

AMMONIA INJECTION: A ROUTE TO CLEAN STACKS

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INTRODUCTION

Reduction in SO₂ emissions from coal-burning powerplant stacks is essential to minimize atmospheric pollution from this source. Projections of energy demand show that by 1980 coal will account for about 25 million tons of total sulfur oxides output, mostly SO₂, unless effective control methods are developed.

A vapor phase ammonia injection process for SO₂ removal is being developed at the Morgantown (W. Va.) Energy Research Center. In laboratory research with simulated stack gas containing 4,200 ppm SO₂ (equivalent to 6.0 percent sulfur in coal), essentially complete removal of SO₂ from the gas phase was effected by ammonia injection (2).¹ Preliminary work has since been carried on with a small pilot-scale installation in which the sulfur products from the vapor phase reaction are removed in a water scrubber. This paper presents additional data from the laboratory work and the pilot-scale installation.

DESCRIPTION OF PROCESS

In the vapor phase ammonia injection process water (or steam) and gaseous ammonia are injected to the stack gas while the gas is at some temperature (>160° F) above that at which ammonium sulfite, the principal product, decomposes (140° to 158° F) (4). After the water is vaporized and the reactants thoroughly mix, the gas is cooled below 140° F and the finely divided salt particles separate from the gas as a smoke or fume ($d_p = 0.01$ to 1.0 micron). The entrained solids, salt particles and fly ash, are then recovered concurrently.

The process offers high versatility in the removal of the entrained solids. They can be removed in either a dry or wet state, and if removed by a wet method, several alternatives are available for regenerating ammonia for reuse. Furthermore, since each salt particle could contain over a million SO₂ molecules, removal of SO₂ as a solid could provide more effective gas cleaning at reduced capital and operating costs. For example, the usual method for cleaning stack gas in modern powerplants is depicted in figure 1(A); after partial recovery of heat, ash is removed in an electrostatic precipitator prior to release of the gas to the atmosphere. Proposed modifications to this mode of cleaning in conjunction with ammonia injection also are shown for dry removal of the salt particles along with the ash in a precipitator as indicated in figure 1(B), or by dry removal of ash followed by wet removal of the salts and residual ash as indicated in figure 1(C). Results of qualitative tests in a precipitator indicate the salts are collectible in the dry state, as suggested, but no attempts have been made to secure quantitative data. If collected dry, the salt-ash mixture could be utilized as a soil conditioner or low-grade fertilizer and regeneration of ammonia would not be necessary.

If a wet method for collection is selected, ammonia can be regenerated from the salt solution by reaction with a readily available metal oxide, such as lime or zinc oxide, with formation of a stable sulfur product for disposal. These metal oxides, however, as well as their reaction products, are insoluble and could cause deposition on heat transfer surfaces and/or clogging in the regenerating equipment. Therefore, as indicated in figure 2, to insure continuity and reliability of the process, a soluble metal oxide was utilized (in the form of sodium hydroxide solution) to regenerate the ammonia in the experimental work described. This procedure also allows more effective utilization of the metal oxide; the soluble oxide (NaOH) can be regenerated in batch equipment outside the continuous portion of the process by reaction with either the aforesaid insoluble reactants, lime or zinc oxide. Better control is afforded in a batch reactor with more efficient use of reactants.

LABORATORY DATA

Published data (2) from the laboratory work on the vapor phase reaction as well as unpublished data on kinetics of the reaction are presented for purposes of clarity.

¹Underlined numbers in parentheses refer to references at the end of this paper.

Figure 3 shows the effect of adding various quantities of ammonia to an SO_2 -laden gas stream in the presence of an excess of water vapor in the laboratory-scale equipment. Essentially complete removal of SO_2 from the gas phase is effected when ammonia additions are actually slightly less than the calculated stoichiometric quantity for sulfite formation. For example, at a gas flow rate of 10 scfh the calculated rate of ammonia addition for 3.6 percent solution is 1.86 milliliters per minute for removing all SO_2 from a gas containing 4,200 ppm, but no SO_2 was detected at the rate of 1.74 milliliters per minute. It is obvious that some bisulfite salt is formed in the reaction of SO_2 with ammonia and water vapor. The kinetics of the reactions are indicated to be adequate for commercial utilization by the curves given in figure 4, wherein residence time in the reactor was less than 0.4 second at a gas flow rate of 70 scfh, the highest tested.

