

India's sulphur problem & its solution

Sulphur is the basic raw material for the manufacture of sulphuric acid which is considered the barometer of India's industrial progress. Of course, in many more advanced countries this rule is no longer valid, as the overall industry grows rapidly with sulphuric acid virtually stable. The current production is at the same level as that of the U.S.A. in 1893 and the per capita consumption of acid in India is only 15% of that in the United States. These figures give indication of the immense development possibilities for India. So the position of sulphur in India should be critically surveyed.

Table II

Name of the Countries	U.S.A.	Germany	.U.K.	India
Per capita consumption in Kg.	81.5	50.8	30.5	1.0

The present need of sulphur in India is 0.4 million tonnes per year. At the end of Fourth Five Year Plan the demand of sulphur is estimated to be 1.86 m. tonnes/year. The present need of 0.4 m. tonnes is entirely imported. This type of absolute foreign dependence for a valuable raw material must go, because it endangers our national security. Although India does

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A critical survey of the sulphur position in India, alongwith the consumption pattern has been depicted. Various possible solutions have been suggested for the acute sulphur problem of the country. Brief outlines on a few important commercially exploitable processes has been given alongwith process flow sheets.

Sulphur is used in various industries, the major consumer being the fertilizer industry. The end user of sulphur and its consumption-distribution will be evident from Table-I.

Table-I

Uses	Distribution
Fertilizer	65%
Titanium & other Pigments	2
Chemicals	5
Iron and Steel	3
Rayon and film	10
Petroleum	2
Miscellaneous	3
Non-acid Industries (e.g. CS ₂ , gun powder etc.)	10

India is lagging much behind the advanced countries in per capita consumption of sulphur, Table II shows how poorly! India is placed.

not have the elemental sulphur deposits she is having various important sulphur resources. These are:—

- A. Natural sulphide and sulphate ores:—Iron pyrites (FeS₂), Chalcopyrites(CuFeS₂), Zinc blende (ZnS), Galena (PbS), Gypsum (CaSO₄, 2H₂O), Calcium sulphate anhydride and baryte (BaS).
- B. Industrial wastes: Spent acid stream like petroleum refining sludge, picking liquor etc., Gaseous effluents from petroleum refinery, Coal and oil combustion units and sewage.
- C. High sulphur content Assam Coals : The, installed capacity for sulphuric acid plants now exceeds 15 million tonnes but the estimated production is only 700,000 tonnes. The short fall is mainly due to scarcity of sulphur, resulting in reduction of fertilizer output.

The present sulphur shortage can be effectively met by adopting the following measures:—

Time of application	Dozeb		
	N/ha	P/ha	K/ha
1) At the time of sowing	40 kg	80	60
2- One month after planting	40 kg	—	—
3) Two months after planting	40 kg	—	—
Total :	120 kg	80	60

conditions Kudrov (1969) working on sugarbeet in U.S.S.R. noticed the higher content of N, P₂O and K₂O in plant and more yield of sugarbeet by incorporating 70.kg. N, 80 Kg. P₂O and 80 Kg K₂O per hectore.

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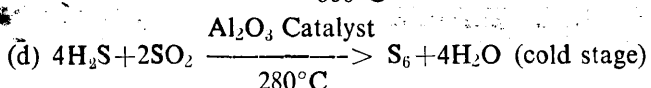
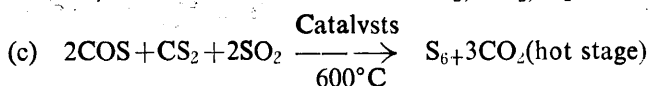
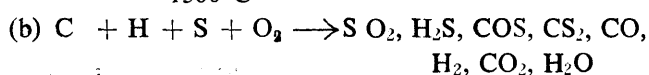
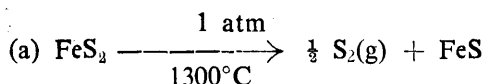
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- (1) Use of indigenously available raw materials for the production of sulphuric acid.
- (2) Adopting methods for the manufacture of chemicals by different routes which do not require H₂SO₄.
- (3) Recovery of sulphur from wastes.

