floor and from one instrument panel. This is shown in Figure 4. The instruments consist of a temperature recorder, a vacuum and pressure gage for blower and absorber, integrating and recording flue gas flowmeter and steam flowmeter, rotameter for liquid flow control, and remote indicating tank level gages. The instruments also included two specially designed sulfur dioxide recorders, one for the head gas and one for the tail gas. This instrument was designed by Thomas, Ivie, and Fitt, of the American Smelting and Refining Company (*8*). These instruments record sulfur dioxide in the presence of carbon dioxide accurately and since the sinter gas at Selby contains a few per cent of carbon dioxide, the analysis of the gas for sulfur dioxide alone is important. Furthermore, the tail gas recorder records minute amounts of sulfur dioxide, and since the tail gas is in the range 0.05 to 0.06% sulfur dioxide this instrument is important for plant operation.

At present three plants are operating producing sulfur dioxide by using anhydrous dimethylaniline: one is the Falconbridge Nickel Company at Kristiansand, Norway; the second is the Selby unit of the American Smelting and Refining Company at Selby, Calif. (Figure 5); and the third, which went into operation a few months ago, is a duplicate of the Selby unit, built by the Tennessee Copper Company, Copperhill, Tenn., under license from Asarco. Several other plants of greater capacity are under consideration.

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Recovery of Sulfur Compounds from Atmospheric Contaminants

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The emission of sulfur compounds, recognized as major atmospheric contaminants, must be reduced as a matter of economics and in the interest of public welfare. Great strides have been made in the control of smelter smoke damage by scientific investigation of sulfur dioxide injury to plant life, and the application of remedial measures, which include use of high stacks and high temperatures for the discharge of waste gases, continuous automatic measurement of ground concentrations and application of meteorological control by accurate forecasting of critical weather conditions, and installation of recovery plants for conversion of excess sulfur dioxide to liquid sulfur dioxide, sulfuric acid, fertilizers, or elemental sulfur. The annual losses of sulfur from products discharged to the atmosphere from zinc plants, lead, copper, and nickel smelters, crude oil refineries, and from coal combustion, are compared with world native sulfur production and by-product sulfur recovery. The extent to which sulfur emission must be reduced, to avoid injury to plant life, is discussed in terms of the permissible levels of ground concentration. Methods for recovery of sulfur compounds from sulfur dioxide and hydrogen sulfide in stack gas include concentration of sulfur dioxide and its conversion to sulfuric acid, recovery as elemental sulfur, and flue gas disposal of the effluent and noneffluent types. New developments of outstanding importance for purification and recovery of sulfur dioxide are embodied in the Trail ammonia process, the dimethylaniline process at Selby, and flash smelting at Copper Cliff in conjunction with liquid sulfur dioxide recovery. An aroused public consciousness of the need of controlling atmospheric pollution has stimulated investigation in many contaminated areas. Sulfur contaminants may be profitably recovered in many industrial operations and thus clean up the air and add to native sulfur reserves, which are rapidly being depleted in the United States. More research is needed in industries confronted with difficult recovery problems—for example, nickel smelters. Cooperation between major native sulfur producers and companies with a large sulfur problem on their hands is desirable.

SULFUR compounds have been recognized as major atmospheric contaminants for many years in the metal smelting and oil refining industries, and in all operations involving the consumption of large quantities of sulfur-containing fuels such as coal. Enormous damage has been caused by the excessive emission and wastage of such products to agricultural and forest areas, and to materials such as metals, stone, cement, paint, paper, leather, and textiles. The annual losses from air pollution cannot be assessed accurately but, nevertheless, amount to many millions of dollars. If one considers that a substantial portion of the sulfur dioxide or hydrogen sulfide lost to the atmosphere may be economically recovered, the real magnitude of such losses and the importance of this problem become apparent.

Within the past 20 years a great scientific effort has been made in the United States, Canada, and elsewhere to determine the causes of air pollution and to develop technical methods of control. The effect of sulfur dioxide on plant life and metabolism, photosynthesis and respiration, and the factors affecting susceptibility have been evaluated with scientific accuracy. Considerable insight has been gained into the role of micrometeorology and the influence of topography on smog conditions accompanied by relatively high concentrations of sulfur dioxide and sulfuric acid mist. The worst fumigations have occurred during periods of temperature inversion. When there is insufficient mixing of the polluted air with fresh air by eddy diffusion, the polluted air spreads like a cloud or blanket over the industrial area and, being unable to diffuse vertically, may be confined within certain lateral limits by the surrounding topography. Although the effects of excessive pollution have been noted mainly on agricultural crops, retardation and killing of forest growth, excessive sulfates and acidity in soils, and corrosion of metals and deterioration of other structural materials, other aspects have affected the public welfare more generally.

The frequent occurrence of smog in densely populated areas accompanied by poor visibility, eye irritation, serious and costly traffic dislocation, and other factors adversely affecting human welfare, has created a widespread public consciousness of pollution and a demand to clean up the air. Two major disasters involving loss of life have been attributed to excessive air pollution with the specific blame placed on sulfur dioxide and sulfuric acid mist.

During a heavy fog of 5 days' duration in the valley of the Meuse River, between Liége and Huy, in December 1930, seventy persons died and several hundred suffered severe respiratory disorders. The symptoms of distress became evident, generally, on the third day of the smog, as it approached maximum density, and disappeared when the fog lifted. Unusual meteorological conditions resulted in a temperature inversion which created an atmospheric ceiling lower than the hills (75 to 100 meters high) bordering this valley. The air was almost motionless, except for a feeble wind from the direction of the Liége industrial area which caused a slow drift of fumes into this narrow bottleneck valley, only about 1 kilometer wide.

It was concluded by the investigating commission that sulfur compounds, emitted mainly from the combustion of coal and existing in the air as sulfur dioxide, sulfurous acid, or sulfuric acid, caused this disaster (*13*, *43*). By calculation, the maximum sulfur dioxide concentration that could have been reached, after the first day of fog, was about 9 p.p.m., and after 4 days, about 35 p.p.m.

A similar smog disaster occurred at two small adjacent communities, Donora and Webster, Pa., in 1948. For about 5 days, beginning October 27, an unusual temperature inversion and still air caused a steady build-up of atmospheric contaminants from zinc smelting, steel and wire industries, railroads, river steamboats, and homes. By October 30 illnesses and fatalities began to mount rapidly. The final toll was at least 20 deaths and 5910 cases of sickness, about 43% of the population being involved. The predominant symptom was an irritation of the respiratory tract, which was especially severe in elderly persons. The dead ranged in age from 52 to 85 years, with a mean of 65.

A well planned and thorough investigation by the United States Public Health Service (*53*) was conducted in cooperation with local and state authorities and consultants of industrial companies. It was concluded that the trouble could have been produced by a combination of several contaminants, chief among which was sulfur dioxide and its oxidation products. Near a zinc smelting plant there was a 5-mile area where tree growth had been devastated by past excessive ground concentrations of sulfur dioxide. Other possible contaminants which were studied were oxides of nitrogen, fluorides, chlorides, hydrogen sulfide, cadmium oxide, and other particulate effluents.

The Donora episode highlighted the need for further research into the whole field of air pollution. Smog investigations have been commenced within the past few years in a considerable number of cities and industrial areas in the United States, such as Los Angeles, Pittsburgh, Whiting, Ind., and Charleston, W. Va. In 1949 the problem of pollution in the international area of the Detroit river was referred to the International Joint Commission and an advisory board of three scientists from Canada and three from the United States created to supervise the investigation. The United States and Canadian chairmen of this board are G. D. Clayton and Morris Katz, respectively.

The lessons gained from atmospheric pollution studies in cities and smelter areas indicate that the emission of sulfur compounds must be reduced, not only as a matter of economics, but also in the interest of public welfare. Sulfur dioxide, and especially sulfuric acid mist, give rise to a tremendous number of condensation nuclei in the air. These nuclei, because of their hygroscopic nature, transform the water vapor in the air to minute droplets, which play a very important role in promoting smog conditions (*44*). However, it is not necessary or desirable to remove sulfur entirely from the air. It is only necessary to reduce the emission by appropriate remedial measures, intelligent plant operation, and meteorological control to the point where injurious ground fumigations do not occur. In low concentrations, sulfur dioxide is nontoxic to plant life and may even exert a beneficial effect by free fertilization of the soil, especially in sulfur-deficient soil areas (*1*, *29*, *30*, *54*, *59*, *63*).

NATIVE SULFUR PRODUCTION AND ESTIMATED SULFUR LOSSES

The production of brimstone in the United States from salt domes by the Frasch process has increased considerably within the past 5 years and commercial reserves of such deposits, at present, have an estimated life of about 25 years (*64*). The trend in world production of native sulfur is shown in Table I. It is now of the order of 5,000,000 long tons annually, most of it produced in the United States. The rapid growth in demand for elemental sulfur is due to the mounting needs for sulfuric acid in the fertilizer, chemical manufacturing, and petroleum refining industries. This continued growth spurs the search for new sources of sulfur.

Table I. World Native Sulfur Production, Long Tons

Year	U. S. Production (*64*)	World[a] Production (*64*)	U. S. Crude Exports (*64*)	U. S. Consumption (*10*)	Canadian[b] Consumption (*8*)
1937	2,741,970	3,300,000	644,005	1,800,000	...
1939	2,090,979	2,700,000	627,814	1,595,000	...
1941	3,139,253	3,700,000	729,464	2,239,000	253,004
1943	2,538,786	3,000,000	654,393	2,532,000	281,280
1945	3,753,188	4,100,000	918,691	2,961,000	266,013
1946	3,859,642	4,200,000	1,189,072	2,907,000	...
1947	4,441,214	4,800,000	1,299,060	3,540,000	...