PILOT-SCALE EQUIPMENT

The entire pilot-scale installation consists of a coal combustor, cyclone separator, two heat exchangers, scrubber, regenerator, and exhaust fan. The scrubber and regenerator are equipped with heat transfer coils and all equipment in contact with the scrubber liquid is made of stainless steel. Gas-sampling ports are installed upstream and downstream of the scrubber. Process data are provided by three recording instruments: a liquid conductivity meter, a pH analyzer, and a flame photometric SO_2 analyzer. This type of analyzer detects sulfur regardless of the compound in which the sulfur occurs.

Combustion gas is generated by burning coal at rates up to 10 lb/hr. A portion of the gas is cooled to about 400° F, is passed through the cyclone to remove most of the fly ash, and is further cooled (to about 160° F) before entering the scrubber vessel above the liquid level as shown previously in the flowsheet of figure 2. A liquid spray in the lower portion of the vessel cools the gas to about 130° F prior to actual scrubbing. After scrubbing, the clean gas, saturated with water vapor, flows through a mist eliminator to a stack at about 115° F. Sulfur dioxide content of the gas is monitored at the cyclone outlet (before reactant injection) and at the scrubber outlet.

Most of the scrubber liquor is cooled (105° F) and recycled in the raw state. Part of the cooled liquor is filtered to remove accumulated ash particles and flows through the pH meter, conductivity meter, and then to the cooling spray. Another portion (without cooling) is filtered and flows to the regenerator at a controlled rate. As shown, sodium hydroxide solution also flows to the regenerator at a controlled rate. The mixture of solutions is heated to about 220° F and chemical reaction releases the ammonia and steam; these products return to the system under the force created by their vapor pressures.

Prior to use of sodium hydroxide, lime and zinc oxide slurries were tested successfully for regenerating ammonia, but these insoluble metal oxides could not be effectively maintained as a suspension. Both reactant and product settled in the regenerator to ruin heat transfer and/or clog the liquid drain. Therefore, as stated earlier, sodium hydroxide was utilized to promote continuity and reliability to the system.

PILOT-SCALE OPERATIONS

Total liquid in the scrubber system in the pilot equipment is maintained at about 16 liters. The raw solution in the scrubber is recycled to the distribution plate at rates from 0.2 to 0.7 gal per minute. The filtered portion that flows through the monitoring instruments and the cooling spray is maintained constant at a rate of 0.2 gal per minute. Flow of solution to the regenerator is controlled from zero to 4.2 liters per hour, depending on the rate at which ammonia is needed for the vapor phase reaction.

At the start of an operation, water or ammonium sulfite solution can be used as the scrubbing liquid. If water is used, primary ammonia and steam must be injected to the gas and the scrubbing operation must continue for several hours prior to regeneration of any ammonia. This builds up a salt solution. If a sulfite solution is used (3.0 percent), ammonia regeneration can begin immediately.

Preliminary tests with the pilot-scale unit confirmed laboratory results and showed that essentially complete removal of SO_2 from the gas phase could be achieved in the larger equipment by injecting ammonia and steam. Many other tests were conducted to isolate the effects of some operating variables, including minimal development of the water scrubber. Results of these tests, however, are not described; the data are outside the scope of this paper.

Final selection of scrubbing medium allowed provision for a liquid reservoir on a distribution plate as described by Kempner, et al (1), and indicated in figure 2. Single or multiple layers of 50-mesh screen were used to obtain liquid-solid contact and to cause wetting and removal of the solids. Results of selected tests of a few hours duration are given in table 1, wherein, unless otherwise noted, 1.0 scfh ammonia and 2.0 lb per hour steam were injected into a flow of 500 scfh combustion gas. Under these conditions mass flow rate was about 350 lb/hr-ft². Calculated salt content of the gas was 0.13 gram per cubic foot based on SO₂ concentration of 900 ppm, as determined by wet chemical analysis (analyzer not installed). Ash content was determined by sampling the gas at the specified isokinetic rate. Because of combustor limitations, higher mass flow rates could not be tested on a continuous basis.

