system modifications are presented in more detail in Chapters 10 and 13.

For fuels which do not contain significant amounts of chemically bound nitrogen, such as natural gas, thermal NO_x is the primary overall contributor to NO_x emissions. In these cases, the technologies described above are particularly effective in NO_x emission control.

Fuel NO_x

The major source of NO_x emissions from nitrogen bearing fuels such as coal and oil is the conversion of fuel bound nitrogen to NO_x during combustion. Laboratory studies indicate that fuel NO_x contributes approximately 50% of the total uncontrolled emissions when firing residual oil, and more than 80% when firing coal. Nitrogen found in fuels such as coal and residual oils is typically bound to the fuel as part of organic compounds. During combustion, the nitrogen is released as a free radical to ultimately form NO or N_2. Although it is a major factor in NO_x emissions, only 20 to 30% of the fuel bound nitrogen is converted to NO.

The majority of NO_x formation from fuel bound nitrogen occurs through a series of reactions which are not fully understood. It does appear, however, that this conversion occurs by two separate paths. These paths, primarily for coal, are represented in Fig 2.

The first path involves the oxidation of volatile nitrogen species during the initial phase of combustion. During the release, and prior to the oxidation of the volatile compounds, nitrogen reacts to form several intermediate compounds in the fuel rich flame regions. These intermediate compounds are then oxidized to NO or reduced to N_2 in the postcombustion zone. The formation of either NO or N_2 is strongly dependent on the local fuel/air stoichiometric ratio. It is estimated that this volatile release mechanism accounts for 60 to 90% of the fuel NO_x contribution.

The second reaction path involves the release of nitrogen radicals during combustion of the char fraction of the fuel. These reactions occur much more slowly than the reactions involving the volatile species.

Conversion of fuel bound nitrogen to NO_x is strongly dependent on the fuel/air stoichiometry but is relatively independent of variations in combustion zone temperature. Therefore, this conversion can be controlled by reducing oxygen availability during the initial stages of combustion. With this reduction, a major portion of the nitrogen released during devolatilization reduces to N_2. This is because hydrocarbon radicals, also released during devolatilization, compete with the nitrogen for the available free oxygen. Techniques such as controlled fuel-air mixing and staged combustion provide a significant reduction in NO_x emissions by controlling stoichiometry in the initial devolatilization zone.

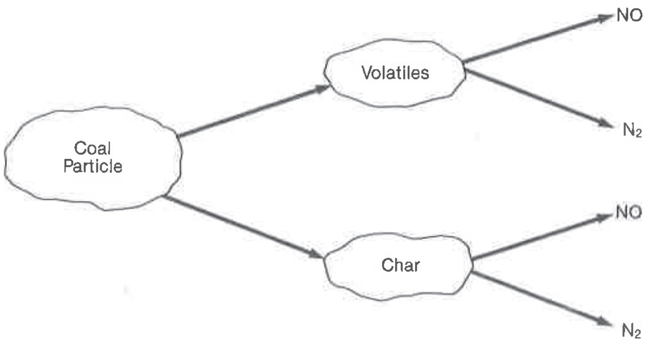


Fig. 2 NO_x formation from nitrogen contained in coal during combustion.

A portion of the NO_x that is formed by oxidation of the fuel bound nitrogen under fuel rich conditions is referred to as *prompt* NO_x, identified through the research of C.P. Fenimore.[3] The name is derived from its formation very early during the combustion process. It was originally identified as the difference between observed and predicted thermal NO emissions.

Prompt NO_x occurs through the formation of intermediate hydrogen cyanide (HCN) species and the reaction between molecular nitrogen and hydrocarbon compounds. This reaction is then followed by the oxidation of HCN to NO.

Although prompt NO_x formation normally has a weak temperature dependence, this dependence can become strong under fuel rich conditions. Modern burners are designed to reduce peak flame temperatures by controlling the rate of fuel and air mixing. Combustion is initiated under fuel rich conditions and this fuel rich zone is where prompt NO_x is formed. Prompt NO_x can contribute from near zero to more than 100 ppmv of NO.

Health and environmental effects of NO_x

Once released into the atmosphere, NO_x becomes a contributor to ozone/photochemical smog, acid rain, particulate matter and potential airborne carcinogens. Each of these pollutants has a significant effect on human health and the environment. However, as discussed in Chapter 32, automobiles and other vehicles are the major source of NO_x with utility power plants contributing less than one third of the total United States (U.S.) emissions.

Ozone/photochemical smog

Naturally occurring ozone, found in the upper atmosphere, is necessary for man's existence. However, man-made ozone, formed in the lower atmosphere, is considered a pollutant. This man-made ozone, formed by a reaction of hydrocarbons and NO_x in the presence of sunlight, is a major component of urban photochemical smog.[4]

Another major component of photochemical smog is NO_2. Once emitted, the NO contained in the flue gas is oxidized to NO_2, which is a yellow-brown gas and is also an oxidant. Urban smog is also made up of a variety of other components.

Acid rain

NO_x and sulfur dioxide (SO_2) contribute to the formation of acid rain,[4] which includes a dilute solution of sulfuric and nitric acids with small amounts of carbonic and other organic acids. The NO_x and SO_2 react with water vapor to form acidic compounds; these acids account for more than 90% of acid rain. Nitric acid is formed through the reaction:

$$NO_2 + OH \rightarrow HNO_3 \qquad (4)$$

Most acid rain control has concentrated on SO_2 contributions instead of those due to NO_x because it is estimated that NO_x contributes less than one third of the acid rain generated.

Particulate matter

NO_x can also contribute to ambient particulate matter. In the atmosphere NO_x reacts with other airborne chemicals to create nitrates. NO_x also promotes the transformation of SO_2 into sulfate particulate compounds.

Controlling NO_x emissions in steam generating equipment

An understanding of the mechanisms and chemical reactions that produce NO_x emissions has enabled engineers and scientists to develop techniques for reducing emissions of this pollutant. Because NO_x is formed during combustion, research has centered on controlling NO_x at the source. The application of techniques that control fuel-air mixing rates and peak combustion temperatures has been effective in reducing these emissions.

NO_x emissions may be controlled through careful fuel selection and selective fuel switching. Once the fuel is chosen, NO_x emissions are minimized by using low NO_x combustion technology and postcombustion techniques. Typically, the fuel is selected by overall economic considerations. Combustion technology based NO_x control is then typically the lowest overall cost approach provided that it will meet local and federal emissions requirements. Where further control is needed, postcombustion NO_x control is added.

Precombustion fuel effects

Unlike sulfur and particulate constituents in coal, nitrogen species contained in the fuel can not be easily reduced or removed. Therefore, the most common precombustion option for reducing NO_x levels is to switch to a fuel with inherently lower nitrogen content. For boilers capable of firing multiple fuels with minimal impact on the steam cycle, this may be the most cost effective solution.

Coal combustion generally produces the highest NO_x emissions. Oil combustion generates less NO_x while gas firing produces even less. When firing oil fuels, a reduction in fuel nitrogen results in reduced NO_x emissions. However, there does not appear to be a similar correlation between coal nitrogen content and NO_x generation. Other factors in coal chemistry including volatile species, oxygen and moisture content appear to dominate the formation of NO_x during coal combustion. Therefore, reducing coal nitrogen content may not provide a corresponding NO_x reduction.

Combustion techniques

NO_x formation is promoted by rapid fuel-air mixing. This produces high peak flame temperatures and excess available oxygen which, in turn, promotes NO_x emissions. Combustion system developments responsible for reducing NO_x formation include low NO_x burners, such as the coal-fired burner shown in Fig. 3, staged burning techniques, and flue gas recirculation (FGR). The specific NO_x reduction mechanisms include controlling the rate of fuel-air mixing, reducing oxygen availability in the initial combustion zone, and reducing peak flame temperatures. Modern systems can emit less than one third of the NO_x produced by older units.

Additional information regarding the details of the combustion process, combustion techniques and hardware used to control NO_x can be found in Chapters 10, 13, 15, 16, 17 and 29. Information on uncontrolled and controlled NO_x emissions is also presented.

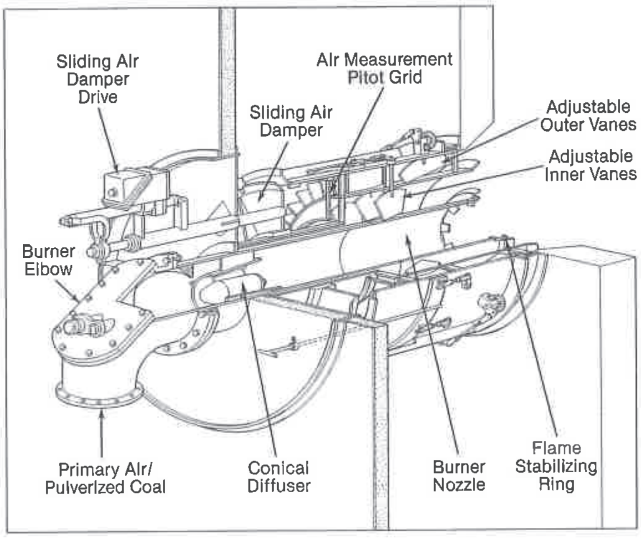


Fig. 3 DRB-XCL™ low NO_x burner for coal firing.