[a] Estimated.
[b] Short tons.

One principal source is the recovery of a substantial amount of the sulfur emitted to the atmosphere as sulfur dioxide and hydrogen sulfide pollutants. The amount available annually from this source is much greater than present world native production and that from pyrites combined. The estimated annual emission to the air from smelting operations, oil refining, and coal consump-

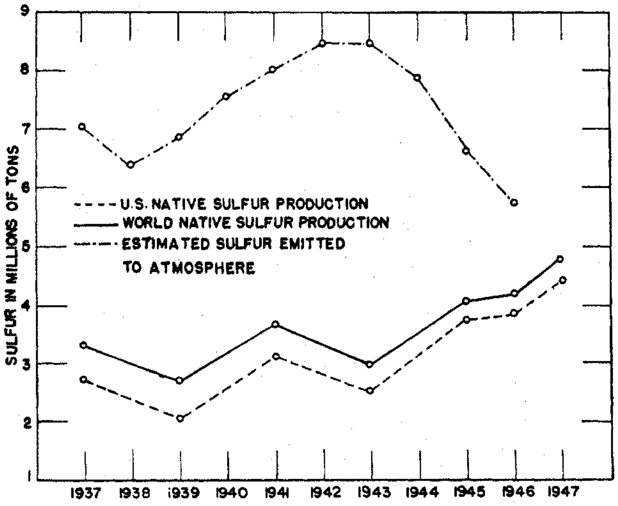

Figure 1. Native Sulfur Production and Estimated Sulfur Loss to Atmosphere from Zinc Plants and Lead, Copper, and Nickel Smelters

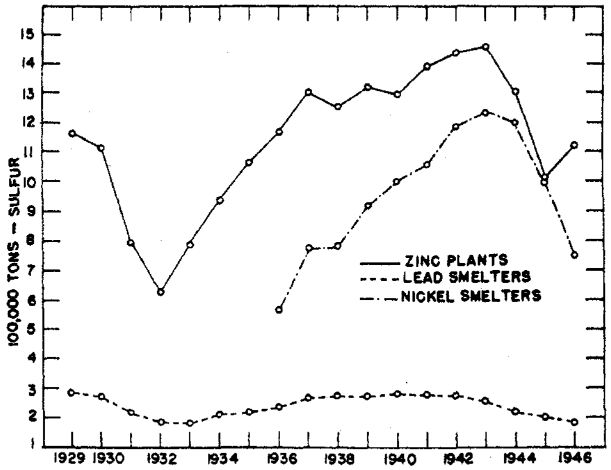

Figure 2. Estimated Sulfur Emitted to Atmosphere Annually from Zinc Plants and Lead and Nickel Smelters

tion is shown in Table II. Most of the sulfur dioxide from zinc, copper, and lead smelters can be readily recovered as sulfuric acid. Hydrogen sulfide from oil and natural gas can also be recovered as elemental sulfur or sulfuric acid. A great deal of the sulfur in coal will be wasted to the air for many years to come because of economic factors. However, in many cases, the stack gases from power plants may be utilized to recover sulfuric acid.

As native sulfur deposits become depleted, the sulfur industry must turn more and more to that available from by-products as well as pyrites. Large tonnages of pyrites and pyrrhotite are removed as flotation concentrates during the milling of copper, nickel, and zinc ores. In coal mining operations a considerable quantity of pyrites (coal brasses) may be recovered as a by-product of coal washing. Many gold mines have large deposits or available supplies of pyrites. In Canada, Noranda Mines, Ltd., has a deposit of several hundred million tons of pyrite ore from which production of elemental sulfur and iron sinter on a pilot plant scale was commenced in December 1947 (*64*).

BY-PRODUCT SULFUR RECOVERY

The recovery of by-product sulfur dioxide in the smelting industry has been closely linked with efforts to control and eliminate excessive atmospheric pollution. An outstanding example is the large lead-zinc smelter at Trail in British Columbia (*30*). Stack emission of sulfur rose from about 4700 tons per month in 1924 to 9000 in 1926, and to nearly 10,000 in 1930. However, remedial measures introduced in 1930 and expanded in subsequent years resulted in conversion of increasing amounts of sulfur dioxide in the stack gas to sulfuric acid, fertilizers, and elemental sulfur, as shown in Table III.

In the United States about 700,000 to 950,000 short tons of by-product sulfuric acid were produced annually at copper and zinc smelters from 1943 to 1948 (Table IV). This represents about 10 to 15% of the total acid manufactured annually. Canadian production of acid increased from 250,000 tons in 1939 to 722,000 tons in 1944, and decreased to 637,000 tons in 1946. About two thirds of this production represents the by-product recovery of acid from smelter fumes, mainly from Trail, B. C. About 50,000 tons of sulfuric acid are recovered annually from stack gas in nickel-copper smelting at Copper Cliff, Ontario. However, the potential amount of acid that could be manufactured from smelter fumes in these nickel-copper operations in Northern Ontario, if it were possible to do so on an economic basis, is greater than the present total by-product acid production of the zinc and copper smelters in the United States.

The sulfuric acid produced in Great Britain in recent years from various raw materials is shown in Table V. The sulfur recovered in the form of spent oxide would be close to 100,000 tons annually. In Germany, before the war, about 70,000 long tons of sulfur were recovered annually from gasoline hydrogenation plants and from manufactured gas. There are a number of small plants utilizing waste gases from zinc smelters in Latin America—one in Mexico, at least one in Brazil, and three in the Argentine.

Table II. Estimated Sulfur Emitted to Atmosphere Annually (*64*), Metric Tons

Year	Zinc Plant	Lead Smelters	Copper Smelters	Nickel Smelters	Crude Oil	Coal
1929	1,161,100	286,000	3,808,000	...	...	...
1930	1,116,000	271,000	3,148,000	...	...	...
1931	797,000	222,000	2,756,000	...	...	...
1932	625,000	186,000	1,864,000	...	2,621,000	16,880,000
1933	790,000	185,000	2,074,000	...	2,882,000	17,790,000
1934	938,000	211,000	2,628,000	...	3,043,000	19,280,000
1935	1,065,000	221,000	3,056,000	...	3,309,000	19,850,000
1936	1,172,000	237,000	3,439,000	566,000	3,604,000	21,800,000
1937	1,300,000	269,000	4,690,000	776,000	4,078,000	23,250,000
1938	1,252,000	272,000	4,076,000	782,000	3,976,000	22,000,000
1939	1,320,000	277,000	4,348,000	922,000	4,171,000	24,650,000
1940	1,297,000	283,000	4,961,000	1,008,000	4,284,000	26,980,000
1941	1,399,000	276,000	5,270,000	1,060,000	4,441,000	27,800,000
1942	1,440,000	273,000	5,581,000	1,192,000	4,186,000	28,250,000
1943	1,462,000	252,000	5,512,000	1,238,000	4,513,000	25,700,000
1944	1,300,000	218,000	5,158,000	1,199,000	5,182,000	...
1945	1,019,000	200,000	4,400,000	999,000	5,189,000	...
1946	1,123,000	187,000	3,670,000	749,000	5,500,000	

Assumptions.
Zn content of concentrates 50%, S content 40%.
Pb content of concentrates 70-80%; ratio of S to Pb taken as 0.16.
Cu content of concentrates 22%, S content 45%.
Ni data obtained from (*46*, p. 35).
Crude oil, specific gravity 0.8–1.0, assumed weight per barrel 300 lb., average S content 1.5%
Coal, conservative estimate of average S content 1.5%.

By-product sulfur obtained from coke-oven, refinery, natural gas, and other industrial gases in the United States as brimstone, sludge, and paste amounted to 34,900 long tons in 1946, 43,427 in 1947, and 44,369 in 1948 (calculated as 100% sulfur). In the same years the quantity of sulfur contained in hydrogen sulfide recovered from hydrocarbon gases by various processes was 18,366, 20,631, and 25,792 long tons, respectively. It is probable that production of such by-product sulfur will be increased considerably in the future in the United States and elsewhere by the erection of many small units of less than 50 tons' daily capacity. Such units are economical to build and operate, and also meet the demand to remove objectionable pollutants near large centers of population (*21*).

Table III. Sulfur Recovered from Sulfur Dioxide at Trail Smelter (*47*) as 100% Sulfuric Acid, Fertilizers, and Sulfur, Short Tons

Year	100% H_2SO_4	Ammonium Sulfate	Other Fertilizers	Sulfur	Sulfur Content[a] of H_2SO_4
1930	8,501	...	...	...	2,775
1931	36,170	6,485	18,571	...	11,811
1932	73,038	46,721	14,420	...	23,850
1933	64,219	65,810	3,058	...	20,980
1934	95,434	55,780	26,717	...	31,150
1935	120,245	42,949	37,697	543	39,300
1936	126,578	71,630	26,429	3,464	41,300
1937	132,194	57,832	44,221	13,533	43,200
			Sulfur and Fertilizer (*11*)		
1938	134,469		170,108		43,908
1939	130,445		178,399		42,594
1940	148,478		188,478		48,483
1941	189,082		176,379		61,801
1942	193,341		205,315		63,132
1943	269,394		283,572		87,965
1944	331,718		327,232		108,316
1945	376,459		369,666		122,925
1946	375,595		484,720		122,633

[a] Calculated.