As shown, the scrubber removes well over 90 percent of the salt and residual ash particles using a single screen atop the liquid reservoir. This degree of removal is attainable at a pressure loss under 2 inches of water and demonstrates that the solids are removed with very short contact time in the cleaning equipment.

After installation of the sulfur analyzer, continuous monitoring was provided. Results of a continuous operation using this scrubber concept in the pilot-scale unit covering 105 consecutive hours (4.4 days) are summarized in table 2. During this period the scrubber was off line only one hour to clean a clogged line. At the start of the operation the scrubber contained a 2.9 percent solution of ammonium sulfite which had been prepared and used previously for almost 8 hours. During extended tests, pressure loss through the scrubber ranged from 2.0 to 2.2 inches of water. The liquid-gas ratio was about 5.0 lb/lb. Throughout the test all ammonia was regenerated from the scrubber liquor using sodium hydroxide solution except for a single 3-hour span during which 1.0 scfh of ammonia was added to test the effect of higher pH in the scrubbing liquid. Operation during the final 20 hours is not representative. This period was devoted to obtaining specific essential data for other purposes.

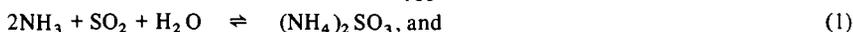
A calculated ammonia balance (using conductivity and pH measurements) over the first 83 hours of operation showed 4.23 g-moles ammonia loss due to all causes, which is representative of a maximum stack loss of 3.53 cubic feet of ammonia. Since a total of 41,500 ft³ of gas was processed, ammonia loss was about 85 ppm. On a once-through basis this represents about a 4 percent loss, using an average SO₂ inlet of 1,050 ppm with 90 percent removal. Other potential losses can occur as solid salts out the stack, unregenerated salt solution, and leakage. Sulfur dioxide concentration in the effluent gas remained consistent, always ranging below about 220 ppm (usually below 100 ppm) and demonstrating a removal efficiency above 77 percent. This removal effectiveness was accomplished at a pH that never exceeded 5.4 and usually was in the range 3.5 to 4.5.

Further analysis of the data in table 2 reveals apparent irregularities in performance of the process. For example, at an elapsed time of 61 hours scrubber solution was being regenerated at a rate of 2.1 liters per hour to supply ammonia for the vapor phase reaction. Removal efficiency was only 77 percent. Six hours later while SO₂ content of the inlet gas was higher (1,000 vs 910 ppm) scrubber solution flow rate to the regenerator was zero, but the SO₂ content of the purified gas was only 10 ppm; removal efficiency was 99 percent. Other similar examples can be isolated. These conflicting data indicate some of the complexities of the process:

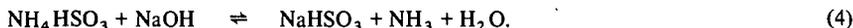
1. If all SO₂ is not converted to the solid state, part or all of the remainder is absorbed during the scrubbing operation. The degree to which this action occurs appears to be directly proportional to the pH of the scrubbing solution and the rate at which scrubber solution is recycled to the distribution plate.
2. At any given flow rate of scrubber solution to the regenerator, the volume of ammonia regenerated appears to vary directly with solution pH, salt concentration, and regenerator temperature (up to about 220° F).
3. Excess sodium hydroxide solution (metal oxide) must be available at all times in the regenerator for reaction with the scrubber salt solution.

PROCESS CHEMISTRY

Initial chemical reactions in the vapor state are postulated as,



After the scrubbing operation, the solution of salts is exposed to sodium hydroxide solution; chemical reaction releases ammonia and steam for recycle,

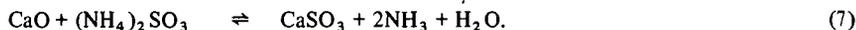


During the scrubbing operation some of the sulfites are oxidized to sulfates; the oxidation products appear to be continuously removed from the scrubbing liquor by similar reactions in the regenerator,



Moreover, it is evident that sulfur trioxide also is removed from the gas as shown by the analyses listed in table 2 (0 ppm SO_2 , 72–89 hours). Ammonia can be regenerated from the sulfates as shown in reactions (5) and (6). Other reactions that may occur could remove selected components from the combustion gas, such as NO_2 or CO_2 , but the high reactivity of the sodium ion should induce reaction with the ammonium salt produced, and thereby minimize this potential loss of ammonia.