Postcombustion techniques

Many localities require lower NO_x emissions than economically possible by combustion modifications alone. To achieve further reductions, additional techniques are applied downstream of the combustion zone. These postcombustion control systems are referred to as selective noncatalytic reduction (SNCR) and selective catalytic reduction (SCR). In either technology, NO_x is reduced to nitrogen (N_2) and water (H_2O) through a series of reactions with a chemical agent injected into the flue gas.

The most common chemical agents used in commercial applications are ammonia and urea for SNCR and ammonia for SCR systems. Most ammonia-based systems have used anhydrous ammonia (NH_3) as the reducing agent. However, due to the hazards of storing and handling NH_3, many systems use aqueous ammonia at a 25 to 28% concentration. Urea [$(NH_2)_2CO$] can be stored as a solid or mixed with water and stored in solution. An additional byproduct of the urea injection is carbon dioxide (CO_2).

Selective noncatalytic reduction technology

There are currently two basic selective noncatalytic reduction (SNCR) processes available. An ammonia-based system has been developed by Exxon and is called Thermal DeNO$_x$®. A urea-based technology has been developed under the sponsorship of the Electric Power Research Institute (EPRI). Although there are distinct differences to each technology, the overall processes are similar.

Both SNCR technologies inject a reducing agent into NO_x laden flue gas within a specific temperature zone or window. In addition, it is important to properly mix the chemical agent with the flue gas. Finally, the mixture must have adequate residence time for the reduction reactions to occur. The chemical reactions for both processes can be represented by:

Ammonia $$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O \qquad (5)$$

Urea $$2NO + (NH_2)_2CO + 1/2\ O_2 \rightarrow 2N_2 + 2H_2O + CO_2 \qquad \textbf{(6)}$$

The acceptable temperature range for either reaction is 1400 to 2000F (760 to 1093C), although temperatures above 1700F (927C) are preferred. Below 1600F (871C), chemical enhancers, such as hydrogen, are needed to assist the reactions. As the temperature increases within this range, the ammonia or urea may react with available oxygen to form NO_x. This reaction becomes significant at temperatures in excess of 2000F (1093C) and may become dominant as temperatures approach 2200F (1204C).

The application of SNCR technology to a municipal solid waste boiler is shown in Fig. 4. Multiple injection levels are used to maintain NO_x reduction efficiencies at acceptable levels as boiler load changes. Based on operating experience, four or more injection levels may be required for larger units. Multiple levels are required because the flue gas temperature profile changes with boiler load and the injection point for the ammonia or urea must be adjusted accordingly.

The SNCR system consists of storage and handling equipment for the ammonia or urea, equipment for mixing the chemical with the carrier (compressed air, steam or water), and the injection equipment. The key component, the injection system, consists of nozzles generally located at various elevations on the furnace walls to match the expected flue gas operating temperature. The number and location of the nozzles are established by the supplier and are based on obtaining good reagent distribution within the flue gas. Fig. 5 provides a simplified flow diagram for an ammonia-based SNCR system.

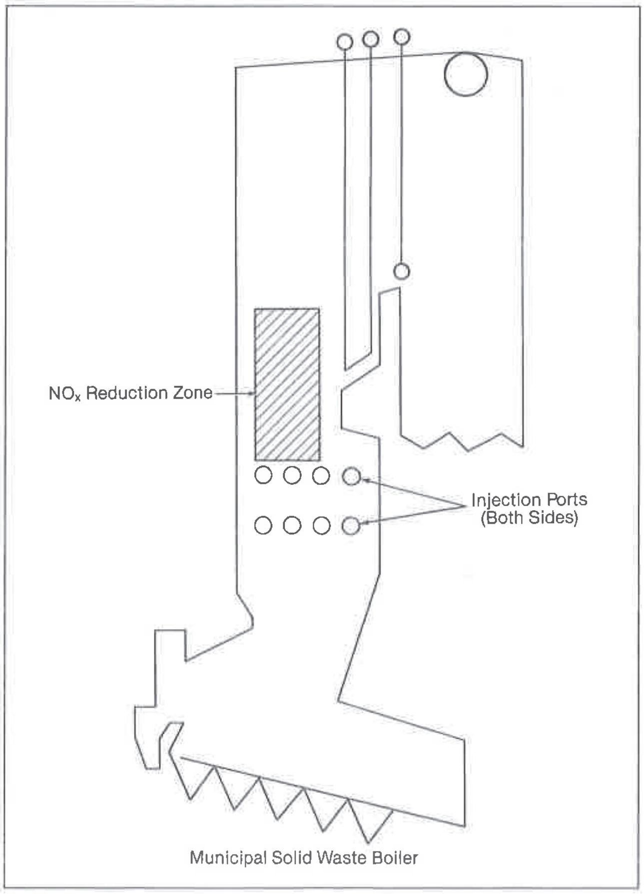


Fig. 4 Typical SNCR application.

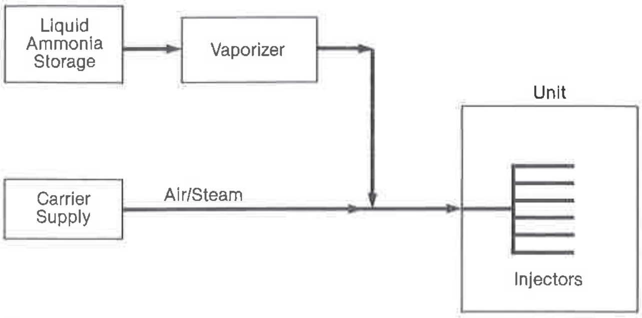


Fig. 5 SNCR deNO_x system.

One major difference between the ammonia and urea based processes is that the ammonia is usually injected into the gas stream in a gaseous state, whereas the urea is injected as an aqueous solution. The urea technology requires a longer residence time for reactions due to the time required to vaporize the liquid droplets once they are in the gas stream. However, as aqueous ammonia systems become more frequently specified, ammonia may also be injected as a liquid with additional residence time required for vaporization.

When injecting ammonia or urea it is important to control the excess unreacted ammonia. As flue gas temperatures are reduced, the excess ammonia can react with other combustion species, primarily sulfur trioxide (SO_3), to form ammonium salts. The major ammonium products formed are ammonium sulfate [$(NH_4)_2SO_4$] and ammonium bisulfate (NH_4HSO_4). Ammonium sulfate is a dry, fine particulate (1 to 3 microns in diameter) that may contribute to plume formation. The ammonium bisulfate is a highly acidic and sticky compound which, when deposited on downstream equipment such as air heaters, contributes to significant fouling and corrosion.

While NO_x reduction levels of 70% are possible under carefully controlled conditions, 30 to 50% reductions in NO_x emissions are more typically used in practice to maintain acceptable levels of reagent consumption and unreacted ammonia carryover.

Most of the current applications for these technologies have been on smaller municipal solid waste or biomass fueled boilers, where the appropriate temperature range is located in the upper furnace, as shown in Fig 4. (See also Chapter 27.) In large utility units, the proper temperature range occurs in the convection pass cavities, making application, especially on retrofits, more challenging. For these applications, overall control may be limited to the 20 to 40% range. New boiler applications may require special design of the boiler convection pass with a dedicated open cavity in an optimal temperature window for the reactions to occur (Fig. 6).

Selective catalytic reduction technology

Fundamental design considerations

Selective catalytic reduction (SCR) systems catalytically reduce flue gas NO_x to N_2 and H_2O using ammonia in a chemical reduction. This technology is the most effective method of reducing NO_x emissions especially where high removal efficiencies (70 to 90%) are required.

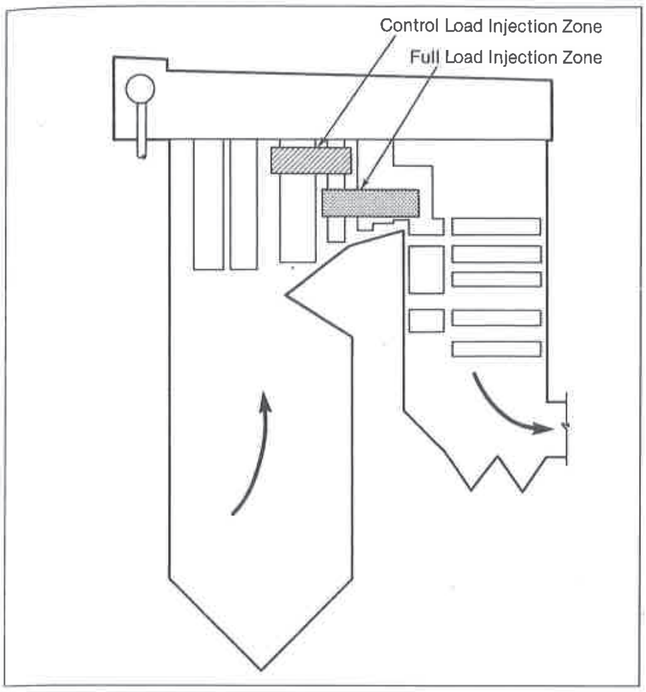


Fig. 6 Coal-fired utility boiler with SNCR temperature window location at full and part load.

