GUIDELINES

FOR LIMITATION OF CONTACT SULFURIC ACID PLANT EMISSIONS

ENVIRONMENTAL PROTECTION AGENCY

APTD0602

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Division of Control Agency Development

ENRIRONMENTAL PROTECTION AGENCY
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INTRODUCTION

This document was prepared by the Air Pollution Control Office (APCO) to assist state and local regulatory agencies in the preparation of emission control regulations for contact sulfuric acid plants. It is advisory in nature, not prescriptive; and it in no way infers or represents national emission standards. It recognizes the importance of of economic considerations, but it does not specifically relate the suggested limits to the economy of any sulfuric acid plant to which they may be applied. This is not to say that any of the emission limits suggested here are economically unrealistic. Most of them have, in fact, been achieved in commercial installations.

The types and sources of air pollution in the contact sulfuric acid plant are discussed, and guidelines based on optimal use of available control technology are presented to assist agencies in developing regulations compatible with local conditions. There is, however, no attempt to give detailed descriptions of either the contact sulfuric acid process or the recommended control techniques. The latter may be found in a study of the sulfuric acid industry sponsored by APCO's Division of Process Control Engineering[1] and in a joint study shared by the Manufacturing Chemists' Association and the U.S. Public Health Service (MCA-PHS).[2]

All emissions are presented as pounds per ton of 98 percent sulfuric acid produced (lb/ton) and as pounds per hour emission rates. The conversion curve (Figure 1) will assist the reader in making a transition between these mass emission rates and the commonly used concentration units, parts per million (ppm) and milligrams per standard cubic foot (mg/SCF). Mass emission rates have been used because they are recommended as more practical for assessing the output of individual plants, and are not subject to circumvention by dilution.

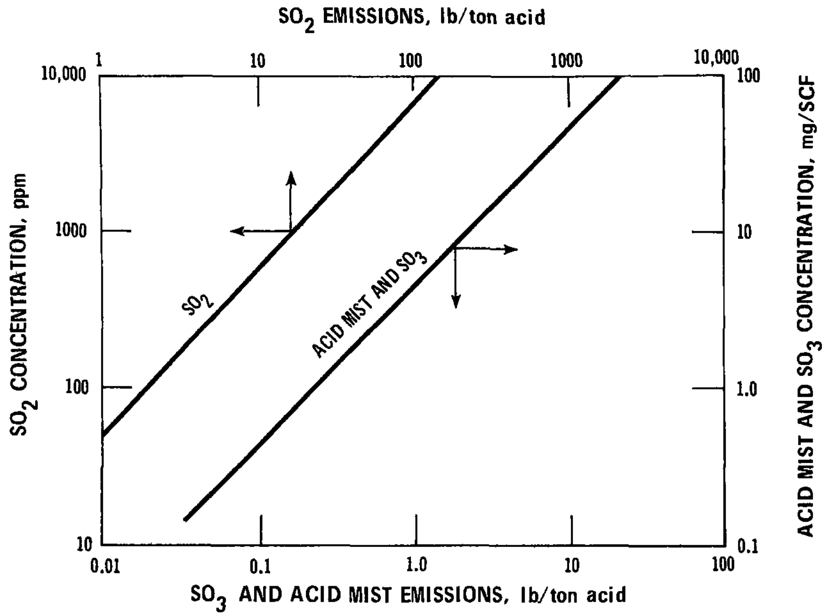

Figure 1. Conversion scale relating concentration and mass emissions for SO_2, SO_3, and acid mist.

The recommendations presented are based on information gathered from the two studies mentioned above; from discussions with members of APCO divisions and representatives of private industries and state and local regulatory agencies; and from the current literature.

Ideal maximum and minimum emission levels for sulfur oxides are dependent on local conditions and cannot be recommended in a document of this nature. The emission levels given herein are offered as guidelines to be incorporated in local regulations.

EMISSIONS AND CONTROL TECHNOLOGY

Sulfur dioxide (SO_2), sulfur trioxide (SO_3), and acid mist in the absorber tail gas are the principal air pollutants emitted from a contact sulfuric acid plant. All three present potential health hazards, and the emission levels can be greatly reduced with the careful application of currently available technology.

Sulfur Dioxide

Sulfur dioxide is emitted from a contact sulfuric acid plant absorber when conversion of the SO_2 to SO_3 is incomplete. Large quantities of unconverted SO_2 then pass through the absorber and into the atmosphere. These emissions, left uncontrolled, can average about 60.0 lb/ton of acid produced, in a plant with a conversion efficiency of 95 to 96 percent; this represents a range of 50 lb/hr for a 20-ton/day plant to about 12,000 lb/hr for a 4800-ton/day plant. It is technologically possible, however, to reduce SO_2 emissions to one of three levels.

