ON THE UTILISATION OF INDIAN RAW MATERIALS FOR THE MANUFACTURE OF SULPHURIC ACID.

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Sulphuric acid is one of the most important of all chemicals, because of the wide use of the acid in many different industrial works. It is to the chemical industry what iron is to metallurgy. The general public, however, do not realise this fact, for sulphuric acid does not appear in the finished product as does iron or steel, but is only an intermediate raw material essential in many industries, such as, for example, the manufacture of phosphatic fertilisers, munitions and explosives, dyes, petroleum products, of various acids and innumerable other chemical and metallurgical products. The demand for sulphuric acid responds much more quickly to a general slump or boom in the industrial world than does the demand for iron or steel, so that it can rightly be said that the demand for this acid for chemical and metallurgical industries is an accurate and sensitive barometer for the general business conditions.

In India the principal manufacturers are the coal, iron and steel companies situated in Bengal, Bihar and Orissa, the ammunition factories and the chemical companies (D. Waldie & Co., with works at Konnagar and Cawnpore, the Bengal Chemical & Pharmaceutical Works, Ltd. of Calcutta (established 1909), Messrs. Parry & Co. of Ranipet (established 1909), the Eastern Chemical Co. with works at Bombay (established 1913), Dharmsi Morarji & Co. of Bombay, the Baroda Chemical Works, Baroda). The entire manufacture of sulphuric acid in India is based on imported sulphur.

Sulphuric Acid from Sulphate Minerals.

One of the most widespread and easily obtainable sources of sulphur is gypsum or anhydrite and the urge towards national self-sufficiency in sulphur is causing considerable attention to be paid to the problem of the utilisation of calcium sulphate, particularly in Russia and France. The Committee appointed by the French Government in August 1937 had recommended (in view of the difficulty of importing adequate supplies of pyrites from Spain) that a large-scale industry should be established for the manufacture of sulphuric acid from gypsum. An extensive report of laboratory and factory scale investigation of a process has been made by the Russian investigators S. M. Rojak, M. I. Gerschman, K. F. Miloslavski and Z. I. Nagerova (*Trans. All. Union Sci. Inst. Cement*, 1935, No. 10, 5). It is said that a suitable composition for the raw mixture is calcium sulphate 80%, dried clay 15%, and coke, anthracite,

etc. 5%. A microscopic study of the clinker shows that the petrographic structure is identical with that of ordinary Portland cement, provided the burning is correctly carried out. A somewhat similar process has been investigated by V. S. Dubey, M. B. Rane and M. Kanakaratnam (*Bull. Indian Ind. Res. Bureau*, 1937, No. 6) in which alumina and sulphur dioxide are produced from bauxite gypsum mixtures. No carbon was added to aid displacement of SO_2 from gypsum. If the mixture of bauxite and gypsum in the ratio of 2 : 5 are heated at 1200–1250° for six to seven hours, the sulphur dioxide is expelled completely from gypsum. The resulting calcium aluminates on hydrolysis furnish pure alumina.

The first published description of the process as employed by Imperial Chemical Industries, Ltd., at Billingham to manufacture high class Portland cement and sulphuric acid from anhydrite and white clay was made by M. Nicolétis (*XVII Cong. Chim. Ind. Paris*).

P. P. Budnikov and E. I. Kretsch (*J. Appl. Chem. Russ.*, 1936, *9*, 1929) have studied the reaction between finely ground calcium sulphate and carbon at 800–1200°. The rate of reduction is proportional to the relative concentration of carbon and inversely proportional to the diameter of the particles. The same authors (*ibid.*, 995) find that the direct decomposition of calcium sulphate by chlorine at 900–950° is accelerated by the addition of various substances, nickelous sulphate having the greatest effect. It is stated that a 100% yield of SO_3 was obtained at 1100–1150° and 86·5% yield at 1000–1050° in the presence of silica. In this projected process the chlorine is recovered as hydrochloric acid.

The reaction between pure calcium sulphate and kaolin was studied by G. Marchel (*J. Chem. Phys.*, 1926, 23, 38–60) and the thermal dissociation in the presence of oxides of iron, silicon, aluminium and chromium has been studied by the Russian chemists (cf. *J. Appl. Chem. Russ.*, 1932, *5*, 897–901).