Initial development of SCR technology began in Japan around 1963. Early laboratory tests included the evaluation of many catalyst formulations and their life expectancies, as well as process design optimizations. Development tests were followed by several catalytic pilot plant installations during the early 1970s; the first commercial installations occurred in 1978. As mandated by environmental regulations, SCR systems have been installed on utility boilers in Japan, Germany and other European countries. SCR technology has also been applied to U.S. installations primarily for gas turbines, combined cycle systems, and small industrial boilers and process heaters. Legislation passed in areas of California requires the use of this technology on utility installations. Environmental permitting considerations will likely require this technology on many new large installations during the 1990s. Typical examples of new and retrofit applications are shown in Figs. 7 through 9. There are more than 400 SCR systems throughout the world, covering a variety of fuels including natural gas, oil, coal and wood.

The NO_x reduction reactions take place as the flue gas passes through the catalyst chamber. Before entering the catalyst, ammonia is injected into and mixed with the flue gas as shown in Fig. 10. Once the mixture enters the catalyst, the NO_x reactions with NH_3 can be represented as follows:

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O \qquad (7)$$

$$2NO_2 + 4NH_3 + O_2 \rightarrow 3N_2 + 6H_2O \qquad (8)$$

As with SNCR systems, the SCR reactions take place within an optimal temperature range. A variety of catalysts are available. Most can operate within a range of 450 to 840F (232 to 449C), but optimum performance occurs between 675 and 840F (357 and 449C). The minimum temperature varies and is based on fuel, flue gas specifications and catalyst formulation. In addition, this minimum temperature tends to increase with flue gas sulfur dioxide content. This results in a smaller operating range as sulfur content increases in order to eliminate the formation of ammonium sulfate salts in the catalyst bed. Above the recommended temperature range, a number of catalyst materials tend to become less effective.

Catalyst formulation is the key to SCR system performance. Although catalyst formulations are proprietary, material typically falls into one of three categories: base metal, zeolite and precious metal.

Most of the operating experience to date has been with base metal catalysts. These catalysts use titanium oxide with small amounts of vanadium, molybdenum, tungsten or a combination of several other active chemical agents. The base metal catalysts are selective and operate in the specified temperature range. The major drawback of the base metal catalyst is its potential to oxidize SO_2 to SO_3; the degree of oxidation varies based on catalyst chemical formulation. The quantities of SO_3 which are formed can react with the ammonia carryover to form the ammonium sulfate salts as previously discussed. Proper system design and catalyst formulation can minimize this problem.

Zeolite catalysts are relatively new to NO_x emission control. These catalysts are aluminosilicate materials which function similarly to base metal catalysts. One potential advantage of zeolite is its higher operating temperature of 970F (521C). This catalyst may also oxidize SO_2 to SO_3 and must be carefully matched to the flue gas conditions.

Precious metal catalysts are generally manufactured from platinum and rhodium. As with the zeolite units, there is little operating experience with these catalysts. They also require careful consideration of flue gas constituents and operating temperatures. While effective in reducing NO_x, these catalysts can also act as oxidizing catalysts, con-

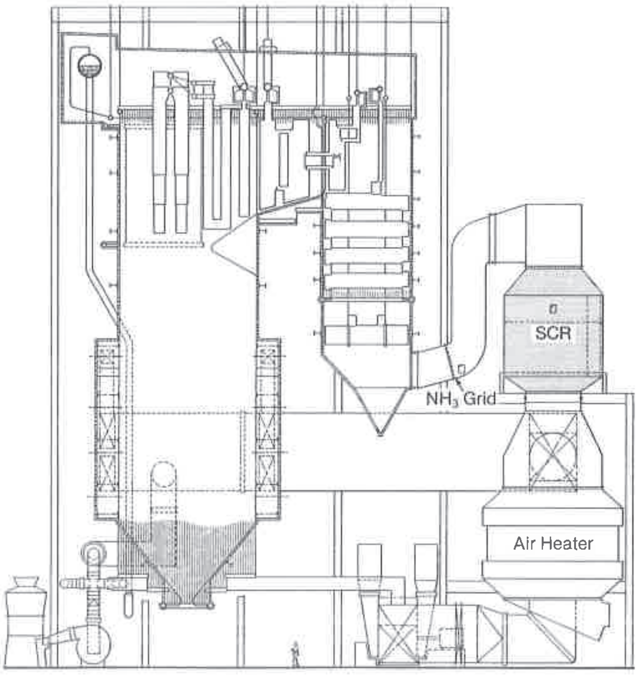


Fig. 7 New utility boiler with SCR.

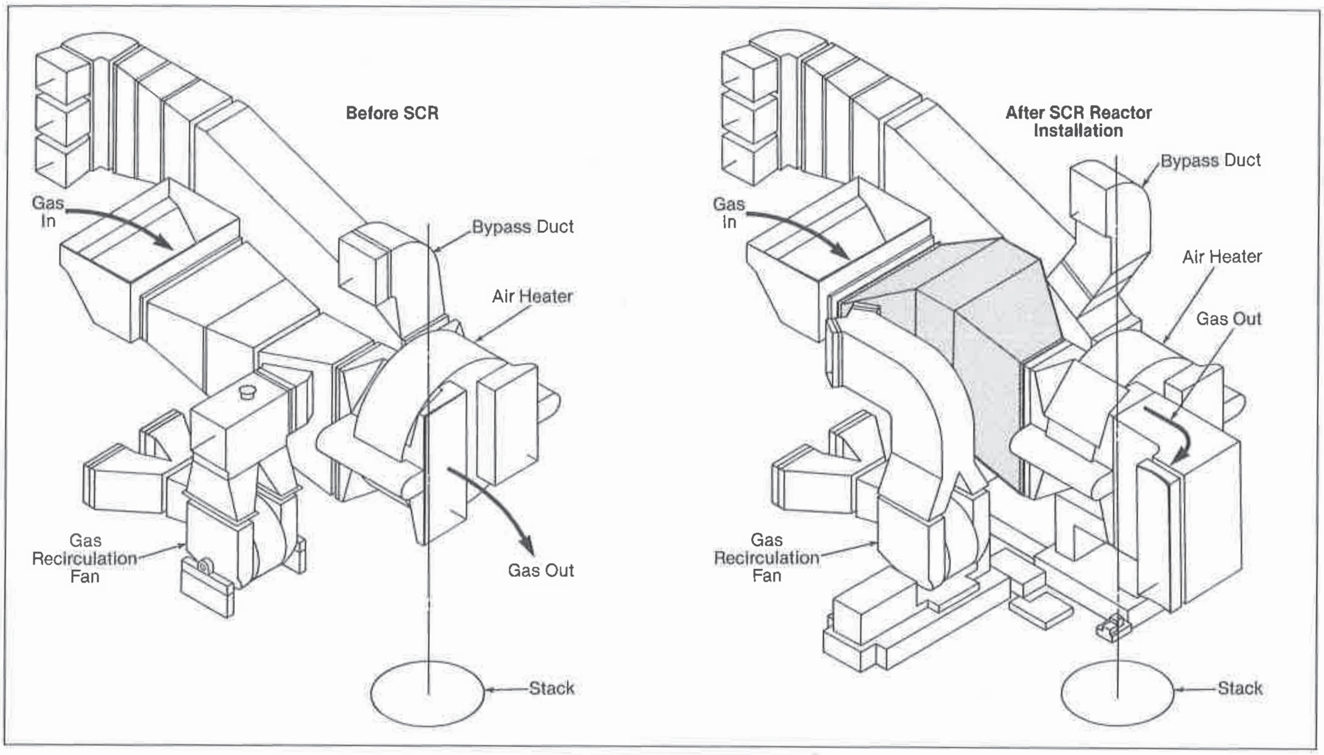


Fig. 8 Retrofit utility boiler application (half of installation shown).

verting CO to CO_2 under proper temperature conditions. However, SO_2 oxidation to SO_3 and high material costs often make precious metal catalysts less attractive.

Early technology used pelletized catalysts in a packed bed configuration. This material was effective for NO_x reduction but could be difficult to handle and frequently added significant pressure drop to the system. As a result, catalyst manufacturing technology evolved to larger, uniform catalyst blocks. Most modern SCR systems use a block type catalyst which is manufactured in the parallel plate or honeycomb configurations shown in Figs. 11 and 12, respectively. For ease of handling and installation, these blocks are fabricated into larger modules.

Each catalyst configuration has its advantages. The plate type unit offers less pressure drop and is less susceptible to plugging and erosion when particulate-laden flue gas is treated in the SCR reactor. The honeycomb configuration often requires less reactor volume for a given overall surface area.

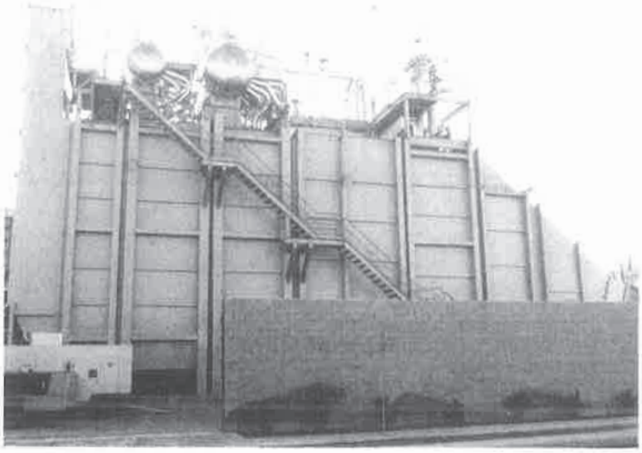


Fig. 9 HRSG with SCR.

