type of reaction i.e. chemically controlled is generally characterised by relatively large energies of activation



and rates being least affected by the change in flow rate or particle size. The order of these reactions can be anything between 0, 1 and 2.<sup>21,22</sup>

A particular reaction may be predominately diffusion controlled under a particular set of conditions but may change over to a chemically controlled reaction under another set of conditions. Thus Cannon and Denbigh<sup>23</sup> have shown that below 830°, the rate of oxidation of 110 faces of zinc sulfide is chemically controlled but above 830° there is evidence of onset of diffusional resistances. Moreover there are some cases when the velocity of the chemical reaction and the rate of diffusion are comparable in magnitude.

However there are some heterogeneous reactions which are predominantly dependent on the properties and texture of the starting material and product. These are categorised as topochemical reactions and have a considerable preparative interest and also have contributed to the understanding of the mechanism of reactions, particularly the reaction between structure and chemical properties.

Topochemical reactions may be grouped into three categories<sup>24</sup>.

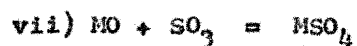
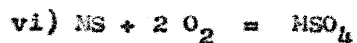
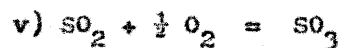
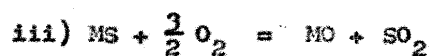
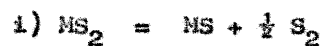
(1) Reactions in which the degree of dispersion of specific surface and the kind and extent of lattice imperfections in the reaction product are dependent on the nature of the starting material.

(ii) Reactions in which the starting material exerts an influence on the crystal structure of the product.

(iii) Reactions where the nature of the starting material determines the chemical composition of the product.

These reactions give rise to compounds which cannot be obtained by other methods or at least not by analogous reactions in gas phase or in solution.

However, the above schemes of general reactions are usually not so simple. These take place through a series of complex reactions as given below :



From the above set of reactions, it is impossible to say which are the actual reaction paths for the formation of metal oxide or metal sulfide, without kinetic data. The metal oxide can be produced through any of the reactions (iii) or (viii), on the other hand, metal sulfate can be produced from reaction

(ii) or (vi) and (vii). It is not known yet, whether  $\text{SO}_3$  formation takes place through reaction (v) at all or not.

#### 1.7. LITERATURE SURVEY

Work on the roasting of sulfides, involving the systems metal-sulfide-oxygen was initiated by German workers in the beginning of twentieth century. The reaction studies involving systems in both equilibrium state and non-equilibrium state, consisted of sulfide-sulfate and sulfide-oxygen system. From a survey of available literature it is generally observed that the informations pertain mainly to the various aspects of conversions of the sulfides to the corresponding oxides. Moreover, these conversions are better achieved at higher temperature. Quite obviously the majority of the work is in the higher temperature range and is mainly on the mechanism of such conversions.<sup>25</sup> This has ultimately resulted in lack of detailed informations on the intermediates formed during the reactions. In the following lines attempt has been made to present a brief review of the available literature, which is of some relevance to the investigations carried out by the present worker.

A review of the work, upto 1957, carried out by Soviet scientists on sulfide systems, has been presented by Frents.<sup>26</sup>

Ashcroft<sup>27</sup> started the studies on the mechanism of the reactions, and concluded that the primary product of oxidation of sulfides were sulfates, which finally dissociates to give oxides along with sulfurous gases. But Peretti<sup>28</sup> suggested that

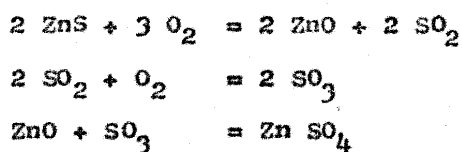
the first product of  $\text{Cu}_2\text{S}$  oxidation was  $\text{CuO}$ , and ultimately copper sulfate forms out of  $\text{CuO}$  in the latter stage.

Tsoidler<sup>29</sup> reported that oxidation of nickel sulfide by gaseous oxygen goes through the formation of nickel oxide, which then gets oxidized to sulfate - by interacting with  $\text{SO}_2$  and  $\text{O}_2$ , present in the system, produced from the reaction.