As previously indicated, other chemical means are available for regenerating ammonia, such as reaction with lime or zinc oxide slurries, both of which have been tested successfully in the pilot installation. These reactions are demonstrated by the equation,



In this reaction, however, both the reactant and the sulfur product are insoluble and could interrupt process continuity by deposition and clogging if installed in the continuous portion of a recycle system. Furthermore, the sodium salt solution from the regenerator can be isolated for batch reaction with a cheap insoluble metal oxide, such as lime slurry,



After concentration, the sodium hydroxide can be recycled. In addition, all disposable salts can be oxidized to the most stable state, e.g., calcium sulfate.

Another means for disposal of a sulfur product could involve reaction of hydrogen sulfide with either the ammonium or sodium sulfite solution to produce elementary sulfur. Additional processing is required, but the weight of disposable product could be reduced by a factor of about four. Moreover, under select conditions sale of sulfur could offset at least part of the processing costs.

DISCUSSION

The vapor phase reaction between water, ammonia, and sulfur dioxide is essentially instantaneous in the presence of an excess of water vapor. The reaction occurs when the mixture is cooled below the decomposition temperature of the product compound(s). In the presence of adequate ammonia virtually complete removal of SO_2 is available providing that the reactants are thoroughly mixed prior to the cooling operation.

The apparent cause for such effective removal of the finely-divided salt particles ($d_p = 0.01$ to 1.0 micron) and the residual ash particles is the process of nucleation that occurs when excess water in the gas condenses on the solids during the cooling operation. This process allows the soluble particles to be dissolved in the scrubbing liquid and the insoluble ones to be enlarged for easier capture. Theoretically, the ash particles could serve as

condensation nuclei for the salt particles; the ash particles then could be wetted by dissolution of the adhering salts and could cause effective size growth in the insoluble solids with concurrent ease of removal.

Scrubber liquid can be recycled to obtain a salt solution of any desired concentration prior to regeneration of ammonia from the solution. The upper limit on solution concentration presumably will be controlled by the vapor pressures of the components, ammonia and sulfur dioxide. At high pH, ammonia vapor predominates; at low pH, sulfur dioxide is the dominant vapor. Therefore, optimum recycle of the scrubber liquid will be controlled at low pH and dilute solution concentration concurrent with and relative to equipment (capital) and operating costs. A solution having low pH (e.g., 6.0) requires stainless steel or protected carbon steel to prevent corrosion.

The process of nucleation apparently is dominant in removal of the entrained solid salts, whereby most of the residual ash also is removed by the scrubbing liquid with low contact time. Whatever the reason, the process is effective at low pressure loss.

Batch processing of the sodium salt solution from the regenerator allows more effective utilization of lime. However, disposal of product salts remains a problem.

Furthermore, after ammonia injection, effective removal of sulfur dioxide as a solid can be accomplished with water or a dilute salt solution. As exemplified by work conducted at Tennessee Valley Authority (TVA) (3) for removal of SO_2 by scrubbing with ammoniacal solution, the scrubber solution must have high pH (~ 6.4) and must be relatively concentrated to provide the required driving force for effective absorption. Under these conditions at least one additional stage of scrubbing is required (with increased pressure loss) to prevent gross loss of ammonia.

CONCLUSIONS

Ammonia injection followed by gas cooling is demonstrated as an effective means for removing SO_2 from the gas phase in combustion gas mixtures. Product sulfur-bearing salts, which are entrained in the gas, can be removed in a single stage water scrubber, and ammonia is effectively regenerated from the scrubber liquid through reaction with sodium hydroxide solution. Ammonia losses are minimal and presumably can be reduced even further through use of a second stage of scrubbing. All reactants and products in the continuous cycle of the process are water soluble, so no equipment clogging occurs; process continuity and reliability are not interrupted.