The catalyst is housed in a reactor which is strategically located within the system. This location permits catalyst exposure to proper SCR reaction temperatures. The reactor design includes a sealing system to prevent flue gas bypassing and to provide internal support for the catalyst. The reactor configuration can be vertical or horizontal depending on the fuel used, space available, and upstream and downstream equipment arrangement. Uniform flow distribution is required for maximum performance. Fig. 13 shows a vertical SCR reactor design and Fig. 14 shows a coal-fired boiler installation.

Ammonia and stoichiometry considerations

A diagram of an ammonia control and supply system is shown in Fig. 15. Ammonia can be anhydrous or aqueous, although most commercial experience has been with anhydrous NH_3. However, due to safety concerns, aqueous NH_3 is required for selected SCR system installations.

Ammonia is transported to the site and stored in specially designed tanks. A controlled amount of ammonia

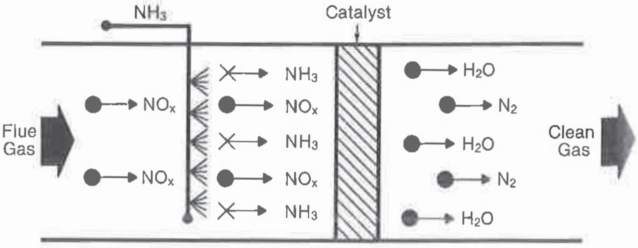


Fig. 10 Principles of NO_x removal process for SCR.

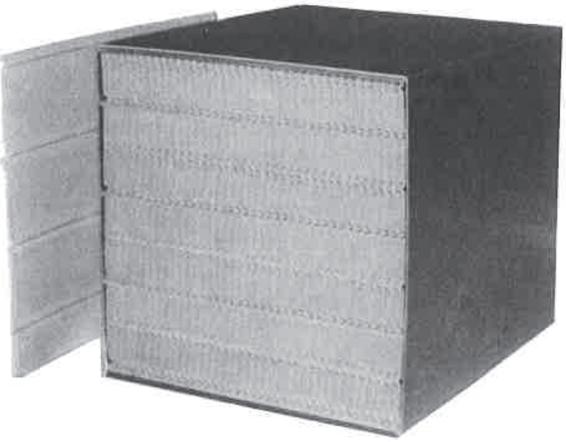


Fig. 11 Plate-type catalyst block.

is then fed to a vaporizer/mix chamber where it is mixed with air or steam at about a 1:20 volume ratio.

The mixture is then introduced into the flue gas through an injection grid system. The unit-specific grid is designed to provide an even distribution of ammonia throughout the flue gas. The grid configuration is based on the duct size and the distance from the injection grid to the inlet of the catalyst bed. Longer distances require fewer injectors for adequate mixing.

The fundamental process control provides ammonia flow at a constant NH_3/NO_x mole ratio. The product of the inlet NO_x concentration and the boiler flue gas flow yields a NO_x flow signal. Ammonia flow control is then established by multiplying the NO_x flow signal by the NH_3/NO_x mole ratio set point. (See Fig. 15.)

In general, the stoichiometry of NO_x reduction is a 1:1 mole ratio of NH_3 to NO_x. Based on this stoichiometry, for example, a theoretical mole ratio of 0.80 is required for 80% NO_x removal. However, the actual mole ratio required is slightly higher to account for unreacted ammonia carryover from the reactor (NH_3 slip). To account for reaction lag time during abrupt boiler load changes, an ammonia-rich ratio is provided for increasing loads. Similarly, a lean mixture is provided for decreasing loads.

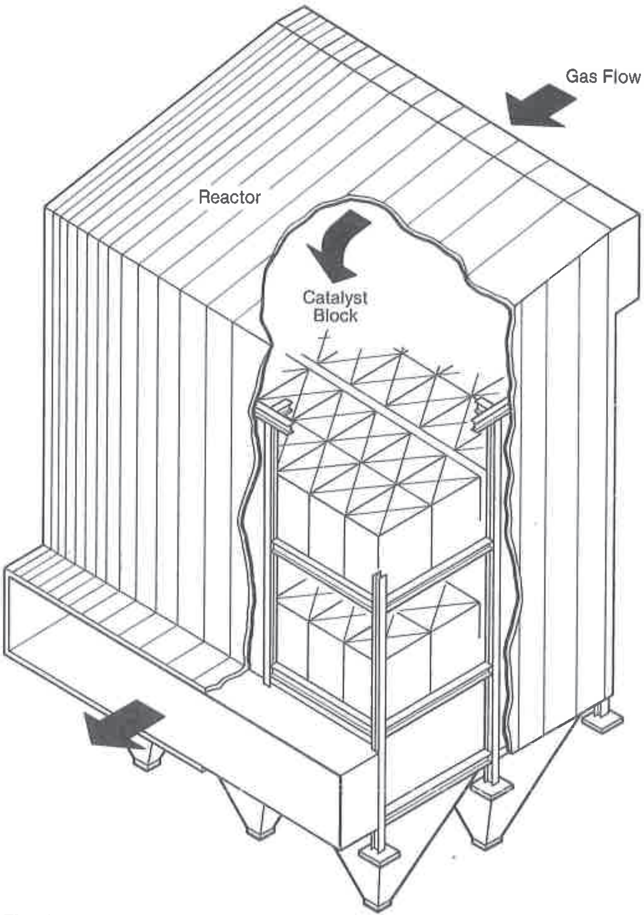


Fig. 13 Typical downflow SCR reactor module.

Related topics

A continuous emissions monitoring (CEM) system is frequently required to monitor all atmospheric pollutants. A detailed discussion of these systems is found in Chapter 36. Data generated from the CEM system can

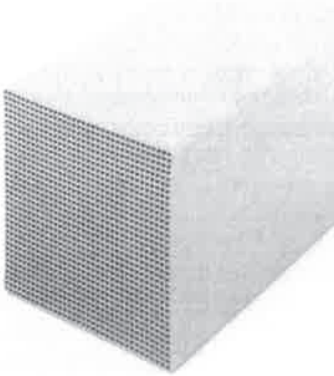


Fig. 12 Honeycomb catalyst geometry.

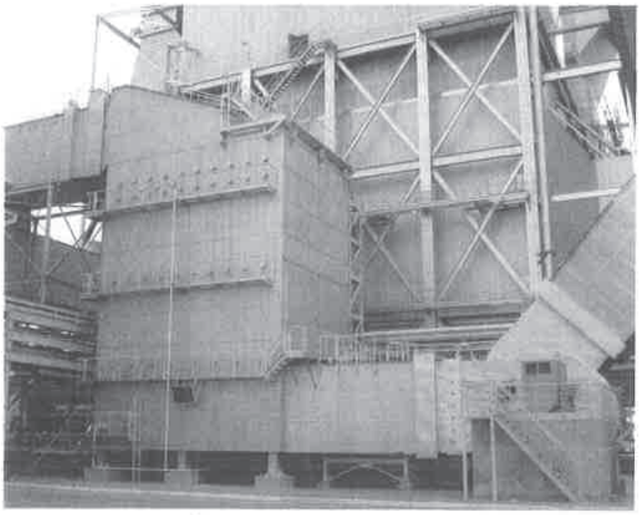


Fig. 14 SCR installation on a coal-fired boiler.

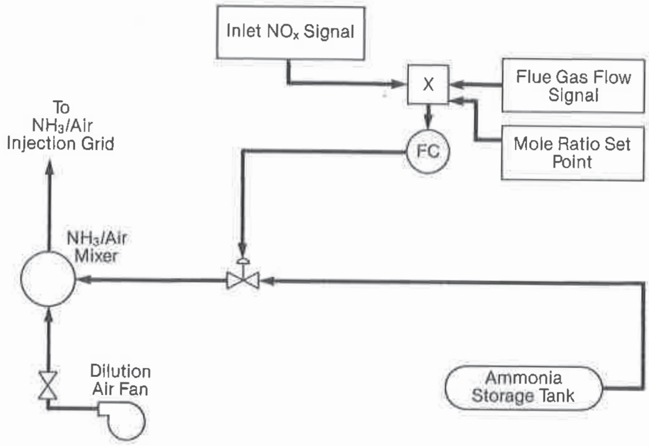
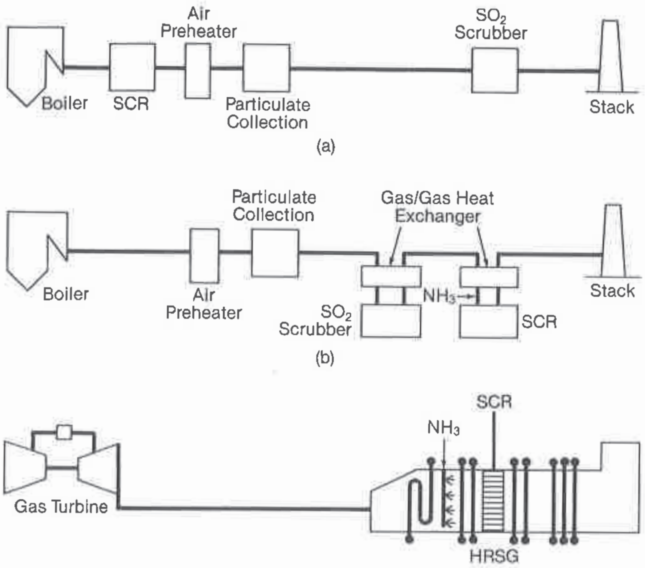


Fig. 15 NH_3/dilution air supply and control system.

be used to control the ammonia flow while achieving the required NO_x emissions level.

