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# MINERALS USEFUL TO CALIFORNIA AGRICULTURE

PREPARED UNDER THE DIRECTION OF  
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## CALIFORNIA SOURCES OF SULFUR AND SULFURIC ACID

BY JAMES W. VERNON

It is estimated that 125,000 tons of sulfur, elemental and combined, were added to California soils during 1948. Of this amount about 20,000 tons was elemental sulfur, the remainder being in compounds such as sulfuric acid, natural gypsum, aluminum sulfate, copper sulfate, and lime-sulfur. At present California's output of natural sulfur does not exceed 1,000 tons per year, Texas and Louisiana deposits supplying the bulk of the natural sulfur used in the state. Sulfuric acid is essential in the production of most of the manufactured sulfur compounds. Most of the sulfuric acid demands of California are met by acid plants in the state using for raw materials, elemental sulfur, sulfide minerals, and hydrogen sulfide obtained from oil refinery gases. Most of the gypsum used for agricultural purposes in California is produced from deposits in the state.

The only sulfur deposits that have been mined commercially in California in recent years are on the west slope of the Last Chance Range, Inyo County.<sup>1</sup> Here sulfur zones are in a series of limestone breccias, conglomerates, sandstone, and volcanics of Tertiary age. These occurrences are attributed to the oxidation of hydrogen sulfide gas, or its interaction with sulfur dioxide gas of volcanic origin. The hydrogen sulfide gas necessary for the reactions was derived from gypsum by the action of organic matter and carbonic acid waters. Some sulfur was deposited here by solfataric action. Lynton, in 1938, conservatively estimated the ore-in-sight in these deposits to be 253,000 tons containing 40.3 percent sulfur. Total reserves were believed to be approximately 2,500,000 tons of sulfur. Both surface and underground methods have been employed in mining Inyo County sulfur. Lack of water in this area has prevented the concentration of the sulfur ore, or the application of mining processes similar to those used at the Gulf Coast deposits which involve the use of large quantities of super-heated water.

Small quantities of sulfur have been obtained from gypsum deposits containing 3 to 7 percent sulfur in Imperial County. At the **Leviathan mine**, Alpine County, sulfur associated with copper represents a potential commercial source.

Most of the minor occurrences of sulfur in California are the result of solfataric action in the vicinity of recent volcanism, or sulfur associated with cinnabar in California's numerous quicksilver deposits. The Sulphur Bank deposits, Lake County, was originally mined for sulfur but it has been principally a quicksilver property.

Production of sulfuric acid in California is centered in the Los Angeles and San Francisco Bay areas. In the bay area, approximately 100,000 tons of pyrite from Shasta County mines are burned annually to produce sulfuric acid. The ores thus used average about 50 percent sulfur. Also, the smelting for metals of sulfide ores from California mines and those of nearby states provides additional material for the production of sulfuric acid.

Pyrite is an iron-sulfide mineral which is widespread in all kinds of rocks and commonly occurs as a gangue mineral in metallic ore deposits.

<sup>1</sup> Lynton, Edward D., Sulfur deposits of Inyo County, California: California Jour. Mines and Geology, vol. 34, pp. 563-589, 1938.



The pyrite being mined in Shasta County occurs as massive replacement deposits in intrusive bodies of alaskite porphyry. The pyrite deposits at the Hornet mine of the Mountain Copper Company, the principal producer, contain more than a million tons of ore averaging 50 percent sulfur. Pyrite is mined here by underground methods. Substantial amounts of pyrite were mined for its sulfur content from Alameda County deposits in the period 1891-1934. In Siskiyou County, large deposits of pyrite occur as irregular replacement bodies and as disseminated grains in a metamorphosed andesite.

Other smaller massive pyrite deposits are known in Mendocino and Santa Clara Counties. Massive sulfide deposits containing principally pyrrhotite, an iron sulfide mineral, in Orange, San Diego, and Trinity Counties also contain substantial reserves of combined sulfur. These deposits represent a potential commercial source of sulfur-bearing material. Small pyrite occurrences of mineralogical interest are known throughout California. Only the deposits of Shasta and Alameda Counties have been exploited for the sulfur in the pyrite.

Hydrogen sulfide gas evolved during petroleum refining is an important source of sulfur for the manufacture of sulfuric acid in Los Angeles and the San Francisco Bay area. The hydrogen sulfide gas is selectively absorbed from refinery gases by use of liquids such as sodium phenolate and diethanolamine. After stripping the hydrogen sulfide from the liquid, the gas is either burned to sulfur dioxide or converted to elemental sulfur.<sup>2</sup> The Hancock Chemical Company now recovers 50 tons of elemental sulfur per day from oil refinery hydrogen sulfide gas of its plant near Los Angeles.

The sulfur dioxide gas necessary for making sulfuric acid is obtained by burning elemental sulfur, roasting sulfide ores, and from burning hydrogen sulfide gas. Two general types of processes are used to produce sulfuric acid from sulfur dioxide; the nitration and the contact processes. The nitration processes involve the oxidation of sulfur dioxide by oxygen, nitric acid (or higher oxides of nitrogen) in the presence of water. The final reaction products are sulfuric acid and oxides of nitrogen. The contact processes oxidize sulfur dioxide to sulfur trioxide, utilizing platinum, a vanadium oxide, or a vanadium silicate as a catalyst. The sulfur trioxide is subsequently absorbed in concentrated sulfuric acid.

Elemental sulfur is used with calcium hydroxide in the preparation of lime-sulfur solution. The California plants that produce lime-sulfur solution are in Richmond, Port Chicago, El Segundo, and South Gate.

<sup>2</sup> New California plant makes sulfur from refinery gas: *Oil and Gas Jour.*, vol. 47, no. 51, p. 241, 1949.

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