1. Use of indigenously available raw materials:—

(i) Use of Pyrites : The pyrites are though not abundant, available in India. The total reserve has been estimated to be 400-700 million tonnes. The survey is still going on; most of this is found at Amjore (Bihar).

The sulphur content of Amjore pyrites is 45-48%. The pyrites can be effectively utilised for the production of sulphur dioxide by the Finnish process (Fig. N. 1) Ground pyrites ore (—200 mesh) is dispersed with hot combustion gases from oil burner in a vertical circular shaft furnace. FeS₂ dissociates into FeS which is tapped periodically in liquid form and granulated. Sulphur is recovered in two stage catalytic reactors from the gases and condensed on molten sulphur droplets in spray condenser. The reactions are as follows:—



The difficulty arises from the fact that the installed plant cost is much higher than based on elemental sulphur. This matter can be overcome by installing economic sizes (300 tonnes/day). One sulphuric acid plant (400 tonnes/day) based on Amjore pyrites has recently been set up at Sindri. A second one will be set up at Durgapur and a third one at Cochin. The Planning Commission has recommended the use of imported pyrites instead of elemental sulphur in two plants in Travancore, one at Visakhapatnam, one in Bombay and the last one at Gujarat. It is estimated that installation of new sulphuric acid plants based on pyrites would save the sulphur imports to the tune of 300,000 tonnes. The conversion proposals when completed will further save 280,000 tonnes of sulphur per year.

(ii) Production of sulphuric acid from Gypsum : Gypsum is already being used for the manufacture of fertilizer at Sindri. For production of sulphuric acid from Gypsum there is a German patent and the process is fully developed in U.K. The process (Fig No. 2) consists of heating in a rotary kiln a mixture of calcium sulphate and coke with silica, alumina and ferric oxide in requisite proportions which yields sulphur dioxide with simultaneous production of clinket. The minimum economic size is 150 tonnes/day. The unit is to be built in such a locality which is favourable for the availability of gypsum, coke and has market for cement. The large reserves of gypsum and coal and increasing demand for cement justify the production of sulphuric acid from Gypsum.

2.. Change of the H₂SO₄ route for the manufacture of chemicals.

Phosphatic fertilizers need sulphuric acid. But it would be better if we can find some alternative route for the manufacture of phosphoric acid other than the H₂SO₄ route.

(i) **Electrothermal phosphorous:** It is true that in this process no sulphuric acid is needed for the manufacture of phosphoric acid but there is one disadvantage that the capital investment is more. Before devaluation capital investment in H₂SO₄ process was Rs. 600/- per 1 ton compared to Rs. 1,000/- to Rs. 1200/- per ton for an electric furnace.

(ii) **Phosphoric acid from hydrochloric acid:** The development of chlorine-caustic industry ensures a large supply of chlorine and as a result hydrochloric acid can be obtained in large quantities without difficulty. The present method of manufacture of phosphoric acid by sulphuric acid can be replaced by the Isreali Mining Industries process, using HCl which will save a considerable amount of sulphur. Even a small scale plant of 10 tonnes H₃PO₄ per day is economic.

(iii) **Substitution of sulphuric acid for pickling of steel:** In the pickling of steel, sulphuric acid can be effectively replaced by hydrochloric acid using suitable inhibitor. The steel industry in India has consumed 21,000 tonnes of sulphuric acid (93% conc.) in 1964 to pickle 1.6 million tonnes of steel. In 1970-71 for an estimated 3 million tonnes of steel to be pickled, sulphuric acid needed would be 40,000 tonnes. If sulphuric acid is completely replaced by hydrochloric acid 1.3x10⁴ tonnes of sulphur can be saved annually.