The design of each SCR system is unique. The major items to be considered include space constraints, location of existing equipment (retrofit projects), temperature requirements, fuel and cost. Fig. 16 shows several potential options of how the SCR system can fit into the boiler system. For new boilers, or when space is available on a retrofit, the preferred configuration is System (a), which provides the optimum temperature profile. The configuration shown in System (b) was originally developed as a retrofit due to space limitations. Unfortunately, its capital and operating costs are substantially higher than those for System (a) due to the required additional heat exchangers and duct burner (external heat source).



(a)

(b)

(c)

Fig. 16 Examples of SCR deNO$_x$ system configuations: (a) preferred SCR location, (b) possible retrofit configuration, and (c) combined cycle heat recovery steam generator (HRSG) location.

The application of SCR technology to combined cycle systems with heat recovery steam generators (HRSG) is shown as System (c). In this application, the catalyst placement within the HRSG is based on gas temperature requirements.

Selective catalytic reduction must be considered when low NO_x combustion technology provides insufficient NO_x reduction to meet local requirements. The SCR technology has proven to be reliable and is capable of up to 90% NO_x reductions and higher in some selected cases.

Future technology

Selective catalytic and noncatalytic processes have been widely accepted since the mid 1970s. SCR advancements have centered on catalyst developments for improved resistance to erosion, resistance to chemical deactivation, lower SO_2 to SO_3 conversion, and an expanded temperature performance range. Catalyst materials such as zeolite and precious metals are recent innovations.

Most SNCR process experimentation has considered alternatives to ammonia injection. Urea is the likely alternative. Two other alternatives receiving attention include cyanuric acid and ammonium sulfate. In addition, the use of methanol extenders (injected with the NO_x reagent) is being studied. The goal is to extend the useful NO_x reduction temperature range.

A special case of injection technology involves organo-amines. For example, methylamine reacts with HNO_2, yielding methanol and nitrogen. This is a low temperature gas phase reaction as opposed to the current high temperature reactions. However, the gas phase concentration of HNO_2 is limited by the oxidation rate of NO to NO_2. This technology, under development, has not been demonstrated on a commercial scale.

A variety of advanced postcombustion NO_x control systems are at various stages of development and demonstration. Many of these are combined NO_x and SO_2 control systems. While the SNCR and SCR systems discussed here basically feature dry reduction of NO_x by ammonia or urea, advanced systems under development offer a variety of options, e.g., wet (aqueous) or dry absorption by solids, absorption plus oxidation by a liquid, and absorption plus reduction by a liquid, among others. However, only the SCR and SNCR systems have achieved widespread commercialization to date. Further development and demonstration of the other systems will be required before significant acceptance is likely and attractive economics are achieved.

References

1. Zeldovich, J.B., "Oxidation of nitrogen in combustion and explosion," *Academic des Sciences de l'URSS-Comptes Rendus (Doklady)*, Vol. 51, No. 3, pp. 217-220, January 30, 1946.

2. Sarofim, A.F., and Pohl, J.H., "Kinetics of nitric oxide formation in premixed laminar flames," presented at the Fourteenth Symposium on Combustion, Pennsylvania State University, University Park, Pennsylvania, August 20-25, 1972.

3. Miller, J.A., and Bowman, T., "Mechanism and modeling of nitrogen chemistry in combustion," Fall Meeting of the Western States Section/The Combustion Institute, Dana Point, California, October 17-18, 1988.

4. "Why NO_x? The costs, consequences and control of nitrogen oxides in the human and natural environment," American Lung Association Report, April 1989.

Bibliography

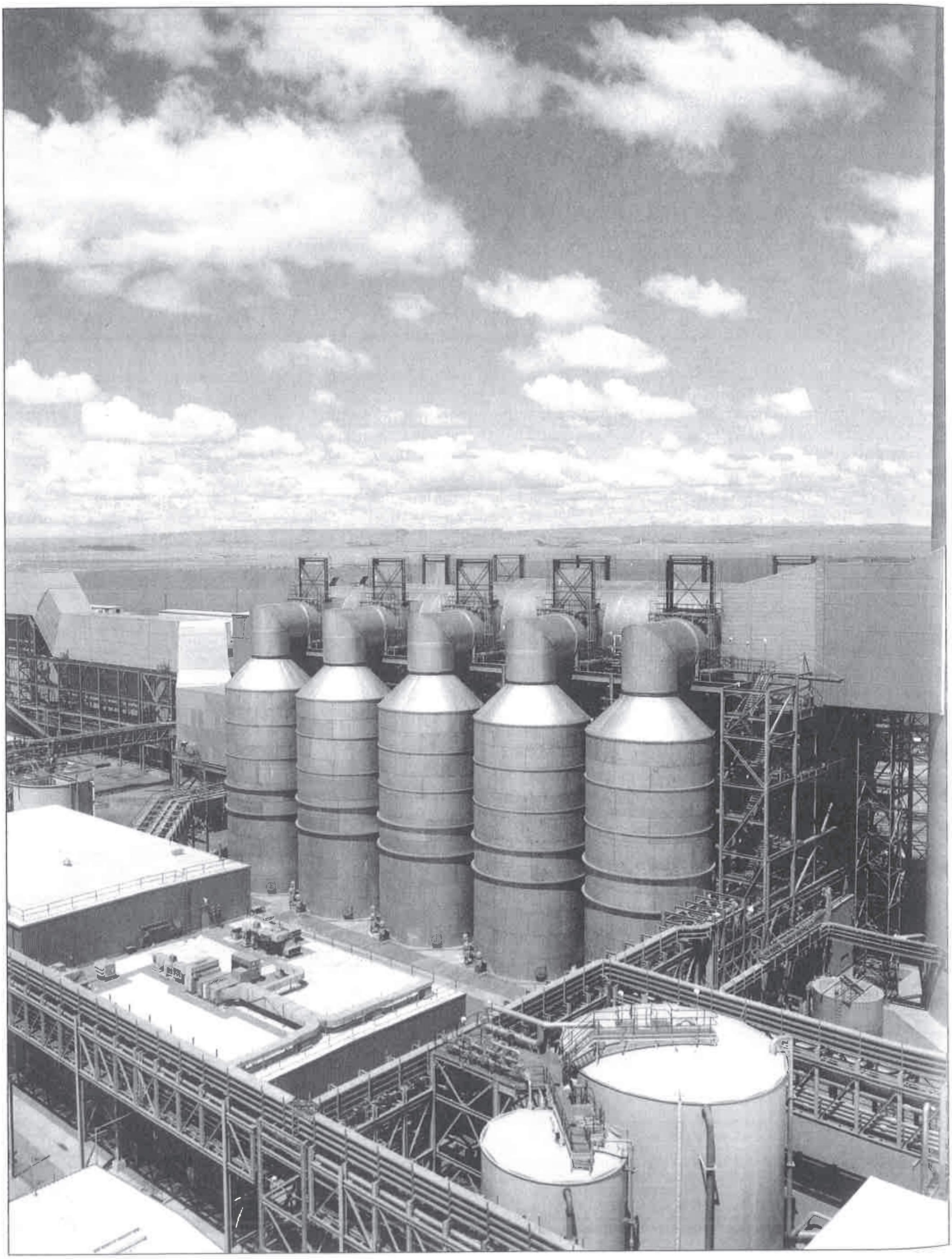
Hurst, B.E., and White, C.M., "Thermal deNO$_x$: A commercial selective noncatalytic NO$_x$ reduction process for waste-to-energy applications," proceedings of the ASME 12th Biennial National Waste Processing Conference, Denver, Colorado, June 2, 1986.

Lim, K.J., *et al.*, "Environmental assessment of utility boiler combustion modification NO$_x$ controls," U.S. Environmental Protection Agency Report, Contract No. 68-02-2160, April 1980.

Perhac, R.M., "Environmental effects of nitrogen oxides," appearing in *1989 Symposium on Stationary Combustion Nitrogen Oxide Control*, Report GS 6423-Vol. 1, Electric Power Research Institute, Palo Alto, California, July 1989.

Pohl, J.H., and Sarofim, A.F., "Devolatilization and oxidation of coal nitrogen," 16th Symposium on Combustion, Massachusetts Institute of Technology, Cambridge, Massachusetts, pp. 491-501, August 15, 1976.

Sourcebook NO$_x$ Control Technology Data, prepared for Control Technology Center U.S. Environmental Protection Agency, October 1990.



1600 MW capacity wet SO_2 flue gas desulfurization retrofit.

Chapter 35
Sulfur Dioxide Control

Sulfur appears in the life cycle of most plants and animals. Most sulfur emitted to the atmosphere originates in the form of hydrogen sulfide from the decay of organic matter. These emissions slowly oxidize to sulfur dioxide (SO_2). Under atmospheric conditions, SO_2 is a reactive, acrid gas which can be rapidly assimilated back to the environment. However, the combustion of fossil fuels, in which large quantities of SO_2 are emitted to relatively small portions of the atmosphere, can stress portions of the ecosystem in the path of these emissions.