Alter Operating Conditions

The emissions can be reduced to about 35 lb/ton acid by altering operating conditions such as catalyst quantity and quality and reaction gas composition, temperature, and residence time in the converter.[1]

Commercial Control Processes

Data from new plants using a dual absorption process in the converter system show emission rates reduced to 6.5 lb/ton acid.[3,4,5] Such plants are in commercial operation in Europe and Japan. In such a process, the SO_2 is first partially converted to SO_3, which is absorbed in the primary absorber. Additional conversion is achieved by sending the off-gases containing SO_2 through a second converter. This gives overall SO_2 to SO_3 conversion efficiencies of 99.5 percent, since equilibrium favors greater conversion at the high O_2/SO_2 ratio that is normally present in the primary absorber off-gases.

No existing contact plants have been converted to dual absorption in the United States, but the systems are being offered commercially. Conversion of an existing contact plant to dual absorption does not represent anything unusual or exotic in the chemical processing industry. It only requires the installation of an additional absorber, heat exchanger, and associated piping.

Other commercially available control processes for existing plants are also capable of reducing emissions to the 6.5-lb/ton-acid level. In most United States plants the Cominco process is being used, but the Wellman-Lord process is operating in one acid regeneration plant.[6,7] The Sulfacid process is in commercial operation in Europe,[1,8] and a slaked-lime scrubbing system is being used to remove SO_2 and SO_3 from a plant in Japan.[9]

Pilot-Scale Reductions

Absorption processes using magnesium oxide and sodium carbonate (Na_2CO_3) have also been evaluated on the pilot-scale level and show particular promise of reducing the total SO_2, in tail gas emissions to 2.0 lb/ton acid.[1]

Relative Merits of Available Controls

A comparison of the total SO_2 emissions from a contact sulfuric acid plant (1) with no control, (2) with either dual-absorption or commercially available SO_2 control processes, and (3) with promising pilot-scale SO_2 control processes is presented in Figure 2.

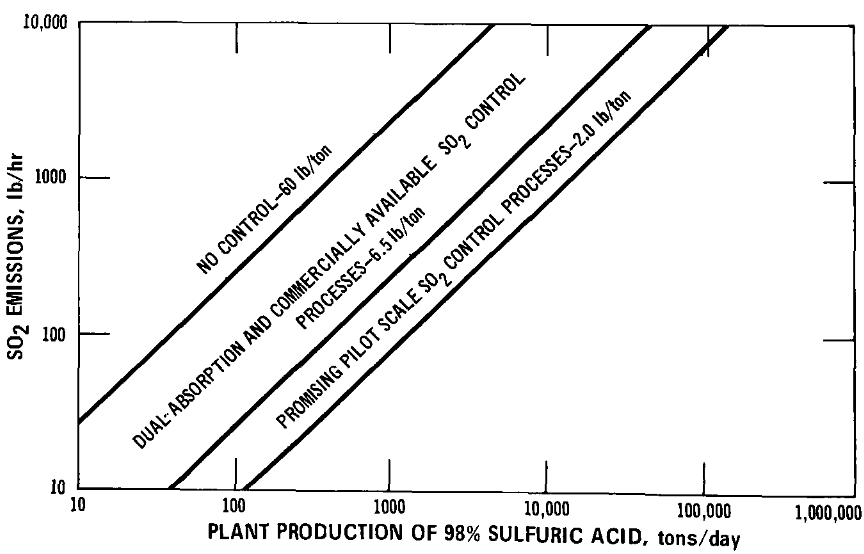

Figure 2. Attainable SO_2 emission levels from contact sulfuric acid plants.

Installation of a dual-absorption plant would not only reduce the SO_2 emissions by 85 to 90 percent from conventional plant levels, but the additional cost of an added heat exchanger and absorption tower would also be partially offset by the increased conversion efficiency.[3] It should, however, be emphasized that the installation of a dual-absorption plant does not necessarily mean that further controls would not be required or that use of the dual absorption process in the converter will eventually solve all of the SO_2 emission problems in the contact sulfuric acid plant. The short stack, high-SO_2 concentration, and cool stack-gas temperature could still present other problems in meeting ambient-SO_2 air quality standards.

Acid Mist

Acid mist formation occurs in the contact sulfuric acid plant in a number of ways, any or all of which may be operative in an individual situation. Hydrocarbons in the sulfur burn and produce water vapor that subsequently combines with SO_3 in the economizer or in the absorber. Operating concentrations and temperatures can favor mist formation in the absorber. Nitrogen oxides formed in the furnace may oxidize the SO_2 in the stack gas to SO_3. When SO_3 is present in a stack gas, it will combine with water in the atmosphere and form a plume of acid mist.