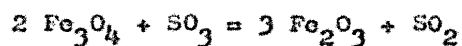
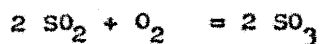


The largest amount of sulfation occurs at  $600^\circ - 800^\circ\text{C}$ , but it disappears due to its instability.

Similar type of conclusion was drawn by Diev and Karyakin<sup>30</sup>, when they studied the  $\text{Cu}_2\text{S}$  system. They stated that  $\text{Cu}_2\text{O}$  is the first product of oxidation, which is then converted to sulfate by reacting with  $\text{SO}_2$  and  $\text{O}_2$ . Same authors<sup>31</sup> claimed same mechanism for the oxidation of  $\text{ZnS}$ . In this report, it has been found that most of the investigators supported the oxide formation to be the primary reaction, which finally leads to the formation of sulfate, the reactions can be outlined as follows :



Same type of reaction mechanism has been established by Smirnov<sup>32</sup>, when he studied the reaction of pyrites-oxygen system. He reported the reactions to take place as below :



This type of reaction mechanism has been termed as oxide theory of sulfation. There is another type of reaction mechanism for the formation of sulfates from sulfides, which has been termed as direct sulfation theory.

Vanyukov et al.<sup>33</sup> supported the direct sulfation theory, when they studied the iron-sulfide roasting. Smirnov<sup>34</sup> also supported this direct sulfation theory in his later work. He reported that the primary product of oxidation was the metallic sulfate which finally reacts with unreacted sulfide to give metallic oxide.

Pazukhin<sup>35</sup> stated that no unified approach can be made to the roasting reactions and the nature of the sulfide involved is very important. He also stated that roasting nature depends mainly on the polarizing force of the cation, the temperature and oxygen partial pressure of the gaseous phase. In his opinion the formation of complex  $\text{SO}_4^{=}$  ion is less probable at higher temperatures, in the excess of oxygen.

McCabe<sup>36</sup> investigated the mechanism of roasting of  $\text{Cu}_2\text{S}$  in lump form. He found that  $\text{CuSO}_4$  is surrounded by oxide on the gas interface and sulfide on the core side.

Wadsworth et al.<sup>37</sup> studied the sulfate formation from pure ZnO, in presence of SO<sub>2</sub> and O<sub>2</sub>. It was reported that no SO<sub>3</sub> was formed when there was no ZnO, for SO<sub>2</sub> oxidation. According to them, the rate of sulfation is proportional to the amount of SO<sub>2</sub> that would be present in the system.

Tratsevitskaya et al.<sup>38</sup> reported that the amount of sulfate produced from sulfide roasting depends on the O<sub>2</sub> partial pressure in the gaseous atmosphere.

Cannon and Denbigh<sup>23</sup> studied on the oxidation of the 110 faces of ZnS between 680°C and 940°C and with a oxygen partial pressure between 0.014 and 0.50 atm. They concluded that below 830°C the rate of oxidation was independent of the thickness of the zinc oxide layer and thus chemically controlled. Above a temperature of 830°C onset of diffusion resistance occurred and at still higher temperature, the whole mechanism changed.

Sommer and Kellogg<sup>39</sup> allowed sphalerite to react with air, mixtures of SO<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub> and mixtures of SO<sub>3</sub>, O<sub>2</sub> and N<sub>2</sub> in the temperature range of 361° to 527°C. Rates of oxidation was negligible in all cases except for the gas mixture containing SO<sub>3</sub>. With this gas the oxidation of finely divided sphalerite was fairly rapid and zinc sulfate was the product. They have suggested that zinc sulfate, besides being produced by reaction of ZnO with SO<sub>3</sub> (or SO<sub>2</sub> and O<sub>2</sub>) might also be produced by direct interaction of SO<sub>3</sub> with ZnS.

Denbigh and Beveridge<sup>40</sup> from their work on oxidation of pelleted spheres of ZnS in air within a temperature range of 500 - 1440°C suggested that the reaction was chemically controlled at lower part of the temperature while at upper part diffusion was predominantly controlling. However within chemically controlled temperature region sintering occurred leading to a great reduction in the overall reaction rate.

