

THE SULPHUR POSITION IN INDIA

BY

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IT is not necessary to enumerate the numerous uses of sulphur. Sulphur and sulphuric acid are indispensable to any country not only for the production of war-time requirements, but also for the needs of all important industries even during peace-time.

It is well known that all sulphur used in India and Burma is imported. Essential supplies cannot be obtained from within the Empire. The quantities in tons of sulphur imported during recent years and the sources from which the supplies were obtained are shown in the following table:

It is obvious from the table that the principal importing countries before the outbreak of war were Italy, Japan, Java and the United States of America.

The rapidity with which the European conflagration is spreading and the threats of war from our eastern neighbours have brought the sulphur problem in India to the forefront and both the Government and the public outside have studied the subject with more than usual enthusiasm and concern. In the second meeting of the Board of Scientific and Industrial Research held in Simla on the 12th and 13th June 1940,

	1933 34	1934 35	1935 36	1936 37	1937 38 (Excl. Imp Burma)
British Empire	60	89	29	55	145
Germany	1,604	492	2,108	918	177
Italy	12,258	10,680	9,226	9,472	18,363
Java	2,091	2,148	1,643	1,837	991
Japan	4,856	5,945	12,376	11,742	9,221
U.S.A.	1,286	541	591	1,729	380
Other countries	10	53	25	1,780	131
Total all countries	22,174	20,221	27,901	27,539	29,408

Note.—The estimated value of the 29,408 tons imported in 1937-38 was Rs. 25,95,306 or approximately Rs. 90 per ton. The present price is approximately Rs. 150 per ton.

Brigadier Wood of the Supply Department emphasised the fact that the most important material which constituted a real shortage from the point of view of supplies was sulphur and the Board decided to constitute the following committee to study the sulphur problem in India from all points of view:

Sulphur Committee.—S. S. Bhatnagar (*Chairman*), Cyril S. Fox, J. C. Ghosh and H. Krall (subsequently added on Chairman's recommendation).

In the earlier stages, the Committee examined the sulphur question from the following points of view:

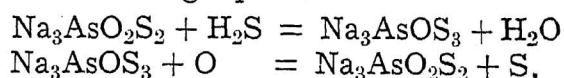
- (1) From the view-point of existing methods of the recovery of sulphur from sulphur-bearing salts and minerals available in abundance in this country.
- (2) From the view-point that the described and the talked of, but probably available sources of natural sulphur and sulphur-bearing minerals, may be examined again with a view to seeing if the likely supplies are expected to be larger than previously estimated. and
- (3) From the point of view of manufacturing or extracting sulphur compounds useful in trade from natural sources such as coal, oil, etc., which have been reported to be sufficiently rich in sulphur content.

As the functions of the Board of Scientific and Industrial Research are to finance those investigations which may lead to some tangible practical results by research, all items under (1) were to be examined from the economic point of view only, but attention was to be particularly bestowed upon (2) and (3) which required research.

As regards (1), particular attention was given to the subject of the recovery of sulphur from coke-oven gases, smelter gases such as those of the Indian Copper Corporation and the Burma Corporation and the utilisation of the deposits of gypsum for the production of sulphur. Various processes have been worked out in industrial countries to carry out one or other of these operations and particular mention has been made in this connection of the "Thylox" process, the "I.C.I./Bolidens" process, the "Orkla" process and others.

Thylox Process.—This process has been developed from the non-recovery Seaboard Process in Germany and the United States

where it is widely employed for the treatment of domestic gas supplies for the removal of hydrogen sulphide and recovery of sulphur from coke-oven gases. In this process the hydrogen sulphide is removed by scrubbing the gas with an absorbing solution consisting of certain alkali metal compounds of arsenic, such as sodium or ammonium thioarsenate and is recovered to sulphur on oxidation by air. These reactions are fairly represented by the following equation:



The solution remains uncontaminated by other substances in the gases both during treatment of the gas and also during regeneration of the foul solution. As a result, the sulphur filtered from the solution is not contaminated by other substances and is so pure that it can be sold both as sulphur and as an agricultural fungicide.

