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METALLIC LEAD PRODUCTS DIVISION

July 9, 1952

CHEMICAL BULLETIN NO. 68

SUBJECT: CONTROLLING
CORROSIVE AIR POLLUTANTS

To Members of the Metallic Lead Products Divisions

Attached is a reprint of an article entitled "Controlling Corrosive Air Pollutants" which was published in the May, 1952, issue of "Air Repair" magazine. This is the official publication of the Air Pollution and Smoke Prevention Association of America.

The article describes how the two principal corrosive air pollutants, sulphur dioxide and sulphuric acid mist, are controlled through the use of modern lead protected equipment.

A limited quantity of additional copies are available. Up to twenty-five copies may be had free of charge; larger quantities may be had at our cost of six cents per copy.

Very truly yours,

Robert L. Ziegfeld
Secretary

N3116

CONTROLLING CORROSIVE AIR POLLUTANTS

by Kempton H. Roll
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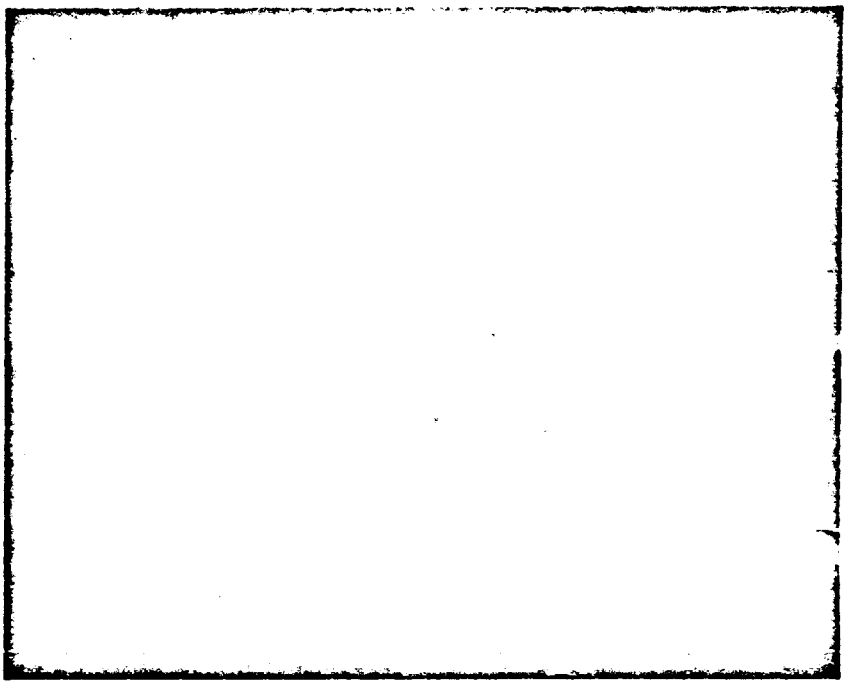


Looking down throat of a Penn Anthony Venturi scrubber. White area is a curtain of fine water sprays for wetting acid mist particles

The Donora Smog Episode*, the Poza Rica Toxic Gas Episode†, the Los Angeles problem with sulfurous gases‡, and, in general, the complaints of many localities situated near industrial operations have all served to point up the importance of controlling air pollution caused by corrosive air pollutants, of which sulfur dioxide and sulfuric acid mist appear to be the chief offenders.

Though the problem has been brought to public focus more recently, it has actually been under study for many years. Forty-two years ago, the American Smelting & Refining Company at Selby, Calif., installed the first satisfactory commercial electrostatic precipitator to suppress acid mists produced during gold and silver parting operations. Converting waste sulfur dioxide gases has been an important source of sulfuric acid for more than half a century, and in the last five years, according to *Chemical Week*, some 20 to 25 chemical plants have spent $19,000,000 on added facilities to control air pollution alone and pay a bill of $5,000,000 a year to operate them.

Problem Not New

Because the air pollution problem is not new, industry has had ample time to develop and perfect appropriate controlling equipment. The approach to the control of corrosive air pollutants has followed two general courses of attack, depending on whether the effluent is an aerosol or a gas.