Abraham et al.<sup>41</sup> from their studies on the oxidation of pure ZnS as well as ZnS-FeS cylindrical compacts suggested that the reaction is diffusion controlled in the range 700-900°C and below 700°C, the oxidation is controlled by a different mechanism. The presence of upto 5% iron as sulfide in the zinc sulfide compact did not affect the roasting rates whereas 10% of this lowered the roasting rate considerably. Similarly Natesan and Phibrook<sup>42</sup> from their studies with ZnS pellets in the temperature range of 740 - 1020°C suggested that the process of oxidation was predominantly controlled by transport through ZnO reaction product layer. They have further observed<sup>43</sup> on the basis of a proposed model that at no stage of the reaction the particle was subjected to a state of instability. Mendoza et al.<sup>43</sup> suggested that the experimental observations on the oxidation of ZnS pellets could be explained on the basis of a model which takes into account the existence of diffusion with simultaneous reaction with some correction factors.

Tamahankar et al.<sup>44</sup> have observed that when samples of CaS, NiS, PbS, ZnS and MoS<sub>2</sub> was heated in air under controlled

conditions, were converted to sulfates, which eventually decomposed to oxides.

Takeo and others<sup>45</sup> studied the kinetics of vaporization and oxidation of ZnS in an oxidising atmosphere in O-N mixture at 1200 - 1250°C. They observed that at first ZnS dissociated to Zn vapour and S vapour. These dissociation products diffuse outwards from the surface of the spherical pellet and form the reaction zone with gas diffusing inwards from the bulk flow. A white shell of ZnO was formed in the reaction zone. This shell finally became impermeable stopping the reaction completely. However Czeslaw and others<sup>46</sup> from their studies on effects of partial pressure of oxygen on the kinetics of zinc sulfide oxidation in the temperature of 850 - 1060°C, suggested that the rate was limited by chemical reactions occurring at the ZnO-ZnS interface and was proportional to partial pressure of oxygen in the gas phase.

Lauchev and Karavastieva<sup>47</sup> carried out roasting of intermediate products containing Zn, Cu, Fe and S of different compositions. They observed that the optimum condition of roasting was 650 - 700°C under high turbulence factor. They observed that sulfation of Cu and Zn sulfides was attained by the simultaneous action of decrease in concentration, ignition temperature due to the presence of other sulfides, improvement of diffusion condition in the solid reaction products and increase in the gas phase due to the catalytic action of Fe oxides.



Results of oxidation of ZnS by  $\text{SO}_2$  in aqueous sulfuric acid, desulfurisation of sphalerite at a temperature range of 760-900°C to suggest the energy of activation of the process at different temperature range and on the effects of grain size and grain shape have been reported by a host of workers<sup>48-50</sup>.

From the studies on the kinetics of oxidation of ZnS concentration in a fluidised bed, Gupta and others<sup>51,59</sup> observed that sulfur removal increased with roasting time while the recovery of sulfur decreased with particle size, other parameters being kept fixed. The rate controlling reaction was first order at particle/gas interface and the activation energy for oxidation was  $30 \pm 2$  Kcal/mol. Similarly Kondo et al.<sup>52</sup> carried out oxidation of ZnS in a fluidised bed at 800-910°. They have observed, by applying a two phase model, that the overall reaction rate in the emulsion phase was controlled by the rate of gas film mass transfer at higher temperature.

From thermogravimetric studies on the oxidation of zinc concentrates, Karwan and others<sup>53</sup> have observed that the ZnS exothermic peak shifted towards higher temperatures by increase in the amounts of Fe, Pb, probably present as sulfides, and dolomite. Pb and dolomite influenced negatively the process of oxidation of ores.

While studying on the processes taking place in the synthesis of ZnO-Zn luminophor from zinc sulfide by the oxidation of ZnS at 900°C Vesker and coworkers<sup>54</sup> observed the simultaneous formation of sulfates. However they also observed that the

primary oxidation of ZnS to ZnO was predominating. Shin and coworkers<sup>55</sup> have observed from their studies on the oxidation of Zn and Cd sulfides that the heterophase oxidation at 850-900° was mainly determined by mass transfer between the gas and sulfide particles.