The Thylox process, or one or other of its alternative developments, such as the Ferrox, Nickel, Phosphate, and Phenolate processes, is now in general use for the removal and recovery of sulphur from various kinds of fuel gases, including coke-oven gas, blue-water gas, carburetted water gas, and oil refinery gases. These processes are best adapted to dealing with fuel gases at ordinary pressure which contain small or moderate quantities of hydrogen sulphide. The newest type of Thylox plant consists of a tower absorber, through which the gases pass and are scrubbed during transit by means of the solution, an aerating tower in which the foul solution is aerated thereby effecting liberation and flotation of the sulphur, a sulphur slurry tank, and a continuous filter for the removal of the sulphur. The whole plant occupies very little ground space. A heater or other means of warming the solution is unusually provided so as to heat the solution entering the aerating tower up to about 95° F., which is the best temperature for effecting the oxidation reaction. About 98 per cent. of the hydrogen sulphide content of the gas can be removed by this process. Pointed attention of the Tata Iron and Steel Company, Jamshedpur, was drawn to the advantage which would accrue if they adopted this process, and they promised to consider the whole question.

I.C.I./Bolidens Method.—A company named Messrs. Sulphur Patents Ltd., London, was formed within recent years by Messrs.

Imperial Chemical Industries Ltd., and a Swedish firm, Messrs. Boildens Gruvaktiebolag, for the recovery of sulphur from smelter gases produced when smelting ores similar to those occurring in India and Burma. The Swedish firm had developed a process for the direct production of sulphur from smelter gases and had operated a plant for several years at their mine in Sweden with a production capacity of up to 70 tons of sulphur per day. During the same period Messrs. Imperial Chemical Industries had developed a process for the production of concentrated sulphur dioxide from weak gas by using an absorbing solution of basic aluminium sulphate. In view of the complementary nature of these processes, an agreement was arrived at in 1936 whereby the patents and processes of the two companies were pooled and the company under the name of Messrs. Sulphur Patents Ltd., was formed to act as sole agents to negotiate licenses for the processes owned by the two companies.

About the same time Messrs. Chemische Industries, Basle (Ciba), had also devised a process for concentrating sulphur dioxide, and this firm entered into an agreement with the Metallgesellschaft of Frankfurt, under which this process was to be developed, and Messrs. Lurgi Chemie (a wholly owned subsidiary of Metallgesellschaft) worked out a process for the production of sulphur from such concentrated sulphur dioxide. For some time these two groups, viz., I.C.I./Bolidens and Lurgi/Ciba worked in competition in regard to developments in the field of concentration of SO_2 and its reduction to sulphur. Subsequently, however, the four companies pooled their patents and processes, with the result that the best process or combination of processes could be applied to each particular problem. In view of the fact that the Lurgi Chemie was a company whose specific object was the design and construction of chemical plants, the members of the pool agreed that the exploitation of the patents and processes should be placed in the hands of Lurgi Gasellschaft fur Chemie und Huttenwesen, m.b.H., Lurgihaus, Gervinusstr 17/19, Frankfurt A.M., Germany.

A branch of this firm, the American Lurgi Corporation, New York, is operating in America, but it may be assumed that Messrs. Sulphur Patents Ltd., have taken over activities connected with these developments.

Negotiations were conducted some time ago between Messrs. The Indian Copper Corporation and Messrs. Sulphur Products Ltd., with a view to investigating the economic possibilities of recovering sulphur from their smelter gases, as it was anticipated that if only a 50 per cent. yield were obtained, about 3,500 tons of sulphur might be available annually from the Singhbaum plant. These negotiations were unsuccessful, however, owing, it is understood, to the Corporation being doubtful whether the gases obtained in their present process of production could be economically utilised and also to their not being disposed to incur the considerable expenses which would be involved in installing the necessary plant. The position was examined recently once again, but the costs and patent positions are prohibitive.

It may be mentioned in this connection that the tonnage of raw material with which the Burma corporation deals is much greater than that treated by the Indian Copper Corporation, but smelting operations, with the exception of lead and silver, have not hitherto been carried so far as the extraction of the metals. Copper and nickel ores received a preliminary concentration to a matte (mainly the sulphides) and speiss (largely arsenides) respectively by means of smelting, and the matte and speiss were subsequently shipped to Germany where the extraction of the metals was carried out. Zinc sulphide was concentrated by ore dressing methods, the "concentrates" being then shipped to Belgium for smelting.

A large amount of sulphur dioxide is produced in the course of these operations and it might be quite feasible to recover sulphur from this and the Burmese Government may well direct their attention to the recovery of sulphur from these gases.

Reference has been made above to the utilisation of gypsum for the production of sulphur. The best known method of recovering sulphur or sulphuric acid from gypsum which has been developed commercially consists in their production from a sintered mixture of powdered gypsum (calcium sulphate) clay, and coal or coke. A process based on this method is operated by the Bayer organisation at Lever Kusen, Cologne, and more recently by Messrs. Imperial Chemical Industries Ltd., at Billingham, Yorkshire.