In the case of an aerosol, such as sulfuric acid mist, the problem is simply one of collection. If the particles which are

* In October 1948, 19 persons died within a period of five days and several thousand more became seriously ill at Donora, Pa. In the words of U. S. Surgeon General Leonard A. Scheele: "It was not until the tragic impact of Donora that the nation as a whole became aware that there might be a serious danger to health from air contamination."

The causes of the disaster, according to U. S. Public Health Service investigators, could be laid to a peculiar combination of three conditions: 1) the presence of sulfur dioxide and some acid mists in the air, 2) the presence of solid particulate matter in the air, and 3) the weather, an inversion trap of impenetrable warm air pressed down on Donora, permitting these pollutants to concentrate but not escape from the enclosed valley.

† Hydrogen sulfide-bearing gases escaping from a refinery flare plus temperature inversion and fog caused 320 casualties, including 22 deaths, on November 24, 1950 in Poza Rica, Mexico, site of the Pemex oil refinery.

‡ Some 822 tons of sulfur dioxide formerly entered the Los Angeles atmosphere every day, and the Director of the Los Angeles Air Pollution Control District

small enough to float in air can be coalesced or agglomerated into larger particles, they can thus be prevented from polluting the air.

In the case of a gas such as sulfur dioxide, an entirely different control technique must be utilized. Two that are in commercial use are: 1) conversion of the sulfur dioxide to sulfuric acid providing the volume warrants the expense, and 2) absorption of the gas in chemicals from which it can be recovered as pure sulfur dioxide.

In the case of hydrogen sulfide, a less corrosive but more toxic gas, the approach has been similar to that used on sulfur dioxide. One method is to burn it in air to convert it to sulfur dioxide and water vapor.

$$2H_2S + 3O_2 = 2H_2O + 2SO_2$$

Another is to burn it in the presence of sulfur dioxide to convert it to elemental sulfur and water vapor.

$$2H_2S + SO_2 = 2H_2O + 3S$$

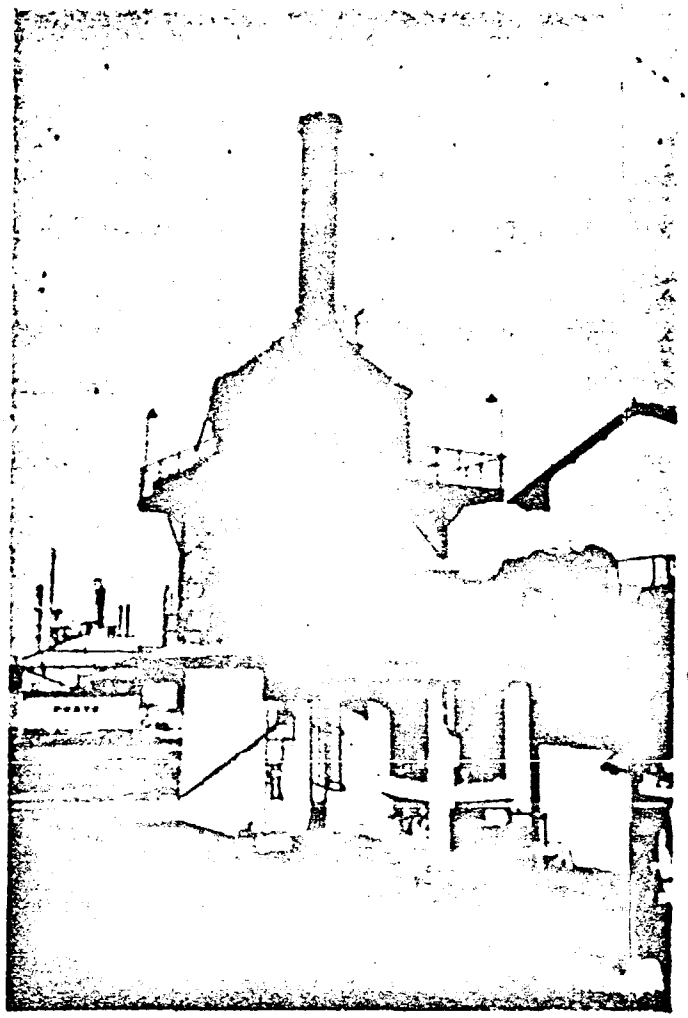
Hydrogen sulfide is now being treated in a number of oil refineries by means of either of these methods. One refinery in the Los Angeles area is producing sulfur at the rate of 50 tons per day from gases that were formerly burned to introduce 100 tons of sulfur dioxide into the atmosphere per day!