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(iv) Substitution of sulphuric acid in Titanium Dioxide Industry: The sulphuric acid in Titanium dioxide industry can be replaced by hydrochloric acid but the chloride process requires enriched ilmenite (94% TiO₂) and the economic size is round 2500 tonnes/year. The present capacity of 6000 tonnes/year is expected to be expanded to about 20,000 tonnes/year. Total sulphuric acid requirement would be 90,000 tonnes. By using chloride process and enriched ilmenite for entire plant the sulphuric acid requirement may further be reduced to 13,000 tonnes saving 77,000 tonnes of H₂SO₄ per annum.

3. Recovery of Sulphur:

(i) From the coke oven gas: The coal charged to the coke ovens on the private and public sector steel plants was 16 million tonnes in 1966 and it will rise to 27 million tonnes in 1971 and 36 million tonnes in 1976. H₂S coming out in the coke oven gas can be recovered by absorption desorption process where H₂S is absorbed first by a suitable solvent and then stripped out of the solution by means of steam.

It is estimated that a coke oven charbonizing 1000 tonnes/day yields approximately 2.5 tonnes of S (sulphur) considering of present intake in coke ovens as million tonnes of coal 50,000 tonnes of S would be recovered which will rise to 0.0625 million tonnes of S in 1971.

(ii) Soft coke Industry : India's need for smokeless fuel for domestic and other purposes is about 4 million tonnes/year which are not devolatilised in the open by the wasteful beehive system. The Central Fuel Research Institute has designed devolatilising equipment with moving grate. If these methods are applied on a large scale basis and simultaneously recovery of sulphur from volatile matter nearly 5,000 tonnes/year of S can be saved from being wasted.

(iii) From Smelter Gas : Sulphur dioxide from the smelter gases is wasted. Proper arrangements should be made to recover the sulphur from wasted sulphur dioxide.

(iv) From Petroleum Industry: Indian crudes contain low sulphur (0.05 to 0.26%). So recovery of sulphur could be limited to refineries using imported middle east crude (1.35 to 2.54% S). By 1971 it is expected that 64% of total crudes will be imported. There is)

no commercial process developed so far which recovered sulphur economically either from the crude or from the liquid products of the refinery. The only possibility lies in recovering H₂S from refinery off gas. The Madras refinery will recover 9000 tonnes of S per annum. The Cochin and Haldia refineries are each capable of producing 8 tonnes of S per day. Burmah Shell, and Esso in Bombay can each recover 9 tonnes of S per day.

(v) Sulphur recovery from sewage: The sewage sludge from the cities when treated with an aerobic micro organism, produces CO₂ methane and H₂S — the sulphur content of the sewage gas varies from 10 grain to 600 grains/100 cft. Installation of sewage digestion plant in all cities followed by sulphur recovery may yield 10,000 to 15,000 tonnes of S per year.

(vi) Sulphur from Assam Coals: Assam coals contain about 6 % sulphur mostly in organic combination. The flue gases resulting from the combustion of such type of coal contain on an average 0.3 to 0.5% SO₂ by volume. This sulphur dioxide can be recovered by the zinc oxide process (Fig. No. 3). The flue gases are scrubbed with aqueous solution of sodium sulphite—bisulphite causing an increase of bisulphite content. Zinc sulphite is precipitated from the clarified solution by treatment with zinc oxide. Filtered zinc sulphite cake is calcined to give a gas mixture containing 70% water vapour and 30% SO₂. Recovered zinc oxide is recycled.



Conclusion: It is estimated that the demand of sulphur by the end of fourth five year plan will rise to 1.86 million tonnes/annum. By utilization of indigenous raw materials, change of the H₂SO₄—route of the manufacture of chemicals and recovery of sulphur from wastes, a huge amount of sulphur approximating 0.75 million tonnes (Table No. III) will be obtained, which will cause a drastic reduction of the import of sulphur, thus saving considerable amount of foreign exchange to the tune of Rupees 45 crores.

Table — III

Total demand of sulphur per annum by the end of Fourth Five year plan = 1.86 million tonnes.

Saving per annum of sulphur by using indigenous available raw material, changing H₂SO₄ route and recovering sulphur from wastes.