The process adopted by the former firm

consists in heating a mixture of powdered anhydride or waste calcium sulphate with powdered coal or coke and shales or clay at 800° in a rotary kiln in an oxidising atmosphere. The kilns are 164 ft. long by 10 ft. diameter and are fired by means of pulverised coal. The burner end is cooled by water drips. The object of the oxidising atmosphere is to prevent the formation of carbon oxy-sulphide in the gases and of calcium sulphide in the clinker. The gases, which contain 6-7 per cent. SO_2 , are freed from dust by electrical deposition, washed, and sent to the chamber or contact plant. The kiln residue is ground up with blast furnace slag and marketed as cement. A description of this process is given in the *Journal of the Society of Chemical Industry*, 1920.

A similar process is used by Messrs. Imperial Chemical Industries at Billingham. Here a dry mixture of 80 per cent. anhydride, 7 per cent. coke and 13 per cent. clay is crushed and passed through tube mills. From the tube mills the raw meals is taken to blending hoppers and then to a rotary kiln similar to the usual type of cement kiln. The kiln process results in the production of clinker and gases.

From the clinker cement is produced, and the gases are passed through an electric precipitation plant of Lodge-Cottroll type and then through scrubbing towers. From the scrubbing towers the gases pass on to a sulphuric acid contact plant where 100 per cent. strength sulphuric acid is produced. Two tons of raw meal produce one ton of clinker and one ton of 100 per cent. acid. The production of the plant at Billingham was, prior to the war, 60,000 tons of 100 per cent. acid annually.

It is clear, however, that sulphur production would be of greater industrial assistance to India than sulphuric acid manufacture. To utilise this process for the production of sulphur instead of sulphuric acid would entail that the kiln gases containing sulphur dioxide, instead of being treated in a chamber or contact plant to produce sulphuric acid, would be treated according to the pooled patents and developments which were being exploited by Lurgi Gasellschaft fur Chemie und Huttenwesen m.b.H and which are now presumably being worked by Messrs. Sulphur Patents Ltd., as described above.

The economics of the process depend greatly on the price obtained for the cement

produced from the clinker and this aspect of the matter is of special importance in regard to India, as there is already a large well-established cement industry in the country with surplus manufacturing plant capacity. Schemes of this type based on the existing or suitably modified processes are being examined by the Associated Cement Company and the Mysore Cement Works. It must, however, be remembered that the cost of a pilot plant for this will be in the neighbourhood of Rs. 20 to 30 thousand and if these experiments prove successful as they no doubt will, the plant itself will cost anything from Rs. 20 to 30 lakhs subject to the patent position and a certain well-known firm would be willing to instal this equipment if the Government is willing to give certain guarantees regarding the purchase of the product now, as well as, after the war, and the matter is, I believe, engaging the attention of the Government.

The Orkla Process.—This process has been developed by Messrs. The Orkla Gurbeaktiebolag of Norway for the production of sulphur from pyrites. In 1927 a 40-ton plant was erected by the firm at their Lokken mine and subsequently in 1931 a much larger plant was erected at Thamshavn on the Orkdal Fjord, having an annual capacity of 200,000 tons of sulphur. The process has now been developed successfully to yield from 85 to 90 per cent. of the sulphur, and the copper in the ore can be obtained at an economical cost. The process consists in first smelting the pyrites in a blast furnace with quartz and limestone and slagging a large part of the iron content of the ore, the copper and other metals of value being collected in the first matte. It is understood that in this smelting operation an excess of coke and a minimum supply of ore are used. The furnace gases contain sulphur vapour, sulphur dioxide and carbon disulphide. With the aid of suitable catalysts (iron and aluminium oxides have been proposed) the constituents of the gas mixture at a temperature of $350/400^{\circ}\text{C}$. are caused to react. Carbon dioxide and elemental sulphur are formed, the latter being thereafter solidified by condensation.

Pyrites.—Several methods have been examined and developed for the manufacture of sulphur from pyrites. In the laboratories of the Director of Scientific and

Industrial Research at Calcutta, Mr. J. N. Sarkar has investigated the possibility of making sulphur by the interaction of sulphur dioxide obtained by burning the iron pyrites and sulphuretted hydrogen obtained by the action of lime, coal dust and steam on heated pyrites. Several catalysts have been tried and the process has yielded fairly satisfactory results and a pilot plant is under construction.

The Orkla process was developed particularly to utilise iron pyrites. Now that several new deposits of pyrites have been recently reported by the Geological Survey of India and the quantity available seems to be ample, the above processes have acquired special significance.