Sulfuric Acid Mist

Sulfuric acid is recognized as the work horse of the chemical process industries, and where it is used as a hot acid, the presence of sulfuric acid mist very often becomes an air pollution problem of considerable magnitude.

The electrostatic precipitator, oftentimes referred to as a "Cottrell," provided one of the earliest effective means for suppressing this corrosive air pollutant. Today it is common practice to add an electrostatic precipitator at the end of the processing circuit through which all gases bearing sulfuric acid mist must pass.

As the gases pass through the precipitator, they receive electrical charges which cause them to agglomerate or coalesce. The charged particles of acid collect on the precipitator walls and, due to their own weight, descend to the bottom for removal.



Modified Cottrell sulfuric acid mist precipitator, part of a drum-type sulfuric acid concentrating unit shown at right

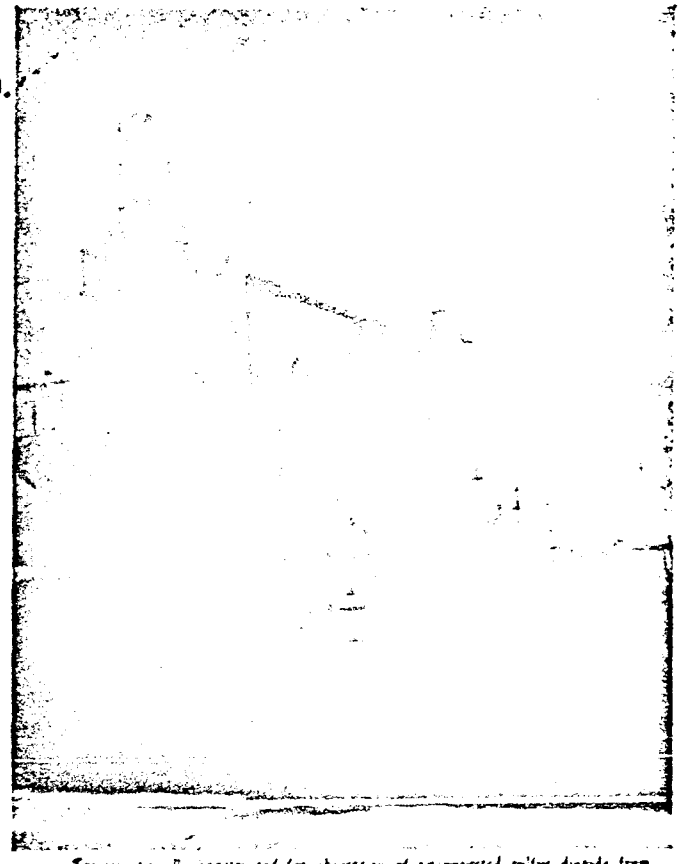
—Photo courtesy Coke Chemical Division

100 Percent Efficiency Possible

The normal efficiency of an electrostatic precipitator generally ranges from 90 to 95 percent; the balance of 5 to 10 percent acid mist still escaping to the air may or may not constitute an air pollution hazard depending upon the locality.

Theoretically, a precipitator can be operated up to 100 percent efficiency, but the extra equipment required generally adds disproportionately to the cost. In the case of a large chemical company located in a heavily populated area of New Jersey there was little choice; collection efficiency had to be raised well up within the 96 to 99 percent range.