PERMISSIBLE LIMITS OF SULFUR COMPOUNDS IN STACK GAS AND ATMOSPHERE

The extent of the recovery steps which must be undertaken to eliminate damage from air pollution will depend among other factors upon the toxicity of the particular type of sulfur compound involved to plant and animal life. In many city and industrial areas, regulations have been set up to limit the discharge of sulfur dioxide, sulfuric acid, and hydrogen sulfide in terms of stack concentration or mass rate of emission. Although there is some uniformity in such regulations from one locality to another, special topographical or meteorological features may render it necessary to impose more severe restrictions than would be advisable if the offending operations were carried on in a region of open terrain with good dispersion of the effluents into the surrounding air. Thus, in the Trail smelter case, the narrow Columbia River valley with its mountain ranges over 3000 feet high served to confine the smelter fumes without adequate mixing, even though they were emitted mainly from 400-foot stacks (*29*). Similarly, in the Los Angeles area, the frequent occurrence of prolonged temperature inversions interfered with effective dispersion of industrial effluents and necessitated severe restrictions to curb the air pollution nuisance (*20*, *39*, *40*).

In the case of many smelters in the United States, restrictions, with respect to the emission of sulfur dioxide, stipulate that the gases should be discharged from as high a stack as is practicable, and the concentration in the stack gas should not exceed 0.75% by volume. It may be further stipulated that smelting operations should be so conducted during the growing season that no damage to vegetation would result. Probably the first precedent for the setting of limits of sulfur dioxide discharge, in terms of ground level concentration and duration, was established by Swain in his investigation of damage from operations of two smelting companies in the Salt Lake district in Utah in 1920 (*57*). A regime was imposed, which, among other provisions, indicated that the discharge of sulfur dioxide during the growing season should be so regulated that at the level of vegetation it should not exceed a concentration of 1 p.p.m. for an hourly average.

In Canada, the smelter at Trail, after prolonged litigation and investigation in proceedings first before the International Joint Commission and later before an International Arbitral Tribunal, was placed under a regime which not only set the maximum permissible discharge in tons per hour, under certain weather conditions, but also restricted the emission in terms of ground concentration and duration (*12*).

Some smelters in the United States have for many years operated a weather plan of avoiding injury to agricultural crops during the growing season by closing down part of the roasters and thus reducing stack emission during periods of calms or temperature inversion (*24*).

In England the emission of sulfur compounds from smelters and sulfuric acid works is governed by the Alkali, etc., Works Regulation Act of 1906. The total acidity of tail gases is restricted to 4 grains of sulfur trioxide per cubic foot before admixture with air, smoke, or other gases.

The first case in history where sulfur emission control in a coal-burning plant was set as a prerequisite to its erection, was the Battersea Station of the London Power Company in 1927. The government had sanctioned the erection of this plant without sulfur restrictions until a protest was made by municipal authorities. The plant disposes of 1,500,000 cubic feet of gas per minute with an initial sulfur dioxide concentration of 0.02 to 0.05%, of which 90 to 92% is extracted by a scrubbing process (*22*).

The trend of modern requirements in urban districts in England is the installation of scrubbing processes for the reduction of sulfur dioxide in the stack gas of power plants to yield an exit concentration of about 50 p.p.m.

Relatively strict standards recently set for Los Angeles County require that no solid discharge shall be in excess of 0.40 grain per cubic foot of gas. Standards in this county have also been set up in terms of the per cent of process weight per hour which can be emitted to the atmosphere, with a top limit of 40 pounds per hour from any one stack, regardless of the process weight involved. The regulations are based on the assumption that the mass rate of emission is the controlling factor in air pollution, the dilution factor being considered unnecessary in control standards. It is, therefore, impossible to meet such air pollution regulations by dilution of stack gases with air. For each plant, these regulations allow a definite emission in terms of per cent of process weight per hour based on a dust collection efficiency of 80% for small industries and 90% for large ones until the above ceiling is reached. It is also provided that the emission of sulfur compounds calculated as sulfur dioxide shall not exceed 0.20% by volume (2000 p.p.m.) in the stack gas (*40*).

The effects of sulfur dioxide on sensitive plant species have been under investigation for many years. In the range of concentrations up to 0.10 to 0.20 p.p.m. there is no adverse influence on growth after prolonged fumigation. Many susceptible plants will tolerate such concentrations indefinitely. In fact, such mild fumigations may have a beneficial effect by supplying sulfur which is an essential element for growth. Injurious effects are usually associated with exposures of sufficient duration to concentrations above 0.25 p.p.m. and, in particular, to those above 0.40 p.p.m., in the growing season. The investigations of Katz and associates (*29*, *30*), Thomas and Hill (*23*, *63*), Swain (*59*), and Setterstrom, Zimmerman, and Crocker (*54*) have determined the permissible level of ground concentrations which may be utilized in control measures. It is probable that no other atmospheric contaminant has been evaluated with such scientific accuracy.

Because green plants are much more sensitive to sulfur dioxide than man or animals, operational measures in industry which result in the virtual elimination of damage to vegetation will also avert any hazard to human health and welfare. The permissible concentrations for man for prolonged exposure have been set at about 10 p.p.m. for sulfur dioxide, 1 p.p.m. for sulfur trioxide, 2 to 10 p.p.m. for sulfuric acid, and 20 p.p.m. for hydrogen sulfide (*49*).

Hydrogen sulfide is only slightly toxic to plant tissue in com-

Table IV. By-Product Sulfuric Acid (Basis 100%) Produced at Copper, Zinc, and Lead Plants in United States, Short Tons

	1943	1944	1945	1946	1947	1948[a]
Copper plants[b]	270,938	248,988	231,697	126,494	126,494	...
Zinc plants	682,926	652,001	610,938	544,529	598,703	...
Total	953,864	900,989	842,635	716,216	725,197	730,000

[a] Estimated.
[b] Includes sulfuric acid produced as by-product at lead smelter.

Source (*64*), preprint.

Table V. Sulfuric Acid Produced in Great Britain and Raw Materials Used (*9*)

	1945[a]	1946	1947	1948	1949[b]
Chamber acid	323,104	721,585	684,083	762,038	396,769
Contact acid	274,965	657,609	695,002	839,400	455,162
Total	598,069	1,379,194	1,379,085	1,601,438	851,931
Pyrites[c]	139,636	312,697	286,237	336,758	175,101
Spent oxide	94,700	191,346	181,447	197,758	97,785
Sulfur and H_2S	78,569	202,051	218,943	267,003	147,708
Zinc concentrates	78,761	163,195	163,013	149,321	75,891

[a] Last 6 months.
[b] First 6 months.
[c] Includes anhydrite "converted" to pyrites.

Acid figures given in short tons, 100% basis.
Raw materials, short tons.

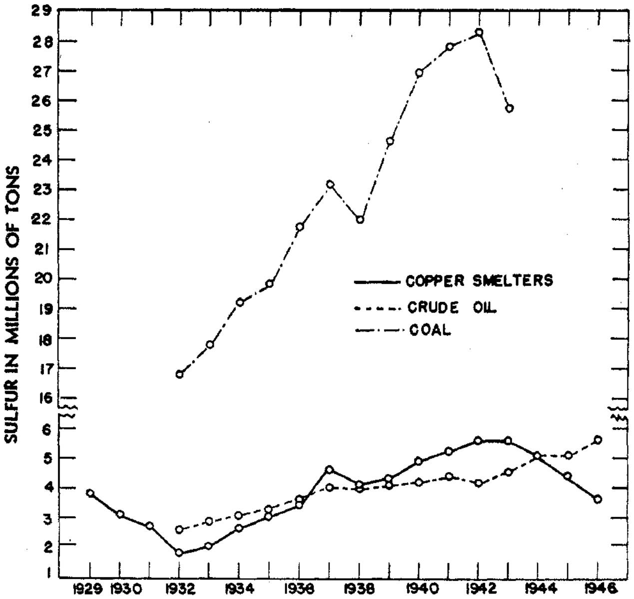

Figure 3. Estimated Sulfur Emitted to Atmosphere Annually from Copper Smelters, Crude Oil Refining, and Combustion of Coal

parison with many other gases, but is more toxic to animals. For this reason, injury to vegetation from hydrogen sulfide is very seldom encountered in the field, except in the vicinity of some refineries using "sour" crudes. Experiments at the Boyce Thompson Institute indicate the following order of toxicity of hydrogen sulfide and sulfur dioxide to classes of organisms: fungi and bacteria, $SO_2 > H_2S$; seeds and sclerotia, $SO_2 > H_2S$; green stems, no difference; animals, $H_2S > SO_2$ (*41*). The characteristic odor of hydrogen sulfide is detectable in concentrations as low as 0.025 p.p.m., is distinct at 0.30 p.p.m., and becomes offensive at 3 to 5 p.p.m. (*49*). Sulfur dioxide may be detected by taste at about 0.3 p.p.m. and by odor at 3 p.p.m.

GENERAL CONTROL MEASURES FOR SULFUR POLLUTION

The use of high stacks to disperse injurious concentrations of sulfur dioxide was one of the earliest methods of control adopted in smelting areas. This was coupled with heating of the waste gases by adding hot boiler gases or by placing a coal-burning stack heater at the base of the stack. In addition, injurious fumigations in the Salt Lake smelting district were often avoided in the growing season during periods of critical weather, when high humidity, temperature, light, and wind conditions were conducive to rapid absorption of sulfur dioxide by growing plants, through the operation of a "sea-captain" plan by which the roasters were shut down until conditions had become less critical (*58*). The dispersal of injurious fumes through high stacks is now accepted practice.