Pure pyrites contains 46.6 per cent. of iron and 53.4 per cent. of sulphur. It burns when heated in air or oxygen and produces sulphur dioxide. It is, however, more difficult to ignite pyrites than sulphur. Ores marketed for the manufacture of sulphuric acid usually contain from 42 to 47 per cent. of sulphur, but material containing as little as 30 per cent. of sulphur can be successfully burnt. On account of the cost of transporting and handling the large proportion of inert material in pyrites, however, the material used for acid making should be as high in sulphur as possible, as the value of the pyrites to the manufacturer of sulphuric acid depends almost entirely on the sulphur content and only to a small extent on the nature and amount of the impurities in the ore. It is also important that the pyrites used for this purpose shall be equally as free as sulphur from injurious components such as arsenic, chlorine, fluorine, antimony, selenium and tellurium.

Because of its considerable content of inert material, pyrites cannot be readily substituted for raw sulphur and burnt in sulphur burners. Owing to the considerable production of cinder and burnt ore when using this material, pyrites burners require to be provided with special grates and facilities for removal of the clinker and burnt ore, and in this respect they differ materially from sulphur burners.

A notable step has been taken by Dr. Kedar Nath of Simla who has installed pyrites burners in his chemical works in Agra and the plant has yielded good sulphuric acid at competitive prices. To persuade existing sulphuric acid manufacturers in India to utilise pyrites, the price

at which the pyrites can be offered to them should be such as to compare favourably with the price of raw sulphur, not only when allowing for the lower sulphur content but also for the capital expenditure necessary to substitute their existing sulphur burners with burners specially designed and made for the burning of pyrites. Owing to the paucity of sulphur, increasing amounts of pyrites both from Simla and the Sone Valley should be employed for manufacturing sulphuric acid.

Sulphuric Compounds from Coal and Oil.

Mr. N. L. Dutta has been associated with the Director, Scientific and Industrial Research, on investigations on the sulphur content of coals and oils. Investigations have been particularly carried out on "Wakting coal" and other coals of high sulphur content obtained from Dr. Fox of Geological Survey of India. The total sulphur of some of these coals have been found to be as high as 6.5 per cent. A substantial quantity of it is in the organic form so that it is possible to extract the sulphur compounds by solvent processes or steam distillation. The sulphur compounds as such or after chemical reaction produce materials which may be useful as anti-oxidants and as accelerators or retarders in vulcanizing processes. Preliminary work on these sulphur compounds has shown that extraction is pretty difficult but a number of important organic sulphur compounds have been extracted and their properties are being examined. This problem is of interest as these sulphur compounds are rather expensive and if they can be removed by a cheap process from the coal, the coal itself will become more useful and a good price could be fetched by developing the sulphur compounds.

Deposits of Sulphur and Sulphur-bearing Materials. Perhaps the most important development in the sulphur position is the location of more than one sulphur mine in India. In literature the largest sulphur deposit in India is described as being located about 12 miles south-west of Sanni in the Kalat State, Baluchistan. Sulphur was at one time mined at the spot but these operations ceased some sixty years ago as a result of a fire. *The Records of the Geological Survey of India*, Vol. L, page 137 (1919) state that the deposit is estimated to amount to at least 36,000 tons of sulphur rock assaying approximately 28.8 per cent. of free

sulphur, which is equivalent to 10,000 tons of sulphur. The mine is 40 miles from Bellpat, the Railway Station. Sulphur also occurs in other parts of Baluchistan, e.g., on the extinct volcano of the Koh-i-Sultan and other volcanic regions in the desert district of Chagai.

Recent work carried out by the Geological Survey under the auspices of the Board of Scientific and Industrial Research and the Sulphur Committee, has proved extremely fruitful and it is estimated that at one place in the surface deposits alone approximately thirty thousand tons of sulphur rock are available and mining operations will probably produce very much more. The deep boring operations in Baluchistan have been reported to be capable of yielding even larger quantities. Proposals are before the Government for working out the deposits in these two places and while the boring opera-

tions in the Sanni district have not yet been resorted to, there is no doubt that the success of the first deposit will lead to greater efforts on our part for obtaining more sulphur by boring. For obvious reasons it is not necessary nor desirable to give fuller details of the quantities of sulphur now required for India and the Eastern Group Nations in the British Empire, but it can be well imagined that the requirements will be large and for this reason, the report that the Simla mines of iron pyrites and the iron pyrites discovered in Sone Valley are not so small as they were at one time pictured, is of special interest. Iron pyrites have also been discovered in the Hyderabad State. The occurrence of sulphur and the large quantity of iron pyrites is a hopeful sign for the rapid development of sulphur sources in this country.