This was accomplished by means of a minor modification on a conventional precipitator. A lead lined steel dome was added to the top and equipped with a short lead stack supported by a steel



Towers specially constructed for absorption of unconverted sulfur dioxide from conventional contact sulfuric acid plant. The lead-lined absorption tower is shown on the left. At the base of the towers are acid storage tanks and sulfur dioxide cooler. —Photo courtesy Cabot Chemical Division

framework, thus bringing the total added height to 30 feet.

The dome served a dual function: to cool the gases further and also insure that the uppermost section of the precipitator chamber would operate effectively regardless of wind and weather conditions. Performance tests on the modified precipitator showed that an intake of corrosive mist containing 325 mg per cubic foot of sulfuric acid was reduced to the very low value of 1.4 to 5.0 mg per cubic foot at the exit.

Made of Chemical Grade Lead

The material of construction of all electrostatic precipitators for handling sulfuric acid mists is principally of chemical grade lead, that is, lead containing 0.002 to 0.02 percent silver and 0.04 to 0.08 percent copper. The method of construction is generally the cage type, that is, the sheet lead is supported in a steel framework which exposes the bulk of the metal's surface to the cooling effects of the outside atmosphere.

Precipitator tubes, electrodes, acid pipe and all other surfaces exposed to either the mist or the precipitated acid are made of lead, either of unalloyed chemical grade or of lead plus 6 percent antimony where greater strength is needed.

Another device that has more recently entered the field of corrosive air pollutant control is the Venturi scrubber. In this device the acid mists are pulled through the constricted throat of a Venturi tube where the particles encounter a high velocity water spray (flow rate of about 250 feet per second).

The water particles are intentionally broken up to approximate the size of the acid mist particles, the object being to combine the acid particles with water and thus increase their weight to the point where they will no longer float.

After passing through the throat, the weighted particles enter a cyclone chamber where their velocity drops, they collect on the sides and then flow down to the bottom of the chamber for withdrawal.

The clean gas, free of acid pollutants, is drawn out of the top of the chamber through blowers and thence to the atmosphere. For handling exhaust gases at the rate of 50,000 to 60,000 cubic feet per minute, about four or five gallons of water are used per minute. However, this is recirculated to reduce the overall water consumption.

Since the spray water picks up acid mist and thus becomes dilute sulfuric acid, all areas coming in contact with it are protected with lead. The cyclone chambers are usually lead lined and the settling chambers, pumps and piping used to recirculate the water are also constructed of lead.

Sonic Agglomerator

Another apparatus developed expressly for air pollution control is known as the sonic agglomerator or collector. This type of collector operates on the principle that high intensity sound will cause particulate matter to agglomerate.

The mist-laden gases are led into a sound chamber where they are exposed to a very high intensity sound field generated by a compressed air operated siren. In one installation, the volume of gas carrying the mist moves at the rate of 24,000 cubic feet per minute and is at a temperature of 125 deg. F.

The lead lined chamber is perhaps 35 feet high and eight feet in diameter. After coalescing, the particles are passed into the sheet lead cyclone where they are separated from the exhaust which proceeds out through the top.

About half of the collection occurs on the inner walls of the tower, the remain-

der within the cyclones. Exit gases leaving the sonic collector are reported to contain between two and three mg of 100 percent sulfuric acid per cubic foot.

Actually ultrasonics are not involved in the operation of this equipment. Originally, research seemed to indicate that ultrasonics or supersonics were the approach to sound conglomeration but later experiments showed that better results were obtained when the sound frequency was dropped down into the audible range though kept at a very high intensity. Fortunately, the noise problem has been overcome through the use of special sound insulating material wrapped around the sound chamber.

By using any of the equipment thus far described it is a comparatively simple matter to control the escape of acid mists. However, our brief descriptions do not imply that other methods are not equally effective, depending upon the conditions encountered.

For example, a simple coke bed will suppress a fair percentage of acid particulate matter. A coke bed is merely a sealed box full of ordinary coke through which mist-laden gases are passed, the mist particles being entrained in the coke interstices. In addition, there are several varieties of cyclones and other types of precipitators, all of which will suppress acid air pollutants to varying degrees.