REFERENCES

1. Kempner, S. K., E. N. Seiler, and D. H. Bowman. Performance of Commercially Available Equipment in Scrubbing Hydrogen Chloride Gas. *J. APCA*, v. 20, No. 3, March 1970, pp. 139-143.
2. Shale, C. C., D. G. Simpson, and P. S. Lewis. Removal of Sulfur and Nitrogen Oxides from Stack Gases by Ammonia. *Chem. Eng. Prog. Symp. Ser.*, v. 67, No. 115, 1971, pp. 52-58.
3. Tennessee Valley Authority. Sulfur Oxide Removal from Power Plant Stack Gas; Ammonia Scrubbing. Conceptual Design and Cost Study Series, Study No. 3. Prepared for Nat. Air Pollution Control Assn., PB 196804, September 1970, pp. 58-61.
4. Weast, R. C., S. M. Selby, and C. D. Hodgman. Handbook of Chemistry and Physics, 45th ed., The Chemical Rubber Co., Cleveland, O., 1964, p. B-152.

TABLE 1. — Scrubber operating data

| Test no. | Scrub. medium, screen | Liquid recycle rate, gpm | Pressure loss in H ₂ O | ^{1/} Resid. NH ₃ , gm/ft ³ x 10 ⁻³ | ^{2/} Resid. ash gr/ft ³ x 10 ⁻³ | Removal eff., percent | |
|----------|--------------------------|-----------------------------|--------------------------------------|---|---|-----------------------|------|
| | | | | | | Salt | Ash |
| 1 | ^{3/} None | 0.4 | 1.5 | 15.5 | 23 | 88.1 | 92.8 |
| 2 | 1 | .4 | 2.5 | 6.8 | .13 | 94.8 | 95.9 |
| 3 | 1 | .4 | 2.5 | 6.4 | 20 | 95.1 | 93.7 |
| 4 | ^{4/} 1 | .2 | 1.8 | 6.6 | 0.6 | 94.9 | 99.8 |
| 5 | ^{4/} 1 | .4 | 2.9 | 5.8 | 0.3 | 95.5 | 99.9 |
| 6 | 2 | .2 | 3.5 | 4.8 | 11 | 96.3 | 96.6 |
| 7 | 3 | .2 | 4.0 | 5.5 | 11 | 95.8 | 96.6 |
| 8 | ^{4/} 3 | .4 | 4.6 | 5.6 | 12 | 95.7 | 96.2 |
| 9 | ^{5/} 3 | .2 | 3.8 | 5.5 | 15 | 95.8 | 95.3 |
| 10 | 3 | .4 | 5.5 | 5.4 | 9 | 95.8 | 97.2 |

^{1/} Calculated salt produced, 0.13 gram per ft³.

^{2/} Ash concentration inlet gas, 0.32 grain per ft³.

^{3/} Distribution plate only, 0.1- in holes.

^{4/} Steam rate 3.0 pph.

^{5/} Steam rate 4.0 pph.