At Ducktown, Tenn., the sulfur dioxide damage problem from copper smelting operations was solved by the adaptation of the lead chamber process to convert the waste gas to 1000 tons of sulfuric acid daily, and ultimately, to produce much needed fertilizer in the phosphate plants of the South. Tall stacks alone could not solve the problem (*58*).

At Trail, B. C., all possible measures to control pollution of the air are in use. The emission of sulfur dioxide is curtailed, when required, by shutting down part or all of the roasters during critical weather conditions forecast many hours in advance. Other control measures consist of concentration of sulfur dioxide in zinc and lead roaster gases for acid manufacture, use of high stacks, the extensive use of electrostatic precipitators, and the continuous recording of ground level concentrations at three fixed stations (*12*, *30*).

In the United States, many by-product plants have been erected in the smelting and oil refining industries, primarily to avoid air contamination problems. The emission of sulfur dioxide or hydrogen sulfide is curtailed by conversion of a part of the waste gas to brimstone and sulfuric acid. The practice of burning hydrogen sulfide to sulfur dioxide mitigates an odor nuisance but may create a damage problem to plant life by converting a less toxic gas into a more toxic one.

In England, in addition to the control measures under the Alkali Act in heavy industry, power stations are under restrictions to control sulfur and grit emission by both effluent and noneffluent removal processes.

RESEARCH IN SULFUR POLLUTION CONTROL

There is hardly a more effective way of illustrating the importance of research, as applied to industry, than to describe its role in the elucidation of smelter smoke damage and its subsequent elimination through successful measures. The first milestone was reached in the report of the Selby Smelter Commission in 1915 (*25*). This classical investigation resulted in the development of the first accurate method of determining low concentrations of sulfur dioxide in air, and in a new method for the controlled fumigation of crop plants in experimental cabinets. Such factors as gas concentration and duration, humidity, temperature, soil moisture, and light were investigated and the effects of fumigation of varying intensity on yield of crop were determined.

The above work was continued in investigations by O'Gara (*45*), Hill and Thomas *et al.* (*23*, *24*, *60–63*), in a broad program of research sponsored by the American Smelting and Refining Company near Salt Lake City. They have contributed numerous papers of high quality on the effects of sulfur dioxide on plants and developed new techniques and apparatus. Among these may be listed the Thomas automatic recorder for the continuous measurement of sulfur dioxide and sulfur compounds in air, the effect of tall stacks and high temperatures on the dilution and dispersion of smelter gases, and the effects of sulfur dioxide on yield, photosynthesis, and respiration.

The research staff of the Boyce Thompson Institute has, for many years, studied in an admirable manner the effects of various gases on plants in greenhouse investigations. Their contributions include studies of the effects of not only sulfur dioxide, but also hydrogen sulfide, ammonia, chlorine, carbon monoxide, and ethylene (*41*, *54*).

The international scope of the Trail smelter problem led to comprehensive and noteworthy investigations by the National Research Council of Canada into nearly all aspects of the smelter fume problem, including the concentration and distribution of sulfur dioxide in the Columbia River valley, its effects on crop plants, tree growth, and soils; and the investigation under carefully controlled conditions of the invisible injury theory, the determination of the effects of low concentrations on photosynthesis and stomatal movement, crop yield and chemical constituents of plants, and influence of environmental factors on susceptibility (*29*, *30*).

The studies by the above groups of investigators have demonstrated that (1) sulfur dioxide does not cause invisible injury; (2) that concentrations between 0.10 to 0.20 p.p.m. may be present continuously throughout the growth of crop of a susceptible plant species, without affecting the yield, photosynthesis, or quality; (3) that only the higher concentrations, in particular those above 0.40 to 0.50 p.p.m., are injurious if the duration is prolonged sufficiently; (4) that the growth of sulfur-deficient plants may be stimulated by the presence of low concentrations of sulfur dioxide in the air; and (5) that wherever such high concentrations have been eliminated in the field, by the operation of control measures involving the use of high stacks and high temperatures for the discharge of waste gases, the installation of recovery plants to reduce the output of waste sulfur gases, or the utilization of meteorological control, no further damage to plant life has occurred.

RECOVERY OF SULFUR DIOXIDE

Many processes have been developed to recover sulfur dioxide from waste gases resulting from such operations as the roasting of sulfide ores, smelting of ores, combustion of coal in power stations, and the burning of acid sludge from petroleum refining. The possible products are liquid sulfur dioxide, elemental sulfur, and sulfuric acid.

CONCENTRATION OF SULFUR DIOXIDE

When sulfur dioxide is to be recovered from dilute gases it is usually necessary or desirable to concentrate the sulfur dioxide to substantially 100%. The gas is absorbed at atmospheric temperature by a suitable absorbing agent, and regenerated by heating the rich absorbant to 100° to 105° C. The moist sulfur dioxide is cooled, dried with sulfuric acid and liquefied, reduced to elemental sulfur, or oxidized to form sulfuric acid. The stripped absorbent is cooled and recycled.

HAENISCH-SCHROEDER PROCESS

The earliest of these processes, the Haenisch-Schroeder process, developed in 1884, employed water as the absorbant (*19*). Lead plate scrubbers and heat interchange for sulfur dioxide absorption were features of the process. Modifications are still in use in about nine plants in the United States producing about 20,000 to 40,000 tons of liquid sulfur dioxide per year. The raw material is brimstone, the sulfur dioxide content of the gas is about 15%, and that of the rich absorbant is 1 to 2%. From 100 to 200 tons of water are required per ton of sulfur and the cost of the sulfur dioxide produced is relatively high. This process is not suitable for the recovery of sulfur dioxide from waste gases because of the large volume of water required, the bulky equipment needed, and the heat losses involved in stripping.

I.C.I.-BASIC ALUMINUM SULFATE PROCESS

The basic aluminum sulfate process developed by Imperial Chemical Industries in England enjoyed a limited success (*56*). A pilot plant capable of producing 20 tons of sulfur dioxide per day was operated intermittently at Billingham before the war. The first commercial plant was put into operation at the Outukumpu Oy copper smelter at Imatra, Finland, in the spring of 1936 and ran for 5 years. Converter gases containing an average of 5% sulfur dioxide were treated in a plant of 52 tons' per day capacity. During the war, the smelter was moved to Western Finland by order of the military authorities, the sulfur dioxide plant dismantled, and the process changed to sulfuric acid production because of increased demand (*3*). The only present plant using this process is that operated by Hardman and Holden, Manchester, England, at a rate of 7 to 8 tons of liquid sulfur dioxide per day (*48*).

The absorbant solution contains 9 to 10 grams of total alumina per 100 ml. prepared by treating a solution of aluminum sulfate with limestone and filtering off the gypsum formed. Phosphoric acid in the amount of 0.6 gram of phosphorus pentoxide per 100 ml. is added to inhibit the formation in the regeneration boiler of a white crystalline precipitate having the approximate composition $Al_2O_3.SO_3.3.5H_2O$. When seed crystals are present, rapid deposition occurs at 100° C. but other basic sulfates and dust have no apparent seeding effect. In practice it was possible to avoid formation of insoluble basic aluminum sulfate by suitable design of the regeneration boiler.

About 1 to 1.5% of the absorbed sulfur dioxide becomes oxidized to sulfur trioxide, depending to some extent on the oxygen content of the gas. This oxidation can be depressed, the best inhibitor being methylene blue. Losses of inhibitor by adsorption on the tower packing and in the gypsum were considered excessive for commercial use. In practice, a side stream of the regenerated absorbant solution is treated with limestone and the gypsum filtered off to control the sulfate content of the solution. Water used to cool the regenerated sulfur dioxide before drying contains dissolved gas and this is used to wash the filter cake to reduce losses of alumina.

To prevent precipitation of elemental sulfur, the oxidizable sulfur content of the absorbing solution is determined on a routine basis. When it exceeds 0.1 gram per 100 ml., part of the absorbant is treated with a solution of copper sulfate at 95° to 100° C. for 2 hours and the precipitated copper sulfide is filtered off (*3*). From a theoretical study of the hydrolytic equilibria involved, Johnstone considered that a solution of basic aluminum sulfate is not suitable for gases containing less than 1% of sulfur dioxide (*27*). The sulfur dioxide content of the tail gas is 0.2% or less and for a 5% gas, the theoretical efficiency of recovery is 94.5%.

AMINE PROCESSES

Much work on the use of aromatic amines as absorbants for sulfur dioxide has been carried out both in this country and in Germany. Roberson and Marks (*52*) have studied diethylenetriamine, triethyltetramine, ethylamine, and diethanolamine. Boswell (*5–7*) patented the use of a mixture of one of the substances pyridine, quinoline, isoquinoline, acridine, aniline, *p*-toluidine, xylidine, or triethanolamine mixed with one of the following—lactic acid, citric acid, glycerol, ethylene glycol, diethylene glycol, and resorcinol in contact with water.

The "sulfidine" process (*66*), developed in Germany, makes use of a suspension of xylidine or toluidine in water as the absorbant. Commercial plants were built at the Norddeutsche Affinerie in Hamburg and at Wolfen, Germany, now in the Russian zone. Only part of the Wolfen plant was in operation after the war and its present status is not known. The process was investigated on a pilot plant scale by Fleming and Fitt (*14*), but discarded in favor of their dimethylaniline process for both technical and economic reasons.

