

Chapter I

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

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1.1 WORLD STATISTICS.

In the present age of industrialisation, the consumption of sulphuric acid is considered as a yard stick of industrial growth. The per capita annual consumption of sulphuric acid in India is only 0.8 Kg per year, as against 91.5 in Australia, 81.5 in U.S.A., 71.2 in Canada, 50.8 in Germany and 30.5 in U.K. (56) The raw material, sulphur required for the production of sulphuric acid is wholly imported in India, as there are practically no workable deposits of elemental sulphur.

U.S.A. produces the maximum amount of sulphur; in 1963 about 8.5 million tons were produced, out of which one million ton was from sour gas and the rest from sulphur deposits by Frasch Operations. Next in order of production are Mexico, France and Canada respectively. Sulphur is mined and refined in smaller quantities in Japan, Italy and in the South African countries. Recovery of sulphur by smelting pyrites is done in Norway, Spain, Portugal, Finland, U.S.S.R. and China. The world's consumption of sulphur was 20 million tons in 1963 and the rate of increase is 9.8% per year. It is apprehended that there would be a severe shortage of sulphur in the world by 1968-70. As a result of survey, it has been estimated that a reserve of only 135 million tons of sulphur exist in the world (56).

1.2 DEPOSIT OF SULPHUR ORES IN INDIA.

There is a huge deposit of pyrites in India. It has been estimated (66) that there is a reserve of 384 million tons of pyrites within an area of 48 square miles at Amjhore in Bihar; of this 78 million tons are proved reserves, which occur in beds 20 ft. below the ground level. The pyrites contain approximately 40-50% sulphur and 36-44% iron.

At Inghaldahl in Mysore there is a reserve of 2 million tons of pyrites, analysing 30-35% sulphur. Smaller deposits of pyrites are also existing in Madras, Panjab and other States.

In order to utilize the Pyrites, the Government of India established a Pyrites and Chemicals Development Corporation (P.C.D.C.) in 1960 with an initial capital of Rs 5.0 crores. This Corporation has prepared a report covering various aspects of utilization of pyrites.

In addition to pyrites, there is a considerable amount of gypsum deposit in Rajasthan, which is being used for the production of ammonium sulphate at Sindri in Bihar.

1.3 SULPHURIC ACID INDUSTRY IN INDIA.

There are 58 sulphuric acid plants in India and the pattern of consumption of sulphuric acid in 1965-66 was as follows :

Industry	Estimated consumption of sulphuric acid, tons	Per cent Consumption
Superphosphate	890,000	59.33
Ammonium Sulphate & Nitrophosphate	200,000	13.33
Pickling of finished steel	30,000	2.00
Aluminium Sulphate	40,000	2.67
Rayon Yarn and Staple Fibre	135,000	9.00
Petroleum Refining	16,000	1.07
Titanium dioxide	24,000	1.60
Miscellaneous	165,000	11.00
	<u>1,500,000</u>	<u>100.00</u>

1.4 P.C.D.C. RECOMMENDATIONS.

The target of production of sulphuric acid during the third five year plan was 1.75 million tons requiring about 0.57 million tons of elemental sulphur. In the year 1965-66, India spent Rs 7.5 crores in foreign exchange for import of sulphur in order to manufacture sulphuric acid. As the foreign exchange position is very critical at present, the Government of India are planning to manufacture sulphuric acid from pyrites. The Pyrites and Chemicals Development Corporation of India (P.C.D.C.) have reported that under the present freight charges and pyrites cost, if the plant is located within a distance of 835 Kilometers from the mines, the cost of sulphuric acid production by burning pyrites will be comparatively lower than that from imported sulphur (66). For distant places it will be economical to transport elemental sulphur after extracting from pyrites.

The progress made till March 1967 (66A) is (a) Rs 439 lakhs have been sanctioned for mining of 2.4 lakhs tonnes/annum of pyrites at Amjhore, (b) Rs 201.51 lakhs for setting up of a 400 tonnes/day H_2SO_4 plant based on pyrites at Sindri (Bihar), (c) sanction has been given for setting up of a plant for production of elemental sulphur from pyrites based on a pilot plant test conducted in Finland by Outocumpo process.

Besides the use of sulphur for sulphuric acid, it is also required in many other industries. During the year 1965-66, consumption of elemental sulphur was 35,000 and 26,000 tons for the manufacture of carbon disulphide and sugar respectively. Vulcanization of rubber and other miscellaneous products consumed about 31,000 tons of sulphur during the same year.