Acid mist usually appears as a dense white plume; however, the absence of a plume does not mean that there is no mist present, only that few of the particles are in the visible-size range. Mist particles range from 0.3 to 5.0 microns in diameter. In plants with an oleum tower, the percentage of submicron particles is greater, compounding the emission problem because the smaller mist is more difficult to collect.

Without controls, the acid-mist emissions can amount to 3 to 12 lb/ton acid. Effective control is possible, however. Commercially available mist eliminators and electrostatic precipitators can reduce the total acid mist emissions to about 0.5 lb/ton of acid produced.[1,2,10]

Sulfur Trioxide

Proper design and operation of the absorption tower is the best assurance against serious SO_3 emissions. Under ideal conditions they should not exceed 0.2 lb/ton acid.[1,2] Serious SO_3 emissions usually occur with plant startup and plant upsets, but continuous SO_3 emissions in excess of 0.2 lb/ton are indicative of inefficient absorber operation.

The SO_3 and acid emission levels recommended in Figure 3 are consistent with attainable levels reported in the literature.[1,2]

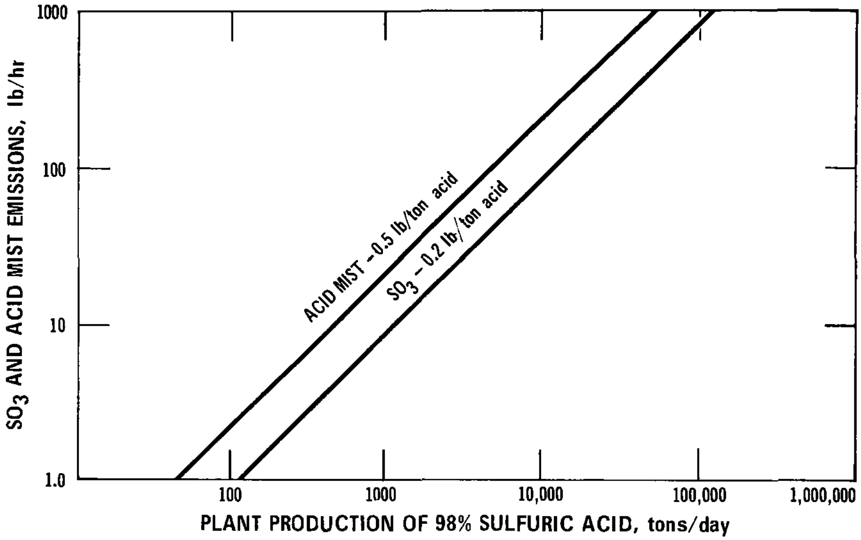

Figure 3. Attainable acid mist and SO_3 emission levels.

SAMPLING AND MONITORING

Since the value of any chemical determination of emission concentrations is only as good as the sampling procedures and analytical techniques used, it is strongly recommended that prescriptions for sound analytical techniques, and the best available sampling equipment and procedures be incorporated into proposed regulations.

It is recommended that the most serious type of pollution, SO_2, be monitored on a continuous basis. Several manufacturers have commercially available equipment that can easily be adapted to do continuous monitoring of the SO_2-tail-gas emissions. It is also recommended that the SO_3 and acid-mist emissions be determined regularly, either once each work shift or every 8 hours.

The modified Monsanto Company technique has been used by APCO for determining the sulfuric acid mist emissions, as have the Shell Development Company and the Chemical Construction Company technique for determining the sulfur trioxide emissions. Detailed descriptions of these analytical techniques can be found in the joint MCA-PHS study mentioned earlier.[2] While these techniques have been acceptable, APCO is currently developing more reliable standard sampling and analytical procedures that will be used for monitoring pollutants emitted from new installations. These procedures will be forthcoming in the near future and it is strongly encouraged that they be adapted for monitoring emissions at both new and existing plants.

SUMMARY OF SUGGESTED LIMITS

1. Contact sulfuric acid plants can be designed to meet an SO_2-tail-gas-emission ceiling of 6.5 lb/ton of acid produced. This is equivalent to the level attainable with both dual-absorption plants and commercially operating SO_2-control processes.

2. Although, at present, commercially available SO_2 control processes and dual-absorption modification schemes can only reduce the SO_2 emissions to 6.5 lb/ton of acid produced, promising pilot-scale studies indicate that SO_2 emission levels of 2.0 lb/ton of acid produced are attainable and probably could be applied to commercial installations.

3. Appropriate equipment is commercially available and could be installed in all new and existing acid plants to reduce the acid mist emission levels to 0.5 lb/ton of acid produced.

4. Efficient absorber operation can limit sulfur trioxide levels to 0.2 lb/ton acid produced on both new and existing installations.

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