TABLE 2. — Representative data on continuous SO₂ removal by NH₃ injection

| Cumulative time, hrs | pH scrubber solution | Solution conductivity, mhos x 10 ⁴ | SO ₂ , ppm | | Solution regen- eration rate, cc/hr | Removal efficiency, pct |
|-------------------------|-------------------------|--|-----------------------|-------------------|--|----------------------------|
| | | | Inlet | Outlet | | |
| 3.0 | 5.20 | 5.40 | 1,000 | 150 | 2,400 | 85 |
| 9.5 | 4.85 | 5.40 | 1,000 | 45 | 2,000 | 95 |
| 15.0 | 4.30 | 5.18 | 1,000 | 120 | 1,056 | 88 |
| 20.0 | 4.45 | 5.01 | 1,225 | 130 | 1,440 | 89 |
| 24.0 | 4.30 | 5.10 | 1,250 | 90 | 1,056 | 93 |
| 29.0 | 4.18 | 5.30 | 1,250 | 220 | 1,056 | 82 |
| 35.0 | 5.02 | 5.50 | 1,650 | 220 | 1,056 | 87 |
| 43.0 | 4.30 | 4.89 | 885 | 25 | 600 | 97 |
| 47.0 | 3.80 | 4.80 | 1,030 | 39 | 240 | 96 |
| 51.0 | 3.03 | 4.83 | 930 | 51 | 240 | 94 |
| 55.0 | 4.23 | 4.11 | 910 | ^{1/} 20 | 2,100 | 97 |
| 61.0 | 4.39 | 3.69 | 910 | 210 | 2,100 | 77 |
| 67.0 | 5.42 | 3.49 | 1,000 | 10 | 0 | 99 |
| 72.0 | 4.02 | 4.45 | 930 | 0 | 0 | 100 |
| 76.0 | 3.16 | 4.74 | 1,090 | 0 | 1,056 | 100 |
| 83.0 | 4.54 | 3.90 | 1,200 | 0 | 2,100 | 100 |
| 89.0 | 4.29 | 3.50 | 1,100 | 0 | 2,100 | 100 |
| 93.0 | 4.02 | 2.90 | 1,030 | 220 | 2,400 | 79 |
| 97.0 | 2.90 | 3.05 | 780 | 760 | 2,700 | 3 |
| 101.5 | 3.98 | 1.93 | 780 | ^{2/} 505 | > 4,200 | 35 |
| 102.0 | 3.78 | 1.80 | 1,030 | 505 | > 4,200 | 50 |
| 104.0 | 4.72 | 1.55 | 1,400 | 590 | > 4,200 | 58 |
| 105.0 | 3.95 | 1.50 | 1,900 | 910 | > 4,200 | 52 |

^{1/} Analysis by wet chemical method, 30 ppm.

^{2/} Analysis by wet chemical method, 510 ppm.