Indian Chemical Manufacturer

Use of pyrites	Use of Gypsum	Using Hcl for H ₂ PO ₄ manf.	Using Hcl for pickling of steel	Using Hcl in TiO ₂	Recovery of sulphur					
					From coke oven gas	Soft coke industry	Smelter gas	From Petroleum Inds.	From sewage	From Assam Coal
0.58 Million Tonne	not estimated.	13,00 ton.	13,00 tonnes	50,000 tonnes	625000 T	5000 ton	not estimated	10,000 T	10,000 T	Not estimated.

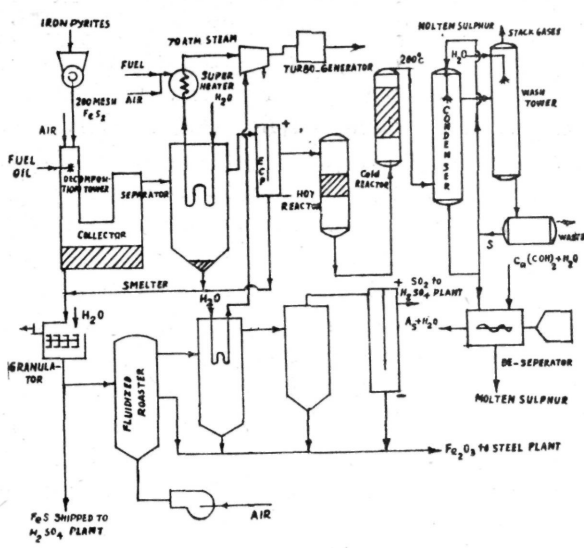


Fig. 1
Sulphur from Pyrites

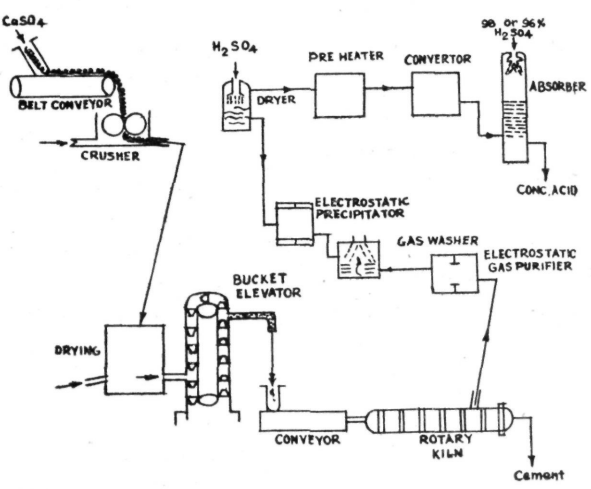


Fig. 2
Sulphuric acid from Gypsum

Total saving of sulphur per annum = 0.7435 million tonnes (Approx. = 0.75 million tonnes)

It is a challenging task before the engineers to reduce the sulphur import in the country by economically recovering from the waste and thus greatly accelerating the country's development, progress and industrialisation.

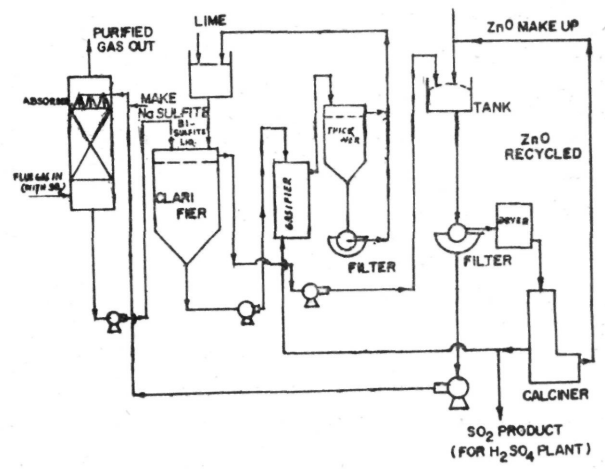


Fig. 3
Recovery of Sulphur Dioxide by zinc oxide process from stack gas

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