1.5 PROCESSES FOR PRODUCTION OF SULPHUR AND SULPHURIC ACID FROM PYRITES.

A very brief synopsis of a few important processes are given below, the details of which are available in (66).

(1) Orkla Process :

Iron pyrites in lump form is mixed with coke, quartz and limestone which is a slag forming material and then smelted in water jacketed closed blast furnace. The gases leaving from the top of the furnace contain S, N_2 , SO_2 , H_2S , COS, CS_2 and CO_2 , which are passed through catalyst, when all the sulphur compounds are disintegrated to elemental sulphur. 80% of the total sulphur can be recovered by this process.

(2) Outocumpo Process :

Dry pyrites fines are flash smelted in a reducing atmosphere, provided by burning fuel oil or pulverised coal. This produces a molten iron sulphide matte, which contains somewhat less than half of the sulphur in the pyrites. The remaining sulphur is volatilised and recovered as elemental sulphur. The molten iron sulphide matte is granulated and roasted in fluid bed roaster producing a gas containing 10% SO_2 , which is suitable for acid production.

(3) Autoclave Process :

A mixture of pyrrhohite and oxygen at a pressure of 30-150 psig are kept in suspension with distilled water in an autoclave and pH of the slurry is maintained at 1.5. The autoclave is heated to 110-125°C. After a period of about 2 hours, the autoclave is cooled and the solidified sulphur nodules are separated from the iron oxide by passing the autoclave contents over a 65 mesh screen.

(4) Trail Process :

The raw material for the process is 100% SO_2 , obtained by roasting pyrites and then concentrating the lean gas by absorbing in ammonia. Concentrated sulphur dioxide is reduced to elemental sulphur by coke.

(5) Bolidon Process :

In this process, lean SO_2 gas is used as the raw material. A modified producer gas is prepared by passing part of the SO_2 fumes through a bed of hot coke. The remaining larger portion of the SO_2 fumes is mixed with the producer gas and is passed through two catalyst chambers in series, where more sulphur is produced. Essential requirement for the process is cheap coke.

(6) Hill Chlorination Process :

The entire sulphur content in pyrites is recovered and iron is removed as iron oxide. Chlorine used in this process is mostly recoverable. By chlorinating pyrites, ferrous chloride and molten sulphur are produced. By passing the mixture of ferrous chloride and sulphur to a chlorinating zone, ferrous chloride reacts with sulphur at about $150-350^\circ\text{C}$, producing a reaction product containing ferrous chloride, sulphur and sulphur chloride. Ferrous chloride is separated substantially free of volatile sulphur compounds from reaction product. Ferrous chloride is then oxidized by passing air at a temperature of about $350-500^\circ\text{C}$, to produce ferric oxide and ferric chloride. This ferric chloride is again used for chlorination zone.

(7) Dorr-Oliver Process :

There are three possible methods for the recovery of sulphur from pyrites by fluosolids technique. (i) Distilling the labile sulphur by external heat source, when only 35% of the

sulphur in the feed can be recovered as elemental sulphur.

(ii) Distilling of sulphur by burning of parts of the pyrites to yield sulphur and SO_2 . Here most of the heat is obtained by burning of pyrites itself. (iii) Recovery of entire sulphur is obtained by part distillation and part reduction of SO_2 .

1.6 INDUSTRIAL APPLICATION OF FLUIDIZED BED IN ROASTING OF PYRITES.

Othmer (58, p.213) reports, "Perhaps the most outstanding commercial application of fluidization in the chemical industry is the roasting of pyrites or pyrrholite (Fe_7S_8) to produce sulphur dioxide used in the Sulphite pulping process or in the manufacture of sulphuric acid". The first Fluosolids system for producing SO_2 was installed in 1952 at New Hampshire and it has been operating ever since at the rate of 9,000 tons of sulphur equivalent per year. The fluidized bed reactor is 16 ft. diameter by 5 ft. deep. The feed is introduced in the reactor as a slurry containing 75% solid and 25% water. Air is introduced in the fluidized bed for oxidation and the bed temperature is maintained at 1610°F. So rapid is the rate of heat transfer that water has to be added to the fluid bed for cooling and a remarkable uniformity of temperature, varying not more than 20°F, can be maintained in the bed. Active oxidation of sulphur to SO_2 and Fe to Fe_3O_4 takes place and normally greater than 99% oxidation is obtained. The feed treated in terms of dry material is 75 tons per 24 hours and the stack gas analysis on percentage volume dry basis shows SO_2 — 13.0, SO_3 — 0.2 and O_2 — 1.0.