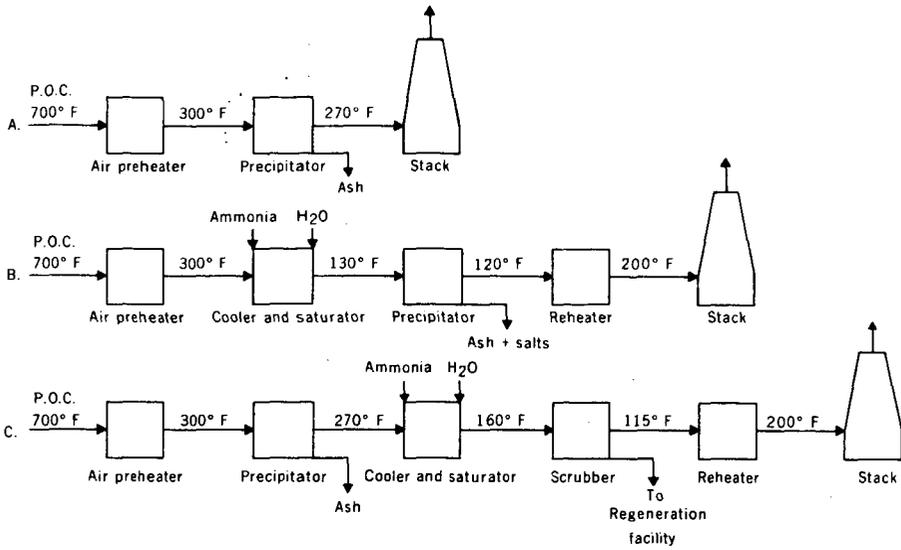


FIGURE 1. — Proposed Modifications for Stack Gas Cleaning Methods

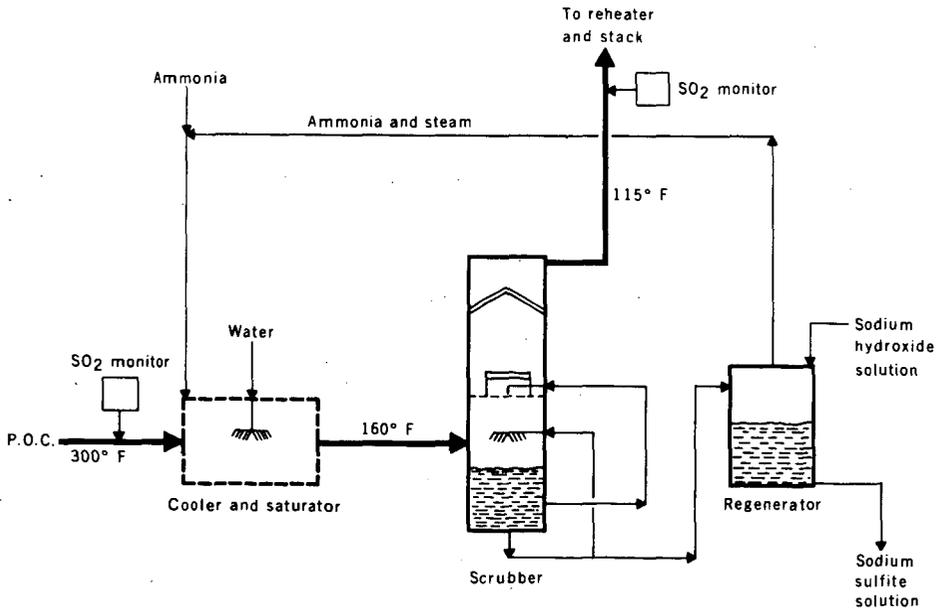


FIGURE 2. — Flow Diagram for Pilot-Scale SO₂ Removal System

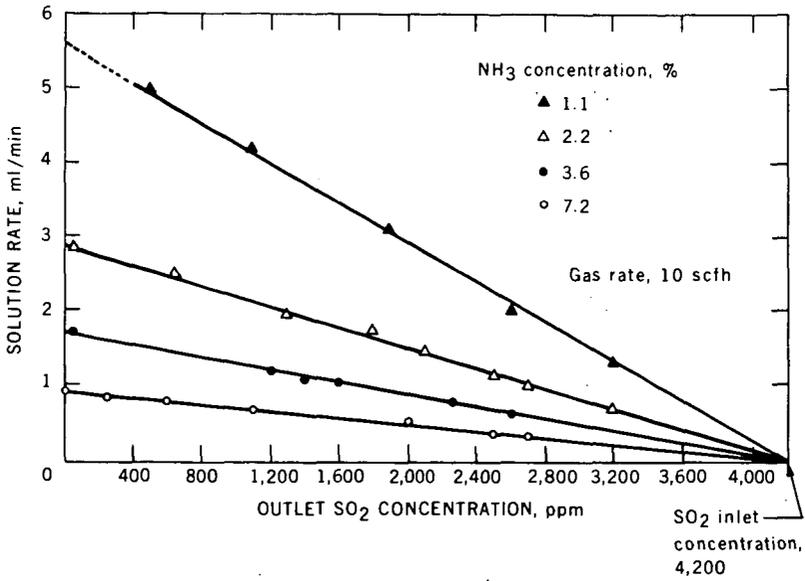


FIGURE 3. - Effect of Ammonia for Removing SO₂ From Gas Phase

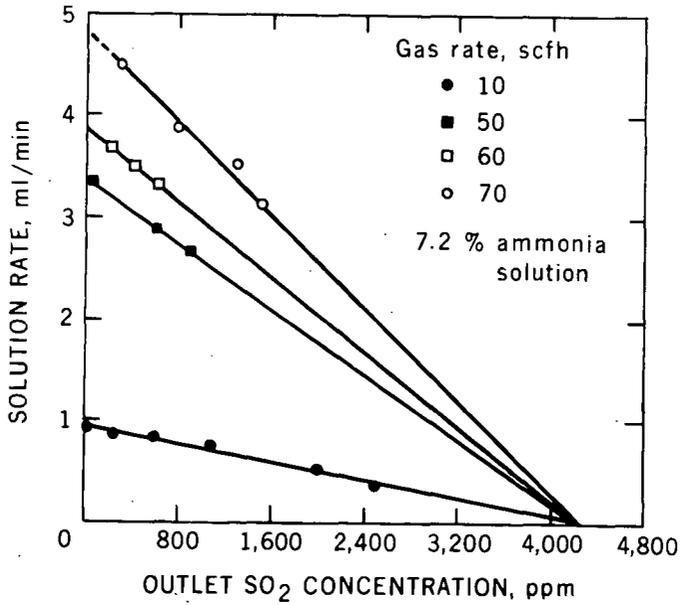


FIGURE 4. - Effect of Gas Flow Rate on Removal of SO₂ Using Ammonia