As sulfur dioxide is absorbed by a 1 to 1 suspension of water in xylidine, the xylidine sulfite tends to dissolve. When the sulfur dioxide content is more than 100 grams per liter the absorbant becomes homogeneous. The absorbing capacity of a 1 to 1 xylidine-water mixture at 20° to 25° C. is 200 grams per liter for a 5% gas and 220 grams per liter for an 8% gas. In practice sufficient absorbant solution is used so that 130 to 180 grams of sulfur dioxide per liter are absorbed. The sulfur dioxide content of the tail gas is reduced to 0.05 to 0.10%.

In operation the waste gases leaving the last absorption tower contain appreciable amounts of xylidine, which is recovered by washing the gas with 4 to 5% sulfuric acid to form xylidine sulfate in a wash tower. About 1% of the sulfur dioxide absorbed in the absorption tower is oxidized to sulfur trioxide and because the oxidation is autocatalytic the sulfate must be removed. At Wolfen, part of the absorption water is removed continuously and part of the dilute sulfuric acid from the wash tower is also taken. The mixture is heated by indirect steam to 80° to 100° C. and 50% caustic soda is added to neutralize the acid. The hot solution is distilled until the salt concentration is 70 to 80% and then discarded. The mixture of distilled steam and xylidine is condensed and run through a water separator and the xylidine is returned to the system. The water phase is used to prepare a 7% caustic soda solution, which is added to the absorption liquor to decrease oxidation of the sulfite which is increased at higher acidities.

Wiedmann and Roesner (*66*) described the addition of sodium carbonate or sodium sulfite in aqueous solution to the absorbant, either after regeneration at temperatures above 50° C. or during the absorption. Part of the sulfate liquor is drawn off and replaced by fresh water or sodium carbonate solution. The liquor withdrawn is saturated with xylidine which is lost.

In pilot plant work, it was shown that oxidation of the sulfite can result in curdling or souring of the absorbant solution, in which case the whole plant has to be shut down and the equipment and solutions cleaned up, with consequent high reagent losses.

The dimethylaniline process described by Fleming and Fitt (*15*) is of considerable interest and may come into widespread use because of the simplicity of operation, the small space requirements, and the economy of materials. The advantages of the process result from the properties of the absorbant, anhydrous dimethylaniline, and from the design of equipment.

The soda ash solution required to treat the dimethylaniline sulfate produced by oxidation and by scrubbing the tail gases with dilute sulfuric acid to recover escaping dimethylaniline vapors is added in a section of the bubble cap absorption tower, thus improving the removal of sulfur dioxide.

The dimethylaniline is continually purified by distillation and stripping, and there is little chance for the absorbant to become soured. By separating off the dimethylaniline before sending the water phase to the regenerator, the steam consumption is reduced. Elimination of aqueous sodium sulfate at the bottom of the regenerator reduces losses of dimethylaniline.

The consumption of process materials is smaller than for the basic aluminum sulfate or sulphidine processes and the oxidation of sulfite to sulfate is less. The sulfur dioxide content of the tail gas is reduced to 0.05%.

AMMONIA PROCESSES

Perhaps the best known process for removal of sulfur dioxide from smelter gases is that developed at Trail (*46*), where substantially 100% gas is recovered from 1% zinc roaster gases through the use of 30% aqua ammonia as the absorbant. Essentially this recovery is a step in the manufacture of ammonium sulfate and the sulfur dioxide is used to increase the capacity of the sulfuric acid plants. The availability of cheap power and of supplies of phosphate rock in Montana has enabled the Trail smelter to build an extensive fertilizer industry.

The use of ammonia as an absorbant for sulfur dioxide by the Guggenheim process (*14*) was investigated at Garfield, Utah, in a 10-ton-per-day pilot plant of stainless steel construction. Numerous corrosion problems arose from the autoxidation of the reaction products to give free sulfuric acid, thionic acids, and free sulfur. Sulfur dioxide was recovered from the ammonium bisulfite solution by heating. The ammonia used was relatively expensive and oxidation of sulfite to sulfate, which was extensive, constituted a loss.

Johnstone (*26*, *27*) has published data on partial vapor pressures over solutions of ammonia, sulfur dioxide, water, and other salts. At Trail, the residual sulfur dioxide content of the exit gases is 0.15 to 0.20%. The sulfur dioxide content can be further reduced, but losses of ammonia to the stack are increased and a fog of finely divided ammonium sulfite particles may be formed. The main operating control in the absorption towers is by pH measurement.

DIRECT COMPRESSION

Recovery of sulfur dioxide by compression and liquefaction is of interest. At Tacoma (*14*) a pilot plant of 1-ton-per-day capacity was built in 1927 to utilize 7% gas from a copper converter. The gas was stored in a holder and only about 50% was rich enough to send to the holder. High power costs made the process uneconomic and, in addition, there was almost 1% sulfur dioxide left in the tail gas.

Recently the development of a flash smelting process at Copper Cliff has made possible the by-product production of a gas containing 70% or more sulfur dioxide (*42*). A pilot plant to produce 5 tons per day of liquid sulfur dioxide was operated by Canadian Industries Limited from June 1947 to November 1948.

In this plant the gas was cooled in a water scrubber and some dust was removed. The remaining dust was removed in a Cottrell precipitator and the gas was dried in a packed tower through which sulfuric acid was circulated. Ninety-eight per cent sulfuric acid was added to the tower and 93% acid was withdrawn for sale. The dry gas which contained 80% sulfur dioxide was compressed to 120 pounds per square inch gage in a single-stage reciprocating compressor and then cooled in a water cooler. Liquid sulfur dioxide was discharged to storage. A second stage in which the gas was cooled to 14° F. by boiling sulfur dioxide was used in the pilot plant, but will probably not be used in a full scale plant. Exit gases were diverted to the inlet flue of Canadian Industries' sulfuric acid plant.

It is expected that the first flash smelting unit will go into operation late in 1950. The gas from this unit will all be used to produce sulfuric acid. If operation of the first unit is successful and if economic studies dealing with distribution of liquid sulfur dioxide show promise, it is expected that flash smelting capacity will be doubled and liquid sulfur dioxide will be produced. Sulfur dioxide not liquefied will be drawn to the sulfuric acid plant to supplement supplies from other sources of the raw material.

MANUFACTURE OF SULFURIC ACID

The manufacture of sulfuric acid from sulfur dioxide contained in waste gases is commonplace. Plants have been built to utilize gas containing as little as 3.5%, which represents about the minimum content that can be economically utilized. In general, contact acid plants are favored over chamber plants. A main requirement is that the gas be rigidly purified to avoid poisoning of the catalyst or production of inferior acid. In treating copper converter gases, careful control over flue pressures is necessary to obtain as rich a gas as possible. Plants are designed to handle a certain volume of gas, so that use of enriched gas will tend to increase capacity. At Trail the use of oxygen-enriched air in the zinc suspension roasters and the addition of 100% sulfur dioxide to the gas to increase the sulfur dioxide content have considerably increased the capacity of the acid plants. Snowball (*55*) has described the use of pure sulfur dioxide and oxygen to produce sulfuric acid. Recirculation of Dwight-Lloyd gases operating on a lead charge is employed at Selby on both first-over and second-over machines to increase the sulfur dioxide content of the gas to 5 to 6%. Since July 1943 such gas has been used to operate the contact acid plant and also in the new liquid sulfur dioxide plant.

In petroleum refining and in the purification of natural gas, appreciable quantities of hydrogen sulfide are obtained which may be burned to sulfur dioxide for the production of sulfuric acid. Chemico sludge conversion plants and contact acid plants are frequently used for this purpose. Monsanto (*2*) has developed a coke deposition process for recovering sulfuric acid from oil refining wastes in which a thin film of sludge acid is deposited on coke of 6- to 10-mesh size and the coke is heated at temperatures of 350° to 450° F. to decompose the acid. The coke recovered from the process is suitable as a fuel, while the decomposed acid gives a gas rich in sulfur dioxide which can be utilized for acid manufacture.

RECOVERY AS ELEMENTAL SULFUR

Several processes have been developed to recover elemental sulfur or brimstone by reduction of sulfur dioxide employing such fuels as metallurgical coke, natural gas, and hydrogen.

TRAIL PROCESS

At Trail brimstone was produced from 1935 to 1943 by a process in which substantially pure sulfur dioxide and oxygen were blown into the bottom of a coke-fired reduction furnace similar to a gas producer. Coke was charged at the top and ash removed on a rotary grate through a water seal at the bottom (*46*).

Lepsoe (*37*) has considered that the reduction of sulfur dioxide by carbon is satisfactorily expressed by the following consecutive reactions:

$$SO_2 + C = CO_2 + 1/2S_2$$
$$CO_2 + C = 2CO$$

The reaction $SO_2 + 2CO = 2CO_2 + 1/2S_2$ is inferred from a study of the apparent and actual rate constants. Above 1200° C. the rate of sulfur dioxide reduction is controlled by gas diffusion rates, inasmuch as about the same depth of fuel bed is required independent of gas velocity. The hot zone in the reduction process is greater than in a conventional gas producer and it was considered that the minimum temperature in this zone should be 1300° C. to maintain rapid reduction rates and smooth operation.