Man is responsible for the majority of the SO_2 emitted to the atmosphere. Annual worldwide emissions are estimated to be 180 to 200 million tons, nearly half of which are from industrial sources. The two principal industrial sources are fossil fuel combustion and metallurgical ore refining.

When gaseous (g) SO_2 combines with liquid (ℓ) water, it forms a dilute aqueous (aq) solution of sulfurous acid (H_2SO_3). Sulfurous acid can easily oxidize in the atmosphere to form sulfuric acid (H_2SO_4). Dilute sulfuric acid is a major constituent of *acid rain*. (Nitric acid is the other major acidic constituent in acid rain.) The respective reactions are written:

$$SO_2(g) + H_2O(\ell) \rightarrow H_2SO_3(aq) \quad (1)$$

$$O_2(g) + 2H_2SO_3(aq) \rightarrow 2H_2SO_4(aq) \quad (2)$$

The SO_2 can also oxidize in the atmosphere to produce gaseous sulfur trioxide (SO_3). Having a high affinity for water vapor, the sulfur trioxide reactions are written:

$$2SO_2(g) + O_2(g) \rightarrow 2SO_3(g) \quad (3)$$

$$SO_3(g) + H_2O(g) \rightarrow H_2SO_4(\ell) \quad (4)$$

While Equations 1 and 2 describe the mechanism by which SO_2 is converted to sulfuric acid in acid rain, Equations 3 and 4 characterize dry deposition of acidified dust particles and aerosols.

The pH scale is the method used to quantify the acidity of acid rain. The scale is defined by:

$$pH = -\log_{10}[H^+] \quad (5)$$

where $[H^+]$ is the concentration of hydrogen ions in solution. A pH below 7.0 is considered acidic, while a value above 7.0 is alkaline. The pH of pure distilled water is 7.0. If rain water contained no sulfuric or nitric acid, its pH would be approximately 5.7 due to absorption of carbon dioxide (CO_2) from the atmosphere. The contributions of man-made SO_2 and nitrogen oxides (NO_x) further reduce the pH of rain water. No uniformly accepted definition exists as to what pH constitutes acid rain. Some authorities believe that a pH of about 4.6 is sufficient to cause sustained damage to lakes and forests in the Northeastern portion of North America and in the Black Forest region of Europe. Rains with pH values of 4.2 have been observed.

SO_2 emissions regulations

Legislative action has been responsible for most industrial SO_2 controls. Major regulations include the Clean Air Amendments of 1970, 1977 and 1990 in the United States (U.S.), the Stationary Emissions Standards of 1970 in Japan, and the 1983 SO_2 Emissions Regulations of the Federal Republic of Germany.

Since the mid 1980s, SO_2 emissions regulations have been proposed in many other industrialized nations. Most members of the European Economic Community are regulated and Canadian laws are similar to those in the U.S. A more detailed discussion of regulation is included in Chapter 32.

SO_2 control

A variety of SO_2 control processes and technologies are in use and others are in various stages of development. Commercialized processes include wet, semi-dry (slurry spray with drying) and completely dry processes. Of these, the wet SO_2 scrubber has been the dominant worldwide technology for the control of SO_2 from utility power plants. As such, wet flue gas desulfurization (FGD) systems will be the primary focus of this chapter with other systems, especially dry FGD systems, also discussed.

From 1970 to 1988, SO_2 emissions in the U.S. diminished from 28.4 to 20.7 million tons per year. In that same time span SO_2 emissions by electric utilities were reduced from 15.8 to 13.6 million tons per year. In 1970 the average sulfur content of coal consumed by these utilities was about 2.3%. The use of coal by the utilities has grown in this time period from 320 million tons in 1970 to 758 million tons in 1988. If no SO_2 emission controls had been implemented in 1970, it is estimated that SO_2 emissions from U.S. electric utilities would have grown to about 34.7 million tons per year by 1988.

The utilities primarily used two strategies for control, switching to low sulfur coal and installing scrubbers. By 1988, the average sulfur content of fuels burned was 1.34% for coal and 1.09% for oil. With fuel switching alone, SO_2 emissions for electric utilities would have been 21.25 million tons in 1988; however, scrubbers, primarily wet, removed 7.65 million tons of SO_2 in 1988. In all, fuel switching accounts for about 64% of the SO_2 control and scrubbers have accounted for 36% of utility SO_2 reductions. (Fuel switching technical considerations are discussed in Chapter 46.)

Wet scrubbers have been used by many utilities since 1970 to meet SO_2 emission regulations. 68,000 MW of FGD capacity were installed in the U.S. between 1970 and 1990.[1] In Japan, 32,000 MW of capacity were added during this period. 48,000 MW of capacity were installed between 1979 and 1990 in Germany. The rest of the world accounts for approximately 4,000 MW. (See Fig. 1).

Wet scrubbers offer the following advantages:

1. As an alternative to fuel switching, the utility can use its normal source of fuel supply.
2. As an alternative to and in contrast to other traditional and emerging flue gas desulfurization methods, wet scrubbers provide high SO_2 removal efficiency and high reagent utilization.

Of the 180,000 MW of worldwide FGD capacity, 85% are wet scrubbers with the balance being predominantly dry scrubbers. Wet scrubbing processes are often categorized by reagent. Table 1 lists several scrubber processes and, of these, the limestone process has been the most widely applied. Within each category several process variations have been developed and commercialized. These are broadly outlined in Table 1 and are discussed later in this chapter. The primary advantages of limestone are its wide availability and cost effectiveness; roughly 5 to 6% of the earth's crust consists of calcium and magnesium carbonates and silicate. Limestone, consisting mostly of calcium carbonate ($CaCO_3$), is easily mined, transported and stored. Its storage and conveying at the plant site are similar to coal handling. (See Chapter 11.)

Wet scrubbers

Design

The first FGD wet scrubbers installed in the U.S. were combined particulate collectors and SO_2 absorbers. However, the energy requirements for the venturi scrubbers used for particulate collection proved to be excessive. High efficiency dust collectors, usually electrostatic precipitators, soon replaced venturi scrubbers. (See Chapter 35.) Fig. 2 displays the typical arrangement.

The dust collector is placed upstream of the wet scrubber. In this arrangement, the induced draft fan is between the dust collector and the scrubber, permitting the fan to operate in a particulate-free, dry flue gas. In Germany, where nearly all FGD systems were retrofits to existing boilers, some induced draft fans did not have sufficient capacity. In some instances, a booster fan is placed downstream of the scrubber to handle the additional scrubber draft. These fans, incorporating a wash system to prevent excessive solid deposition from the scrubber, generally have rubber-lined housings and high alloy rotors.

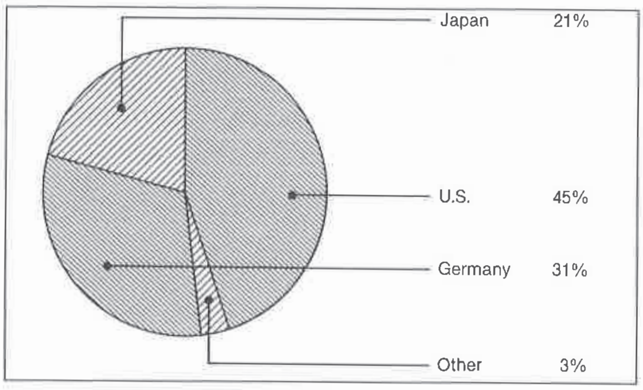


Fig. 1 Wet FGD systems installed throughout the world, on a capacity basis — through 1990.

The maximum size of a wet scrubber depends upon several design factors. Scrubbers which treat more than 6×10^6 lb/h (756 kg/s) of flue gas have been built and no fundamental engineering limits to wet scrubber size have been identified. Prior to 1990, U.S. environmental regulations encouraged utilities to purchase FGD systems which included multiple module designs with spare capacity. Current regulations now provide a framework within which single module scrubber systems can form a part of the compliance strategy. In Germany and Japan, utilities have favored large single modules for each boiler; in some instances, one scrubber treats the flue gas from two or more boilers.

The most popular wet scrubber design is the *spray tower* depicted in Fig. 3. The tower is designed so that, at maximum load, the average superficial gas velocity does not exceed the design gas velocity. For most spray towers, the average gas velocity varies from about 8 to 13 ft/s (2.4 to 4 m/s) based upon scrubber outlet conditions. A typical design velocity for a limestone wet scrubber is about 10 ft/s (3.1 m/s).