Corrosive Gases

Sulfur dioxide is one of the principal corrosives associated with air pollution that is of a truly gaseous nature. The time-tested method for preventing air pollution by sulfur dioxide has been to collect, clean and convert the gas to sulfuric acid, a method which has proven in many cases to be not only effective but economical as well by providing a readily salable product.

Non-ferrous metallurgical operations which usually involve the roasting and smelting of sulfide ores produce substantial quantities of waste gases bearing sulfur dioxide. The early problems that arose as a result of permitting these gases to escape freely to the atmosphere are common knowledge.

The so-called "smoke farmers" who located in areas adjacent to metallurgical smelting operations, it is reported, made more money from law suits than crop raising. But today they'd not fare so well, for waste gases, particularly sulfur dioxide, are almost universally removed before entering the atmosphere.

Standard practice is to first wet the hot gas to cool it and also knock down some of the heavier particulate matter, pass the gas through mist Cottrells or electrostatic precipitators which remove the balance of the solid suspended matter, cool the gas by passing it through lead pipe cooling coils and then convert it in conventional contact process equipment to high concentration, high purity sulfuric acid.

In many installations where the volume of gas is large and the percentage of sulfuric dioxide is in the neighborhood of 2 to 3 percent, it is more economical to convert the gas to sulfuric acid in modern Mills-Packard chambers which operate more efficiently than a contact plant under low sulfur dioxide concentrations.

Since a ready market exists for liquid sulfur dioxide, a more recent practice on the part of many operators faced with the task of eliminating sulfur dioxide air pollution is to collect, purify, and compress the gas for sale as liquid 99.997 percent sulfur dioxide.

Dimethylaniline Used

One of the newest and most successful methods involves dissolving the impure gas in cold dimethylaniline and extracting it as pure sulfur dioxide by heating the pregnant dimethylaniline solution. The dimethylaniline is, of course, regenerated and returned to the circuit for re-use. Here again, because dimethylaniline sulfate (dimethylaniline plus sulfur dioxide) is corrosive to practically all materials of construction with the exception of lead, almost the entire absorption, regeneration, and purification process is conducted in lead-protected equipment.

Depending on their availability, sulfur dioxide may be absorbed for regeneration in other chemicals: various alkalies, ammonium compounds, tri-potassium phosphate, diethanolamine, etc. One chemical company, for example, dissolves waste sulfur dioxide in by-product sodium sulfite to form sodium acid sulfite.

In this case, the problem arose from the fact that in a typical contact acid plant all of the sulfur dioxide that enters the converter does not normally come out as sulfur trioxide. This means that anywhere from one to three percent sulfur dioxide may escape into the atmosphere.

To prevent this, plant engineers constructed equipment to utilize by-product sodium sulfite, which has the ability of absorbing sulfur dioxide to form sodium bisulfite.

The sulfur dioxide is recovered by heating the bisulfite with steam, thus freeing the sodium sulfite and returning it to the circuit. The absorption tower in this particular case consists of a steel shell 45 feet high, lined with bonded lead (lead bonded directly to steel; in effect a lead clad steel), then a layer of mill board, and finally a layer of refractory brick.

The regenerating tower is three feet in diameter, 30 feet high, and lined with bonded lead and carbon brick. The final exit gases in the process are said to contain only 2 mg. per cubic foot sulfuric acid mist and 8 mg. per cubic foot sulfur dioxide.

This is considerably lower than the exit gases and mists of a standard contact acid plant which emit approximately 20-25 mg. per cubic foot as mist and 200 mg. per cubic foot as sulfur dioxide.

Incidentally, this plant manages to recover about 10 tons of sulfur dioxide per day from this one operation – a fair indication of what would normally be escaping into the atmosphere.

Recovery Methods Vary

Since each problem is different, the recovery, disposal or treatment scheme for the same gas may vary widely. These variations depend on the amount of material to be disposed of, market value of recovered product, local plant conditions, etc.

Much more has been said and written about the various types of equipment mentioned above as well as other less commercially used methods. All those described are known to be systems in use in industry today for overcoming the problem of controlling corrosive air pollutants.

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