India is quite rich in deposits of high grade gypsum. Most of the gypsum now mined is being used in the cement industry, where gypsum is added to the ground cement clinker to control the setting properties of the cement. The production of gypsum is increasing as the following statistics show:—

Period.	Average annual production.
1914–18	18,857 tons.
1919–23	35,133 ,,
1924–28	41,199 ,,
1929–33	50,112 ,,

70% comes from the Punjab, the remainder from Kashmir, Rajputana and Madras. In the Jhelum district of the Punjab the mineral occurs in enormous quantities and extends through Shahpur and Mianwali districts along the whole length of the southern flank of the range from Jalalpur to Kalabagh on the Indus. At Khewra in the Jhelum district, the Department of Northern

India Salt Revenue undertake the quarrying of gypsum as a subsidiary industry.

Immense deposits also exist in the trans-Indus salt region of the Kohat district, North-West Frontier Province, where more or less continuous masses up to 200 ft. in thickness are found with bands of shale and clay. Huge deposits also occur in Spiti and Kanaur, in the Punjab Himalayas.

The Kashmir deposits are also immense and are stretched for fifteen miles to the north of the Jhelum valley cart road near Braripara in the Urie Tehsil.

In Rajputana, the Bikaner State accounts for 54% of the production, the Jodhpur State for 45% and the Jaisalmer State for the rest.

In Southern India gypsum is widely distributed in the cretaceous rocks of the Trichinopoly district. The mineral is mined at Karai in the Perambalur Taluq and at Ottathur in the same Taluq and at Maravathur in Udaiyarpalayam Taluq.

In his evidence before the Indian Tariff Board on Heavy Chemical Industry (1930, Vol. II, p. 481) Sir Edwin Pascoe stated that gypsum of a very superior quality occurs in immense quantities in Burma, and can be picked up by hand labour over large areas of the country.

Another mineral which has a promising future in India is barytes, the sulphate of barium, a heavy white mineral which finds its chief application at present in the paint industry. India has very rich deposits of this mineral. The largest deposits occur in the Madras Presidency. Mining was started in 1918 at Betumcherla in Kurnool district and over 24,500 tons had been exported from this district by the end of 1931. As a result of systematic investigation in 1932, Mr. A. L. Coulson listed sixty localities in this region.

District.	Taluq.	No. of places.
Cuddapah ..	.. Pulivendla	8
Cuddapah ..	.. Other Taluqs	5
Anantapur ..	.. Tadpatri	8
Anantapur ..	.. Other Taluqs	3
Kurnool ..	.. Dhone	29
Kurnool ..	.. Other Taluqs	7

According to the estimate of Mr. A. L. Coulson (*Mem. Geol. Surv. Ind.*, LXIV, Pt. 1, 1933) at Kottapalle in the Pulivendla Taluq of the Cuddapah district there are over 30,000 tons of barytes in the first 20 ft. of depth. The Mutssukota deposit may contain 75,000 tons. Four veins have been found near Nerijamupalle in Anantapur the largest of which is from 3 to 11 ft. wide and has been traced for more than half a mile along its strike.

Barytes has been mined in the Alwar State of Rajputana since 1921, the total output up to the end of 1932 being 14,302 tons. There are four separate deposits, the most important being situated four miles north by east of Parisal, where a vein of pure white mineral has been got.

It will thus be seen that we have extensive deposits of barytes in India, and it will be worth the while to examine the possibilities of obtaining sulphuric acid from this mineral. According to a patent granted to Mr. M. Kanakaratnam, sulphur dioxide is completely expelled by heating mixtures of bauxite and barytes in suitable proportions. The Brown Co. patented a process (U.S.P. 2,205,929) in which sulphuric acid and caustic soda are produced from barium sulphate and sodium sulphate as raw materials. Barium sulphate is reduced by carbon to barium sulphide which is treated with aqueous sodium sulphate to give a solution of sodium sulphide. This is then causticised with cupric oxide, using a method similar to that employed by Boguslvoski and his co-workers.

It has been reported that sulphur in considerable quantity can be had from Baluchistan and that pyrites occur in the Simla Hills and in the province of Bihar. Detailed information about these deposits is not, however, available; the possibility of recovery of sulphur from well-known sulphate deposits cannot therefore be ruled out of consideration.