Because the flue gas enters the absorber from the side, gas flow nonuniformity in the tower is a potential prob-

Table 1
Wet Scrubber Processes

- Limestone —
  - with no oxidation inhibition (*natural oxidation*)
  - with inhibited oxidation
  - with in situ forced oxidation
  - with ex situ forced oxidation
  - with soluble organic or inorganic buffers
- Lime —
  - with inorganic buffers (such as magnesium oxide)
  - without buffers
- Dual alkali —
  - sodium carbonate/calcium hydroxide
  - sodium carbonate/calcium carbonate
- Soda ash —
  - with regeneration by steam stripping
  - without regeneration
- Magnesium oxide with thermal regeneration

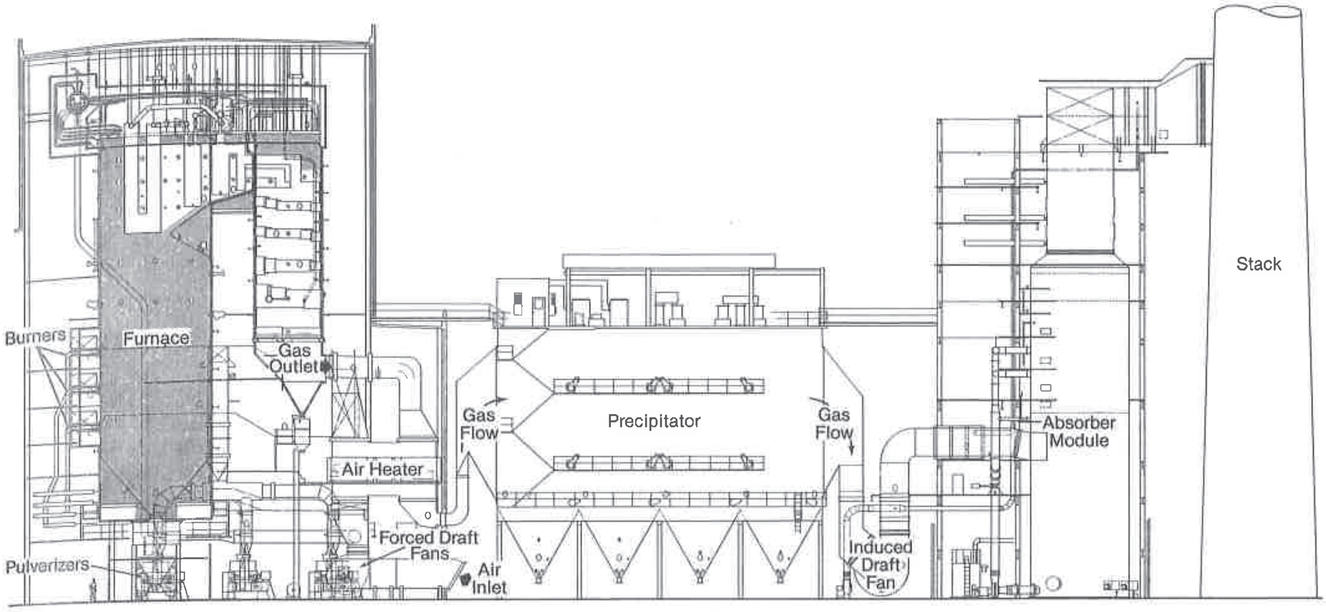


Fig. 2 Typical emission control systems for a coal-fired utility boiler.

lem. This nonuniformity reduces overall SO_2 removal performance and aggravates mist eliminator carryover. The absorber design depicted in Fig. 3 incorporates a sieve or perforated plate tray which reduces flue gas flow maldistribution. The pressure drop across the tray is usually between 1 to 3 in. wg (0.2 to 0.7 kPa). Towers with multiple trays have also been built. The design of the tower is influenced by the reagent (lime or limestone, for example), the desired SO_2 removal level, the tradeoff between fan power and recirculation slurry pump power, and several other factors.

The dominant design variable for all FGD wet scrubbers is the ratio of slurry flow to gas flow in the tower, known as L/G. In the U.S., this term is expressed as gallons per thousand cubic feet of flue gas evaluated at scrubber outlet conditions. In Japan and Germany, the L/G units are l/m^3. A wide range of L/G values have been used on wet scrubbers. Soda scrubbers operate at as low as 10 gal/1000 ft^3 (1.34 l/m^3) and some limestone scrubbers operate at up to 150 gal/1000 ft^3 (20 l/m^3).

Spray nozzles are used in wet scrubbers to control the mixing of slurry with flue gas. The operating pressures typically vary between about 5 and 20 psi (34 and 138 kPa). Spray nozzles without internal obstructions are favored to minimize plugging by tramp debris. Although plugging could be minimized by using a minimum number of large spray nozzles, flow maldistribution would most likely occur. Therefore, several smaller nozzles are usually preferred. Ceramic nozzles are commonly used.

The large tank at the bottom of the tower is called the *reaction tank* or the *recirculation tank*. The volume of this tank permits several chemical and physical processes to approach completion. Some of these rate processes will be described in more detail later.

Flue gas/scrubber considerations

Flue gas enters the side of the scrubber module at a temperature of 250 to 350F (121 to 177C) and is evaporatively cooled to its adiabatic saturation temperature by a slurry spray. The scrubber inlet must be designed to prevent deposition of slurry solids at the wet-dry interface. Because the inlet flue is at the flue gas temperature [for example 300F (149C)] and the shell of the scrubber is at the saturation temperature [typically 125F (52C)], there is a point where the surface temperature abruptly changes. Deposits are most likely to form at this point. Deposition is minimized by a combination of features which prevent periodic slurry splashing on the hot, dry side of the wet-dry line.

Flue gas passes vertically upward through the scrubber. In the unit illustrated in Fig. 3, the gas flow is uniformly distributed by a specially designed perforated plate or sieve tray. This tray serves as a gas-liquid contacting device. Gas-liquid contact is enhanced by a froth of slurry which forms on the tray.

Above the tray, flue gases pass through several spray levels where additional gas-liquid contact is achieved. Each spray level consists of a set of headers and spray nozzles as illustrated in Fig. 3. The spray nozzles produce a relatively coarse spray with mass median droplet diameters of about 2000 to 2500 microns. This suspension of droplets is in countercurrent contact with the flue gas for about one to three seconds. A majority of the SO_2 absorption occurs during this short contact time. The spray zone in combination with the froth on the tray is referred to as the gas-liquid contact zone of the wet scrubber.

A disengagement height is provided above the top spray zone before the flue gases reach the mist eliminators. The purpose is to allow disengagement and return of the largest slurry droplets to the spray zone. For a scrubber operating at an average gas velocity of 10 ft/s (3 m/s), droplets larger than about 600 microns may have sufficient time and mass to fall back to the spray zone.

The mist eliminator design in most wet scrubbers uses *chevrons* to remove additional moisture from the flue gas (see Fig. 3). Chevrons are closely spaced corrugated plates which collect slurry deposits by impaction. They efficiently collect droplets larger than about 20 microns in diameter.

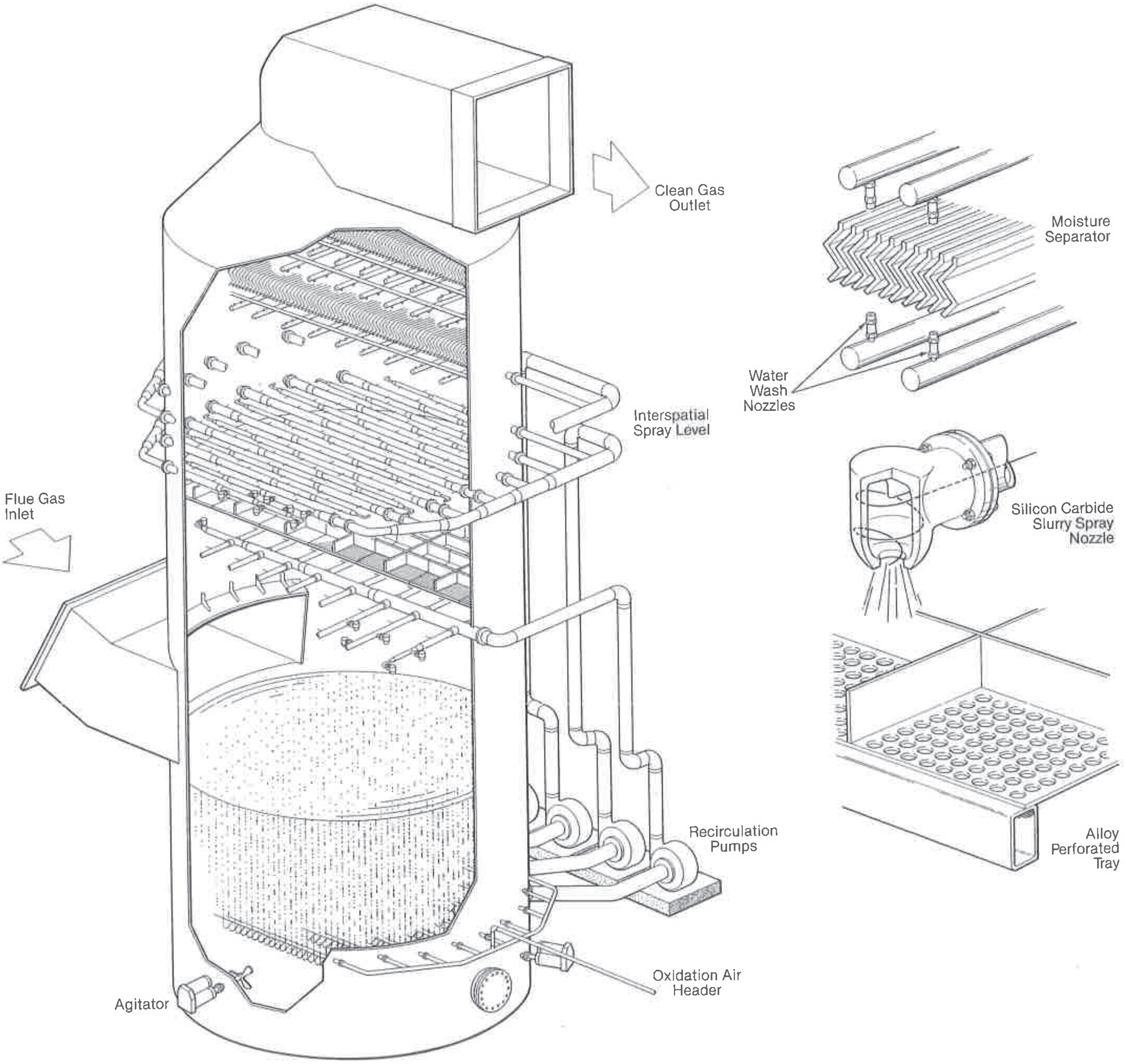


Fig. 3 Wet flue gas desulfurization scrubber module.