Gradual oxidation of zinc sulfide has been observed when it is kept in humid condition, the rate depends on the presence of pyrites and chalcopyrite. It has been observed that the rate of oxidation is also dependent on the degree of the zinc sulfide ore dispersion.

During the storage of ground pyrite ores, having a high content of metacolloidal (structure) minerals the oxidation of ZnS has been found to proceed with a high rate.

#### 1.8. SCOPE OF THE WORK :

From the foregoing discussions it is seen that during roasting of zinc sulfide some zinc sulfate is directly obtained. Such formation is favoured at lower temperature, while at higher temperature the production of zinc oxide is favoured. It is also seen from various works that zinc sulfate is unstable at higher temperatures and decomposes to zinc oxide more or less completely beyond a temperature of about 600°C. Hence if the roasting of the sulfide is carried out at lower temperatures, in presence of some catalysts/additives which will not only increase the conversion to sulfate, but also stabilise the sulfate, the recovery of both zinc and sulfur can be achieved very easily. This will also help to avoid various drawbacks of

the existing process for the recovery of zinc from zinc sulfide ores namely (i) high temperatures, (ii) detrimental effect of sulfur dioxides evolved in the process on the plant at high temperatures and finally the numerous steps necessary for the recovery of both zinc and sulfur from the roasted material and the effluent gases. Hence if the development of a single step process by which substantial conversion of sulfide to sulfate is possible, not only the whole recovery would be simplified but also open up new avenues for ore utilisation.

It is also known that some sulfide ores, zinc sulfide ores being one of them, undergo weathering process leading to direct sulfation of these sulfides. The weathering is a slow process occurring at a comparatively low temperature, almost at room temperature and takes place in presence of moisture and oxygen. Hence it is quite likely if a similar condition is simulated at higher temperature, it may lead to not only increase in rate but also higher conversion to sulfate. One may further presume that such a possibility may further be increased by incorporating suitable catalysts which will not only increase the rate but also stabilise the zinc sulfate.

With these <sup>in view</sup> i.e., formation of zinc sulfate at lower temperature, possibility increasing with incorporation of steam/moisture along with air and in presence of a suitable catalyst if necessary, attempts have been made to convert sphalerite ore, available at Zawar Mine of Udaipur, India.

These investigations have been divided broadly into two parts : one without using steam and the other in presence of steam. Since the ore contains iron sulfide, some experiments were carried out with it. However, later on  $\text{Fe}_2\text{O}_3$  was added to the ore and experiments were conducted with it to find out the reaction conditions necessary for highest conversion to sulfate. The oxides of transition metals were attempted as additives/ catalysts as because these are known to be good oxidation catalysts. The underlying principle is to find out the feasibility of such a process at lower temperature and also the maximum conversion to zinc sulphate possible under suitable optimum conditions. Such a conversion directly to zinc sulfate will indicate the possibility of converting zinc and sulfur to an easily recoverable form by a single step. It is needless to mention that subsequent recovery of both zinc and sulfur as sulfuric acid is obtained through the electrolysis of the aqueous solution obtained by water leaching of the product. Zinc thus obtained will be of high purity. The sulfuric acid generated during the electrolysis will have to be occasionally replaced or treated as is done in other electrolysis cases.

Finally attempts were made to delve into the mechanism of the reaction through studies conducted with pure zinc sulfide. These studies were first conducted to find out whether the conversion of zinc sulfide to sulfate would be augmented by steam alone or some additives (oxidation catalysts) were necessary as observed in the cases involving oxidation under humid conditions. Subsequently the influences of various operational parameters on

the conversions were studied. This would help not only to arrive at the optimum conditions necessary for such conversions but also to find the probable mechanism and kinetics of the reaction. However such reactions which involve gas solid interactions leading not only to various simultaneous reactions but also other catalysed reactions are not that simple to tackle.