Carbonyl sulfide is formed above the hot zone by a reaction between carbon monoxide and sulfur vapor. Sufficient sulfur dioxide is added to react with the carbon monoxide and carbonyl sulfide as follows:

$$\begin{aligned} 2CO + SO_2 &= 2CO_2 + 1/2S_2 \\ 2COS + SO_2 &= 2CO_2 + 3/2S_2 \end{aligned}$$

The greater part of the reaction occurred in a column filled with firebrick. The gases were cooled in a waste heat boiler and further reacted in a catalyst tower. At 800° C. almost any hot surface will catalyze the reaction. At lower temperatures slightly hydrated and acid-soluble forms of alumina are very efficient. Lightly calcined alumina and activated alumina are said to be satisfactory. The alumina may also be used on a carrier of porous cement or sintered to crushed firebrick. Water vapor was undesirable because of the formation of hydrogen sulfide, and coal was unsatisfactory as a reducing agent because of the copious quantities of hydrogen sulfide formed.

I.C.I. PROCESS

Imperial Chemical Industries (*56*) operated a 5- to 6-ton-per-day pilot plant intermittently before the war.

In this plant 100% sulfur dioxide diluted with air to 50 to 60% and preheated to 300° C. was passed through a bed of coke. The gases left the reducer at 800° to 900° C. and the rate was adjusted so that some unconverted sulfur dioxide remained to react with the carbon monoxide, carbonyl sulfide, and hydrogen sulfide in a catalyst tower. The hot gas was used to preheat the incoming gas, then passed through a waste heat boiler where sulfur condensed, followed by a steam-jacketed mist Cottrell. After a final scrubbing with steam and water, the tail gases containing 1.5 to 2% of gaseous sulfur compounds were mixed with waste gases from the absorption plant and sent to the stack. At least 0.75 ton of coke is required per ton of sulfur produced, so that cheap coke is an essential requirement.

BOLIDEN PROCESS

The Boliden process (*4*, *46*, *56*) for the direct reduction of sulfur dioxide in raw gas was operated for several years in Sweden, but was taken out of operation in 1943 because of increasing coke prices during the war.

A part of the roaster gases, called the direct gas, was diluted with air to obtain a suitable temperature in the gas producer. A typical analysis would be sulfur dioxide 5%, oxygen 12%, nitrogen 83%. The direct gas preheated to 250° to 300° C. was passed through a deep coke bed in a mechanical gas producer of special design where carbon dioxide, carbon monoxide, sulfur vapor, carbonyl sulfide, carbon disulfide, and hydrogen sulfide were formed. The temperature above the coke layer was about 900° C.

By-pass gas having a typical composition of sulfur dioxide 9%, oxygen 5.5%, and nitrogen 85.5% was added at the top of the reducer and passed through two catalyst chambers. The oxygen in the mixture was rapidly consumed, raising the gas temperature to 1000° to 1100° C. in the first chamber while in the second chamber the temperature was 900° to 1000° C. The gases were cooled by atmospheric cooling and in a preheater for the raw gas to about 300° C. After the preheater there was a third catalyst chamber operating at 300° C. where further quantities of hydrogen sulfide and sulfur dioxide were converted.

The gases were then further cooled in a large sheet-iron cooler, where some liquid sulfur condensed and then passed through two Cottrells in series. The temperature of the gases leaving the Cottrell was about 130° C. The analysis of tail gases other than nitrogen and carbon dioxide would be carbon monoxide 0.2 to 1.0%, sulfur dioxide 0.5 to 1.0%, hydrogen sulfide 0.5 to 1.0%, carbonyl sulfide 0.3 to 0.5%, and sulfur vapor 1 to 2 grams per cubic meter (0.4 to 0.9 grain per cubic foot).

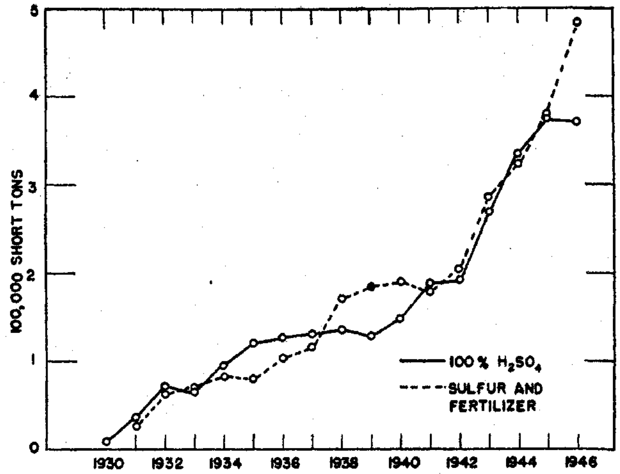

Figure 4. Sulfur Recovered from Sulfur Dioxide at Trail Smelter

The catalyst in the first two catalyst chambers was prepared by casting 60% bauxite (alumina 75%, ferric oxide 25%) and 40% high-alumina cement in blocks armored with iron.

Steam requirements for sulfur purification and transportation to storage bins were about 1.7 metric tons per ton recovered. If a waste heat boiler is installed between the second catalyst chamber and the preheater, an excess of 2.7 tons of high-pressure steam will be obtained. The coke requirements were about 1.7 metric tons per ton of sulfur while labor requirements were 9 man-hours per ton of sulfur.

The capital cost of the plant, which had a capacity of 20,000 to 25,000 metric tons per year, was about 5,000,000 Swedish kronor (1933-36) or 220 Swedish kronor per ton per year. The operating costs for the years 1936 to 1938 were about 85 Swedish kronor per ton of sulfur produced.

OTHER PROCESSES

Fleming and Fitt (*16*) have patented a process for the reduction of sulfur dioxide with natural gas which is considered to be economically feasible if natural gas at 12 cents per thousand cubic feet can be obtained. Boswell (*5*) has patented a reduction process with hydrogen at a temperature of 300° C. using a catalyst prepared by reacting iron, nickel, or cobalt oxide with hydrogen and sulfur dioxide to cause the oxide to take up sulfur. The use of vanadium pentoxide distributed over asbestos, pumice, or other inert material for reduction with hydrogen at 600° to 800° C. has also been patented.

FLUE GAS DISPOSAL PROCESSES

A group of processes designed to remove sulfur dioxide from the flue gases of power stations has been developed.

EFFLUENT PROCESS

At the Battersea station in London (*17*), flue gases are scrubbed with Thames River water in five banks of steel channel scrubbers followed by a final wash with water containing suspended chalk. The rusty surface of the steel channels is considered to be more efficient than other surfaces tested, while traces of iron in the effluent promote oxidation of sulfites to sulfates. The volume of water required for scrubbing is about 35 tons per ton of coal burned. In 1937, 480,000 tons of coal with an average sulfur content of 0.86% were burned. The gas treated was 1.9×10^{11} cubic foot, the average total acidity of the effluent was 0.032 grain (as sulfur) per cubic foot of dry gas, and the sulfur eliminated was 3734 tons. This process was not operated during the war for se-

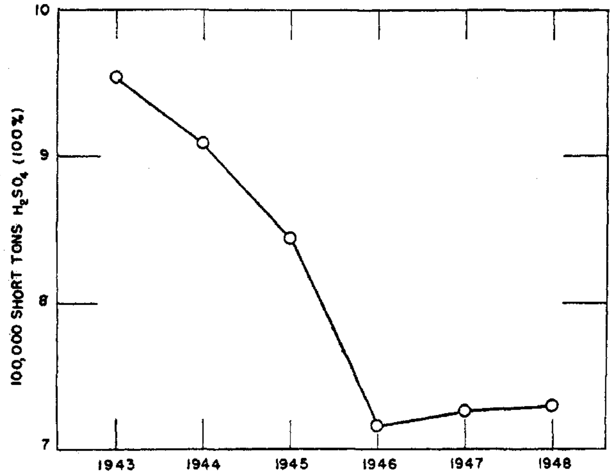

Figure 5. By-Product Sulfuric Acid Produced at Copper, Zinc, and Lead Plants in United States

1948 estimated

curity reasons. Gas washing has been restarted to a limited extent and the whole plant will soon be in operation.

NONEFFLUENT PROCESS

The Howden-I.C.I. process (*17, 38, 50*) employing a lime or chalk slurry in wooden grid-packed towers was installed at the Fulham and Tir John power stations in Britain. The process requires the circulation of about 250 tons of a slurry of calcium sulfite and calcium sulfate crystals per ton of coal burned to prevent crystallization on the scrubber surface. Part of the circulating liquid is continuously withdrawn, the sludge settled out, and the clarified liquor returned to the system. Addition of alkali after the scrubber to maintain the pH between 6.5 and 7.0 is regulated by a glass electrode pH controller.

At both power stations, while scaling of the scrubber surfaces was avoided, the high sludge concentration in the circulating liquor caused blockage in the narrow cells of the scrubbers. At Swansea operating difficulties became so great that the washing plant was shut down and electrostatic precipitators were installed. At Fulham less trouble was experienced, but maintenance costs were high because of the necessity of replacing the scrubber packing or mechanical cleaning every few months. By increasing the cross section of the vertical wooden cells from 0.625 to 3 inches square, silting troubles and maintenance costs were considerably reduced. The efficiency of sulfur removal was 90 to 92% for the Battersea station, while at Fulham the efficiency was reduced from 96 to 98% to about 92% by the change in scrubber packing. In 1937, 270,190 tons of coal with an average sulfur content of 0.89% were burned, 9.59×10^{10} cubic feet of gas were treated, the total acidity of emissions was 0.0063 grain (as sulfur) per cubic foot, and the sulfur eliminated was 2371 tons. The flue gas washing plant was shut down during the war and has not yet been restarted.