1.7 LITERATURE SURVEY.

A. ELEMENTAL SULPHUR FROM PYRITES

Recovery of elemental sulphur from pyrites was tried by Ronken (68) by burning pyrites in air. Pyrites particles of 1/4 inch to 3/8 inch in size were ignited in a container and allowed to burn in an atmosphere of air mixed with recirculated gases from the combustion process. The temperature of the mass was about 1070°C. The gaseous combustion products were passed through a condenser to recover the sulphur. Between 35 and 40 per cent of the sulphur originally contained in the pyrites was recovered.

Khundkar (41) studied the thermal decomposition of iron pyrites in an atmosphere of carbon dioxide. He found that the dissociation was practically nil below 550°C. The dissociation was considerable at 600°C, and at a temperature slightly above 800°C, approximately half of the sulphur content in the ore was liberated.

Yazaki and Nakajima (88) studied several Japanese and Canadian ores. The continuous desulphurization by ignition was determined with a thermo balance. They reported that the ores with no free sulphur were stable at 400°C., and they began to decompose from 400-500°C, which continued upto 800°C. The ores rich in free sulphur were stable at 150°C and lost both free and combined sulphur partially at 200-300°C, and complete_{ly} at 600-700°C in air or oxygen. When heated slowly in an atmosphere of nitrogen,

the ores showed two characteristic thermodynamic curves, one indicating the vaporization of free sulphur and the other the decomposition of combined sulphur.

West (85) conducted experiments to recover elemental sulphur in nitrogen or sulphur dioxide at a suitable temperature to drive off one atom of sulphur, which was recovered and the residue was pyrrhotite. A portion of the pyrrhotite so produced was later fluidized with an oxygen bearing gas at a temperature required to convert it to magnetite with the generation of SO_2 and S. Another portion of the FeS was fluidized with previously formed SO_2 , again to produce sulphur dioxide and sulphur vapor. The vapor was condensed and SO_2 was used for pyrrhotite treatment.

Parker (60) worked with finely divided sulphide ores, which were fed into a fluidized bed supplied with an oxidizing gas, such that only part of the sulphur was oxidized. The temperature was controlled so that the SO_2 formed reacted with the remaining sulphides to form sulphur vapor without sintering of the bed particles (for pyrites 800-950°C). In this connection Davis et al (15) suggested on the basis of their experimental study, that by increasing the maximum size of particles from 1/8 inch to 3/8 inch diameter and decreasing the proportion of fines, sintering could be avoided. They suggested that concentration of particles bigger than 10 mesh should be 2-50% by weight.

Fredrik (20) studied roasting of iron sulphide ore with steam. Pyrites was ground to 325 mesh and mixed with 5% CaSO_4 (also 325 mesh) with addition of 10% water. The material was

formed into 0.5-1.0 inch pellets, dried and charged into a pre-heater at 750°C, flushed with nitrogen. The pellets passed continuously into a reaction furnace to form a bed 18 ft. deep. Steam at 1100-1200°C was passed through the bed. In the reaction zone, labile sulphur was distilled off largely as H₂S and SO₂ in approximately 2:1 mole ratio. A large amount of hydrogen was generated and passed off with the steam. The steam and the gases from the reaction furnace were passed to a condenser, where all the labile sulphur and part of the sulphur from the reaction were deposited in almost a colloidal state. The water carrying this sulphur and the uncondensed gases were sent through a sulphur recovery plant, where the SO₂ and H₂S mixture was passed through a bauxite catalyst. The sulphur in the water was recovered by coagulation. The sulphur yield was approximately 90% of the theoretical.

Kjullerud and Yoder (42) have recently reviewed the works on the thermal decomposition of mineral pyrites (FeS₂) to yield pyrrhotite (FeS_{1+x}) and sulphur.

Recovery of elemental sulphur from pyrites by thermal decomposition has been studied by Allen (3), Kamura (39), Raeder (67), D'orr, L (17), Rosenqvist (70), Dickson (16) and various other workers. Recently the feasibility of conversion of high sulphur tertiary coals of Assam (India) to energy products and chemicals has been discussed by Lahiri ~~and~~ et al. (43).

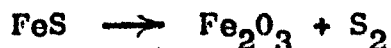
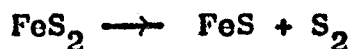
B. KINETICS & MECHANISM OF REACTION

Thermal decomposition of Iron Pyrites was studied by Schwab and Philinis (71) at 600-650°C. The per cent decomposition was calculated on the basis of the reaction :



It was noted that the reaction proceeded quite rapidly even at 600°C and at 650°C, it approached completion within an hour. In agreement with Udintseva and Chufarov (81) no induction period was noted. But in contrast with many other reactions in the solid phase, a sufficient number of active spots were present in pyrites lattice from the start. The authors also found out the activation energy required for the reaction and reported values of 29 Kcal for the initial period of the reaction and 33 Kcal for the final period of the reaction. Those values were attributed to the chemical process and not to a transport phenomenon, since the alteration in the rate of flow of the carrier gas, CO₂ between 40 and 170 ml/min, had no influence on the rate of decomposition.

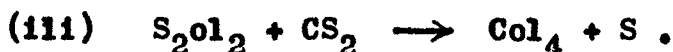
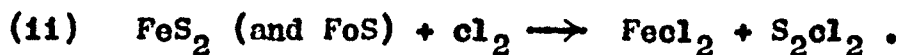
An interesting work was carried out by Morawietz (55) in the field of preparation of elemental sulphur from iron pyrites. FeS₂ loses sulphur on heating in presence of sulphur dioxide in two stages with FeS as an intermediate as follows :



The calculation of equilibrium constant is made difficult by the fact that both FeS and Fe_2O_3 are non-stoichiometric compounds, whose composition depends on the S_2 pressure. It was determined by suspending a sample of FeS with large pore volume from an arm of a thermo balance, while $\text{SO}_2 - \text{N}_2$ mixtures at partial pressures of SO_2 at 0.9, 0.5 and 0.1 atmosphere were circulated through the chamber held at temperatures of 620, 720, 820 and 920°C. The heat of formation of $\text{FeS}_{1.104}$ was found to be 12.2 Kcal at 870°C, which is in good agreement with the theory. In the kinetics of the reaction, the rate determining step was the diffusion of SO_2 through the surface layer of Fe_2O_3 to the unreacted FeS in the centre of the spherical sample. Diffusion takes place predominantly in the gas phase through the pores in the solid, with some activated diffusion through the surface absorption film.

Kinetics of roasting of ferrous sulphide in fluidized beds was studied by Malets (48). Pyrites was treated for 3-4 hours at 800-850°C in a nitrogen atmosphere, when loss of elemental sulphur was 45-47%. From the percentage of FeS_2 roasted versus time curves, the plots of $\log K$ vs. $1/T$ were constructed. These consisted of three linear sections, the intersection of which located the temperatures of transition of roasting pyrites. The kinetic zone was found to be upto 532°C, and the diffusion started at 647°C. In the intermediate range, 532-647°C, both factors affected the roasting.

Ishikawa (34) studied the reaction conditions for the following industrial processes :

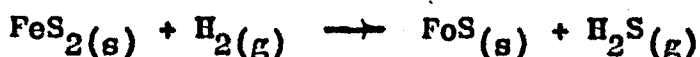


The thermal decomposition of reaction (i) was 592°C. The reaction was performed in a nitrogen atmosphere. The yield of this reaction, dependent on the grain size of the pyrites, was maximum at 10 mesh. The optimum conditions for the reaction (ii) were a temperature of 250°C, and a rate of chlorine gas supply of 20 ml/min per gm pyrites. Pyrites acts as a catalyst for the reaction (iii), which did not occur without catalyst.

In a recent work by Habashi and Bauer (26) elemental sulphur was utilised to produce sulphuric acid by aqueous oxidation. They mentioned of the possibility of utilizing sulphide ores. If the aqueous oxidation of sulphide ores is conducted at a temperature below 120°C and in acidic medium, elemental sulphur is always a reaction product. Once this temperature is exceeded, no sulphur is formed. The reaction $\text{S} + 1.5 \text{O}_2 + \text{H}_2\text{O} \longrightarrow \text{H}_2\text{SO}_4$ is greatly dependent on temperature and oxygen partial pressure. Below the melting point of sulphur the rate is extremely slow, and above this temperature the rate is appreciable and increases rapidly with temperature. The reaction is chemically controlled, and the activation energy is 11.75 Kcal/mole. The rate is proportional to $p_{\text{O}_2}^{3/2}$, thus suggesting that it takes place in two steps : $\text{S} + 1.5 \text{O}_2 \longrightarrow \text{SO}_3$ and $\text{SO}_3 + \text{H}_2\text{O} \longrightarrow \text{H}_2\text{SO}_4$, the first being

the rate determining step. Sulphur dioxide is not an intermediate reaction product. The rate is affected by the presence of some foreign ions.