The utilization of the sludge produced in the Howden-I.C.I. process for the manufacture of cement clinker and a gas rich in sulfur dioxide has been considered. To the sludge of calcium sulfite, calcium sulfate, coal ash, carbon, and calcium carbonate, sufficient clay and coal dust must be added to decompose the sulfite and sulfate completely and provide enough alumina and silica to produce a good quality of cement clinker. The reaction temperature is 1050° to 1200° C. and a gas containing 4.8% sulfur dioxide is produced. In 1939, slurry from the Fulham station was sent to Germany for a trial run in a small producer type of cement kiln connected to a contact sulfuric acid plant. The process is said to have operated satisfactorily.

KATASULF PROCESS

The use of ammonia in a process in which the concentration of the ammonia salts is allowed to increase to just below the saturation point is reported to have worked satisfactorily on a pilot plant scale. The strong solution of ammonia salts is filtered to remove grit, a small proportion of sulfuric acid and free sulfur is added, and the solution is heated in autoclaves at about 200 pounds per square inch. Ammonium sulfate and sulfur are produced. The sulfur is run off from the base of the autoclave and the ammonium sulfate is crystallized out by evaporation. The proposed advantages are that ammonia is recovered at an increased value as sulfate, there are no charges for slaking of lime and sludge disposal, and difficulties with silting in the scrubbers are avoided.

ZINC OXIDE PROCESS

A chemical regeneration process developed by Johnstone and co-workers (*28*) to recover sulfur dioxide from flue gases has been proved on a pilot plant scale but has not been utilized commercially.

The flue gases are scrubbed with an aqueous solution of sodium sulfite-bisulfite. The solution is clarified and treated in a mixer with zinc oxide, where zinc sulfite is formed and crystallizes from solution.

$$ZnO + NaHSO_3 + 2^1/_2H_2O \longrightarrow ZnSO_3.2^1/_2H_2O + NaOH$$
$$NaOH + NaHSO_3 \longrightarrow Na_2SO_3 + H_2O$$

The zinc sulfite crystals are filtered off and the filtrate is recycled to the scrubber. The zinc sulfite is dried, milled, and calcined in a flash calciner from which a gas containing 70% water and 30% sulfur dioxide is driven off. The gas is cooled, dried, and liquefied. The calcined zinc oxide is re-used.

The over-all oxidation of sulfite to sulfate is about 10%, so that desulfation of the absorbant with lime is required. The underflow from the clarifier is treated with sufficient sulfur dioxide to convert the calcium sulfite present to bisulfite and form some free sulfurous acid. The sulfate precipitates as gypsum, which with the ash is filtered off. Sufficient lime to convert all the free sulfurous acid and part of the bisulfite to sulfite is added. The calcium sulfite slurry at about the same pH as the main stream is returned to the clarifier.

The estimated cost is equivalent to $15.40 per ton of liquid sulfur dioxide recovered or $1.08 per ton of coal burned. At Fulham the cost is estimated at 58 cents and at Battersea at 36 cents per ton of coal burned. The latter two figures are for low-sulfur coals without by-product recovery, and would be substantially greater for high-sulfur coals.

MISCELLANEOUS PROCESSES

Several processes have been considered for recovery of sulfur from pyrite. The Orkla process has been operated for many years in Norway, Spain, and Portugal, producing about 105,000 tons of sulfur in 1948. In the process developed by Lenander (*31-36*) pyrite is smelted with coke, limestone, and quartz in a furnace similar to a water-jacketed blast furnace at a temperature of about 1600° C. Copper and the precious metals form a matte with sulfur, and iron is slagged off. About half the sulfur is removed by distillation of the labile atom of sulfur. Air blown in the base reacts with iron sulfide to provide much of the heat required. The coke feed is so regulated that some sulfur dioxide is not reduced in the furnace but left to react with carbon sulfur compounds in the upper part of the furnace and in subsequent catalytic reduction chambers. Sulfur is recovered by condensation, followed by electrostatic precipitation. The exit gases are finally scrubbed in a battery of six limestone towers. The recovery of sulfur and copper is 85 to 90%.

Noranda Mines Limited (*21, 64*) have carried out development work for a number of years with the object of utilizing a large body of low-grade ore. The most promising of the various processes investigated involves the distillation of the labile atom of sulfur in pyrites with recovery of iron oxide of low sulfur content.

The sulfur produced would be sold to pulp mills and the iron oxide to the steel companies. The process has been proved on the pilot plant scale and the economics are favorable.

RECOVERY OF HYDROGEN SULFIDE

The removal or recovery of hydrogen sulfide is of major importance in petroleum refining and in the purification of natural and manufactured gas. In isolated areas hydrogen sulfide may be vented directly to the atmosphere, but the usual practice is to separate it from refinery gases and burn it as a fuel. About 20,000 tons of sulfur per year from hydrogen sulfide in refining gases are utilized for sulfuric acid manufacture in the United States.

GIRBOTOL PROCESS

Reed (*51*) has reported that the Girbotol process is at present the only one being installed on a large scale for the removal of hydrogen sulfide from refinery and natural gases. It was first used commercially in 1929 and has since been installed in several hundred plants. The process is said to be extensively used for the separation and recovery of carbon dioxide from gas mixtures and is in use for purifying such hydrocarbon liquids as propane, butane, and straight-run and cracked gasoline as well as for purifying and dehydrating natural and refinery gases.

In the process the absorbant solution passes down through a bubble tray absorber countercurrent to the gas flow. The rich absorbant solution flows through heat exchangers to a second bubble plate "reactivator" tower in which hydrogen sulfide or carbon dioxide is stripped from the solution by steam generated in a reboiler at the base of the tower. Steam is condensed at the top and the condensate is returned to the solution. The stripped absorbant is cooled in a heat exchanger and cooler, and returned to the absorber. The absorbant solution may be an aqueous solution of monoethanolamine, diethanolamine, or a mixture of one or both with diethylene glycol, depending upon the particular application. The basic process is similar to the cyclic processes for sulfur dioxide recovery. Reed has discussed solutions to various operating problems and described improvements in the process.

ELEMENTAL SULFUR FROM HYDROGEN SULFIDE

In recent years considerable interest has developed in the recovery of elemental sulfur from hydrogen sulfide by limited oxidation with air. Hay and others have listed the plants which have been or are being built to manufacture brimstone by this method. In 1947, 43,400 tons of sulfur were recovered from natural gas by this process and it is estimated that the total annual production in all plants built or started since 1947 may be about 220,000 tons per year. Weber (*65*) described the first commercial plant built in Arkansas. Graff (*18*) discussed the adaptation of the original Klaus process developed in Germany about 100 years ago to present-day practice. The operating cost of an elemental sulfur-recovery plant producing 50 tons per day is given as approximately $6 per ton including labor, amortization, and fixed charges, and the initial investment is said to be about $350,000.

In the original process, hydrogen sulfide with added air was burned in a large combustion chamber containing a catalytic material where the following reaction took place:

$$3H_2S + 1^1/_2O_2 = 3S + 3H_2O + 159 \text{ kg.-cal.}$$

High and uncontrolled operating temperatures resulted in incomplete conversion. In later plants, part of the vent gases were recycled to allow some temperature control.

I. G. Farbenindustrie A.-G. (*18*) modified the process by burning one third of the hydrogen sulfide under a steam boiler. Products of combustion at 900° F. were mixed with the remaining hydrogen sulfide and reacted in a catalytic reaction vessel at about 700° to 750° F.; 92 to 94% conversion to elemental sulfur was obtained, and 99% conversion could be obtained by adding an additional catalytic reactor and sulfur condenser.

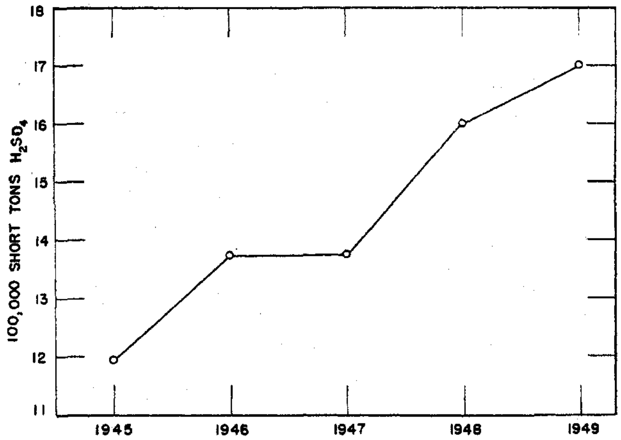

Figure 6. Sulfuric Acid (100% Basis) Produced in Great Britain

1945 and 1949 estimated

$$H_2S + 1^1/_2O_2 = SO_2 + H_2O + 124 \text{ to } 138 \text{ kg.-cal.}$$
$$SO_2 + 2H_2S = 3S + 2H_2O + 21 \text{ to } 35 \text{ kg.-cal.}$$

In a further modification the mixture of hydrogen sulfide and air was burned under a steam boiler, where 60 to 65% conversion occurred, and the partially cooled flue gases passed into the catalytic reaction vessel to obtain final conversion. These modifications have resulted in increased efficiency and reduced size of plant.