Schwab and Philinis (71) measured the extent of the reaction



at 450°, 477° and 495°C. Their results indicated a first order (with respect to hydrogen) irreversible reaction. Hydrogen at high flow rate was passed at atmospheric pressure through a bed of FeS₂ particle ranging in size from 0.01 to 0.1 mm. The conversion was 95% in 2 hours at a temperature of 495°C.

Coats and Bright (11) studied the kinetics of thermal decomposition of pyrite to pyrrhotite and sulphur in a dynamic argon atmosphere over the temperature range 600-653°C. Pyrite containing appreciable amount of quartz was crushed to -200 mesh and the quartz removed as far as possible by heavy liquid separation with tetrabromomethane. Final product on analysis, corresponded to the formula FeS_{1.99} containing 0.3% silica. The reaction was followed by the rate of progression of the pyrite/pyrrhotite interface into a cylindrical, compressed, polycrystalline pellet. The temperature coefficient of the reaction was found to be 69.5 ± 5.9, 64.7 ± 3.3 and 66.9 ± 5.1 Kcal/mole, when the results were processed in three different ways. The pyrite/pyrrhotite interface was found to progress at a linear rate

into the pellet at a given temperature; equations were derived to express the variation of reaction rate with temperature and the equation of Mo.Kewan (51) :- $r_0 d_0 [1 - (1 - \theta)^{1/3}] = K_2 t$ can be used to represent the decomposition, where r_0 , d_0 are the initial radius and density of pyrites respectively, θ the fraction decomposed, K_2 the reaction rate constant and t the time. Attempts to follow the early nucleation stage of the decomposition, using massive mineral crystals, proved unsuccessful.

According to Pavlyuchenko and Samal (61), the kinetic equation of the form $[1 - (1 - \theta)^{1/3}] = Kt$ describes experimental data on the dehydration of $\text{LiCl} \cdot \text{H}_2\text{O}$ and the thermal decomposition of CuS , $\text{LiBr} \cdot \text{NH}_3$ and FeS_2 . The progress of isothermal decomposition of CaCO_3 , calcite and magnesite was reported to follow the equation.

$$-\frac{dv}{dt} = k 4\pi (r - \xi)^2 \lambda$$

where r is the initial spherical equivalent radius of the carbonate particles, ξ is the thickness of the product layer at time t , v represents the volume of undecomposed carbonate and λ is the shape factor.

Lin and Palermo (46) in their recent review on kinetics and Reaction Engineering, have mentioned that much work on the kinetics of reactions dealing with Pyrites have not yet been done.

1.8 SCOPE OF THE PRESENT INVESTIGATION.

Because of the nonavailability of sulphur in India, alternative sources for obtaining sulphur from pyrites, gypsum and high sulphur coals, which are available must be developed. The importance of sulphuric acid for manufacture of ammonium sulphate for increasing the food production in the country cannot be overestimated. Consequent on the devaluation of Indian currency, alternative process for producing sulphur from sulphur bearing ores will be more economical than importing sulphur.

The present investigation was undertaken with the object of recovering elemental sulphur from pyrites available in plenty in India. Experiments were conducted on the following lines.

- I. Fundamental studies, o.g., X-ray analysis, microscopic study, fluidization characteristics etc.
- II. Thermodynamic feasibility studies on thermal decomposition of pyrites as well as reaction of pyrites with steam and SO_2 gas.
- III. Study of thermal decomposition of pyrites in presence of an inert gas, CO_2 by a thermograv balance. Kinetic models were fitted to the decomposition reaction and rate equation derived. Activation energy for the decomposition reaction was also calculated.

IV. Decomposition of pyrites in a fluidized bed using steam as the fluidizing medium. Heat and mass transfer coefficients were also calculated from the experimental results.

For carrying out these investigations, 2 tons of 'Amjhora Pyrites' were obtained through the courtesy of Pyrites and Chemicals Development Corporation of India.