Where the quantity of hydrogen sulfide in the gas is insufficient to support combustion under a steam boiler, the air and acid gas may be preheated. The catalysts used are alumina, bauxite, pumice, porous iron oxide, and silica gel, the most common being natural bauxite containing 5 to 10% iron oxide.

In the plant described by Weber (*65*) the gas stripped from the diethanolamine absorbant solution averaged 55% hydrogen sulfide, 43% carbon dioxide, and 2% hydrocarbons. The gas admixed with air was burned in a special furnace, the temperature reduced in a waste heat boiler to about 530° C., and the flue gas passed to a first-stage converter containing bauxite catalyst. The suspended sulfur was scrubbed out with liquid sulfur in a packed column and the scrubbed gases passed through a second converter and packed column. The liquid sulfur went to a measuring tank maintained at 250° F. and from there was sprayed in thin layers on a sulfur pile. Better than 93% recovery was obtained.

MISCELLANEOUS PROCESSES

Several liquid purification processes have been developed. Of these the ferrox, nickel, Thylox, phosphate, phenolate, and Seabord processes are the most important. The Seabord process was the first commercial liquid purification process used in the United States. Hydrogen sulfide is not recovered. Because of its simplicity, about 50 plants were built in the United States and Canada. The absorbant is a 3% solution of soda ash. Regeneration of the spent solution is effected by blowing with air in an "actifier" tower.

The Ferrox and nickel processes employ a solution of soda ash containing ferric hydroxide and nickel hydroxide, respectively, in suspension. In the Thylox process the absorbant is a solution of sodium ammonium thioarsenate. In all these processes, regeneration of the spent solution is accomplished by blowing with air in which a suspension of sulfur is formed and removed by filtration. It may be sold as a paste or treated in an autoclave to form brimstone.

CONCLUSION

The control of pollution is necessary in this age where population and industry cannot be effectively segregated, but in the application of control measures, the interests of the community as a whole must be considered. The arbitrary application of injunctions is not the answer to a problem which can always be solved by the use of sound scientific and engineering principles. It is impossible to eliminate all the products of combustion of fuels, internal combustion engines, and all effluents from metallurgical and chemical operations. A certain amount of pollution is unavoidable and will always be present. Standards should be reasonable within the capacity of existing methods and known engineering equipment to achieve, and not discriminatory. On the other hand, careless, inefficient, and wasteful methods of combustion and production of avoidable smoke, dust, and gases of injurious proportions in a manner contrary to sound engineering practice should be prevented.

In the case of sulfur dioxide and its effects on vegetation, the permissible limits of ground concentration are now known with certainty. Wherever such ground concentrations have been maintained by proper plant operation below 0.30 to 0.50 p.p.m., normal forest and agricultural crops have been obtained and no damage has resulted to the most susceptible species. In fact, science has shown that not only is sulfur an essential plant food, but vegetation may benefit from the application of sulfur either in fertilizers to deficient soils or in the form of low concentrations of sulfur dioxide in the air to sulfur-deficient plants.

The investigations into the recent Donora disaster and increasing evidence from other heavily smoke-polluted districts indicate that the most common irritants to which the general public may be exposed are sulfur and its compounds, halogens, halogen acids, and oxides of nitrogen. These contaminants in the presence of soot and tarry material from incomplete combustion of fuels may cause an intensified irritation of the upper respiratory tract, resulting in coughing and other symptoms which may only fatigue persons in good health but can lead to much more serious effects in people weakened by pulmonary or cardiovascular diseases. However, such irritating solids and gases can be effectively diluted by emission at high temperatures from tall stacks, or the mass rate of discharge reduced by recovery installations at the source, to the point where the ground concentrations are insufficient to constitute a health hazard, except under abnormal weather and topographical conditions. Where such conditions exist it is wise to invoke a form of meteorological control to avert a possible repetition of the Donora episode, when it is not economically possible to convert most of the harmful wastes into useful by-products.

For those industrial operations which result in a considerable tonnage of waste sulfur-containing gases which are not too dilute—e.g., 1% or more of sulfur dioxide—it pays to clean up the air and transform this waste into elemental sulfur, sulfuric acid, liquid sulfur dioxide, or fertilizers and insecticides. The agricultural demand for fertilizers is huge and constantly increasing as the pressure of population and soil depletion makes it necessary to maintain world production of foodstuffs at a proper nutritional level. Increased requirements of sulfur must also be met for the ever-spreading chemical, pulp and paper, explosives, paint, and miscellaneous industries. For smelters, oil refineries, and sour natural gas producers, the problems involved in the recovery of atmospheric contaminants are largely technical and have, in many cases, been solved successfully with profitable results. Very few industrial plants cannot, for economic reasons, apply one or more of the known processes mentioned in this paper to recover some by-product sulfur, provided there is ready access to markets.

The major producers of native sulfur are faced with the problem of eventual exhaustion of reserves at present rates of depletion. It is logical, therefore, that they should cooperate with companies which have a large waste sulfur problem in the interests of conservation of sulfur resources and to alleviate atmospheric pollution. Steps in this direction have already been taken by Texas Gulf Sulphur Company to recover hydrogen sulfide from natural gas in Arkansas. Recently this company, in cooperation with Pure Oil Company, has started construction of the largest plant of its kind at Worland, Wyo., to treat 30,000,000 cubic feet of natural gas containing 28% hydrogen sulfide by stripping the gas with an amine solution and use of a modified Claus process for recovery of elemental sulfur. Texas Gulf Sulphur also controls the use of the Orkla process in the Western Hemisphere and in Australia.

In Canada, Canadian Industries Limited is cooperating with the International Nickel Company at Copper Cliff in the production of sulfuric acid and in the proposed new plant for liquid sulfur dioxide. Such ventures between producers that have ready access to markets and those that have waste sulfur available are likely to increase.

There is need for continued research on the problem of sulfur recovery. In the nickel smelting industry, such research might be aimed at developing a process which would produce iron oxide as a useful by-product. In the Sudbury, Ontario, area there are available in the waste gases discharged to the atmosphere about 1,000,000 long tons of sulfur annually. Most of the sulfur evolved in this area, however, comes from pyrrhotite which is closely associated with the chief nickel and copper minerals, pentlandite and chalcopyrite. An economical solution to this problem may depend upon developing improved concentration processes to eliminate a greater proportion of the pyrrhotite without loss of appreciable metal values.

The use of oxygen-enriched air for smelting to yield higher concentrations of sulfur dioxide in roaster gases is already established. Other fields of investigation which might be attempted are acid leaching to yield hydrogen sulfide which could react with sulfur dioxide, and reaction of sulfur dioxide with sulfide ores at high temperatures to give elemental sulfur and the oxide of the metal.

The reduction of sulfur dioxide, resulting from the roasting of sulfide ores, to sulfur is inherently wasteful and is not likely to come into widespread use because the coke required approaches or exceeds in value the sulfur produced. Research directed toward partial oxidation of the sulfide ores to produce the oxide of the metal and elemental sulfur might permit more economical operations.

The achievements of industry and research in the metallurgical and oil refining operations may, in the future, transform all sulfur wastes from undesirable air contaminants to valuable by-products. The same is true of flue gases from coal-burning power plants, coke ovens, and coal-gas plants. Various programs of smoke abatement and control in large cities and industrial areas are now under way to curb the evils of coal smoke. All these efforts are directed toward ultimately banishing smog from our atmosphere.

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Removal of Hydrogen Sulfide from Industrial Gases

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Removal of hydrogen sulfide from natural and manufactured gases has become of great importance in recent years because of more rigid specifications for pipe-line distribution, higher sulfur content in raw materials, and the depletion rate of mineral sulfur deposits. This paper reviews the various commercial processes used for this purpose. The only dry process in extensive use is the iron oxide process, largely used by utility companies for purification of city gas. The wet processes used fall in the following classifications: nonregenerative processes, including caustic soda, lime slurry, potassium permanganate, and bichromate–zinc sulfate; regenerative nonrecovery processes (the only process in commercial use in this classification is the Seaboard process); regenerative processes with recovery as hydrogen sulfide, including vacuum carbonate, Girbotol, phosphate, Alkazid, and phenolate; and regenerative processes with recovery as sulfur (the principal process used here is the Thylox process; the earlier Ferrox and nickel processes are now becoming obsolete). Various processes are selective in varying degrees for the removal of hydrogen sulfide in the presence of carbon dioxide. Potassium permanganate and bichromate–zinc sulfate processes may be used for the removal of small quantities of hydrogen sulfide. Manufactured gas may be purified by the use of iron oxide, Seaboard, vacuum carbonate, and Thylox processes, which are highly selective. Natural and refinery gases may be treated with the Girbotol process using the tertiary amine, the phosphate process, or the Alkazid Dik solution for semiselective removal of hydrogen sulfide.

THE removal of hydrogen sulfide from natural and manufactured gases is not a new problem; the objectionable properties of this impurity are well known. Hydrogen sulfide not only has an objectionable odor, but also is highly poisonous, being almost as toxic as the more notorious hydrogen cyanide and five to six times as toxic as carbon monoxide. In addition, hydrogen sulfide is corrosive to pipe lines, compressors, and combustion equipment. When burned it produces sulfur dioxide, which is also obnoxious and corrosive. Lastly, its presence in synthesis gases may result in catalyst poisoning and product contamination.

Although an old problem, the importance of hydrogen sulfide removal has increased considerably in recent years, owing to several factors. Probably the most significant of these is the increased usage of raw materials of higher sulfur content. These include natural gas, crude oil, and coal, from which most of the industrial gases considered here are produced.