The design of the flue from the exit of the wet scrubber to the stack is an important facet of the system design. The potential for severe corrosion and deposition in these flues is well documented. This potential for severe corrosion arises from a combination of facts. First, the flue gas leaves the mist eliminator saturated with water vapor. Second, some carryover of slurry droplets smaller than 20 microns is inevitable. These droplets will usually be slightly acidic and may contain high concentrations of dissolved chlorides. The flue gases will contain some residual SO_2 and ample oxygen to oxidize some of the SO_2 to SO_3. Because the flue gas is saturated with water vapor, surface condensation is inevitable. This condensate can become severely acidic (pH less than 1.0), and calcium salts can deposit on the walls.

Two approaches are used to minimize these effects, flue gas reheat and flue/stack lining. The former option involves reheating the flue gas so that no more droplets remain. Reheating the flue gas that is leaving the scrubber has been accomplished by various systems:

1. steam coil heaters,
2. mixing with some hot flue gas which is bypassed around the scrubber,
3. mixing with hot air,
4. mixing with hot gases generated by combustion of a clean fuel, and
5. regenerative heat exchangers which transfer heat from the hot flue gas inlet to the cooler flue gas outlet.

Several problems are associated with each of the reheat methods. Deposition and corrosion occur in the heat exchangers. Reheating with bypass gas reduces the overall FGD system effectiveness. Finally, the evaporation of droplets from the scrubber concentrates the corrosive constituents in the slurry. As a result, operation without flue gas reheat, i.e., with a *wet stack*, has become popular in the U.S. Under these conditions, the flues from the scrubber to the stack are lined with corrosion resistant materials, and the stack is lined with acid resistant brick or other suitable material. A drainage system is also included to accommodate condensation of water vapor.

Wet scrubber — limestone and lime FGD processes

All of the limestone and lime processes listed in Table 1 are classified as nonregenerable. This means that the reagent is consumed by the process and must therefore be continually replenished. A generic diagram of nonregenerative processes is illustrated in Fig. 4. Each consists of four process steps: reagent preparation, SO_2 absorption, slurry dewatering and final disposal. Within each of these process steps many variations exist. Essentially all wet FGD installations have some unique aspects. A description of some of the more frequently used approaches to each process step is presented below followed by examples of two specific processes.

Reagent preparation

Limestone In North America, most limestone wet FGD systems feature on-site wet grinding for slurry preparation. In most cases, the system of choice is a closed loop ball mill. A typical ball mill circuit is shown in Fig. 5. The energy required to achieve a given grind size is estimated by the Bond relationship:

$$W = \frac{10\ W_i}{\sqrt{D_P}} - \frac{10\ W_i}{\sqrt{D_F}} \tag{6}$$

where

W = power, kWh/t of product
W_i = Bond work index, kWh (micron)$^{1/2}$/t
D_P = diameter in microns for which 80% of product is finer
D_F = diameter in microns for which 80% of feed is finer

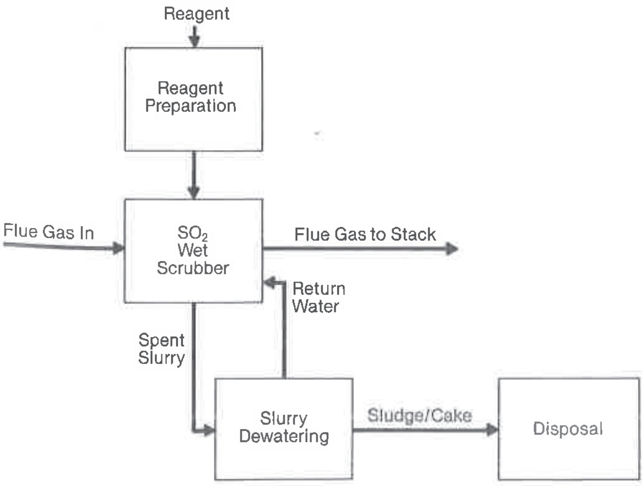


Fig. 4 Wet FGD system diagram.

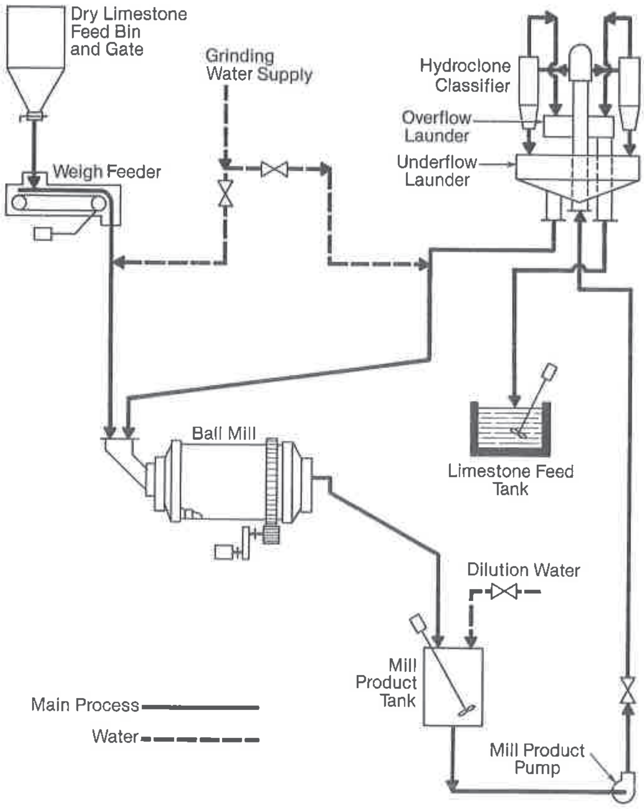


Fig. 5 Limestone reagent preparation system.

The Bond work index for calcitic limestones typically ranges from about 8 to 15 kWh (micron)$^{1/2}$/t.

For on-site grinding systems, the limestone is typically received with a diameter of about 1 in. (25 mm) or less and is fed through a weigh belt feeder to the ball mill. Either fresh or recycled water is added at the feed chute in proportion to the feed rate of the stone. The output from the mill overflows to the mill product tank where it is pumped to a set of hydroclones. These hydroclones separate the fines from the coarse fraction. The coarse fraction (*underflow*) is returned to the ball mill and the fine material is sent to the limestone feed tank. The water balance is maintained to provide 25 to 35% suspended limestone solids in the feed tank.

The limestone grind is usually expressed as a percent passing a certain sieve size. The coarsest limestone grind used in wet FGD systems is one where about 70% passes through a 200 mesh (75 micron) sieve. Fine limestone grinding produces a product where about 95% of the limestone is finer than a 325 mesh (44 micron) sieve. Fine grinding requires a larger ball mill system and higher operating expense. The finer material provides higher limestone utilization, better reactivity with SO_2, and higher SO_2 removal for a given stoichiometry, while permitting a smaller reaction tank for some systems. Stoichiometry is defined as the molar ratio of the reactant, $CaCO_3$ for limestone systems, to the SO_2. It is common practice in the U.S. to define the stoichiometry by using the quantity of SO_2 removed for wet scrubbing systems and by the inlet quantity of SO_2 for other removal systems.

In Germany, off-site grinding is preferred. Limestone is dry ground at a central location and transported by truck to the FGD system. At the site, the pulverized limestone is pneumatically conveyed to a storage bunker. It is then fed to water-filled slurry preparation tanks. This system requires less space than on-site grinding facilities and reduces some of the FGD operating burden.

Lime Lime based FGD systems are common in the U.S. Three types of slaking systems are used: the detention slaker, the paste slaker and the ball mill slaker. The detention slaker is the simplest but produces the poorest quality slaked lime. The paste slaker, while producing high quality lime, is the most complex system and grit separation can be troublesome. The ball mill slaker produces an intermediate slaked lime quality but requires no postslaking separation of the grit and slaked lime.

A typical slurry preparation system is shown in Fig. 6. This system consists of storage for pebble lime, a weigh belt feeder, slaker, grit removal system, dilution system and slaked lime storage tank. Lime storage is usually maintained at 20 to 25% suspended solids.

Slurry dewatering and disposal

The disposal of reaction products from lime/limestone wet scrubbers has taken many forms. Several approaches, some unique to U.S. units, are used.

Ponding of the spent slurry without dewatering is the simplest disposal method. However, limited site availability and the cost of pond management have restricted its use. The combination of primary dewatering, secondary dewatering and landfilling is the most common approach used in the U.S. Primary dewatering is accomplished using thickeners or hydroclones. A thickener (Fig. 7) is capable of concentrating slurries with particle sizes as small as 5 microns to between 20 and 30% suspended solids. Lime/limestone systems with natural oxidation produce fine crystals and therefore require thickeners.

If the slurry is limited to particles larger than about 15 microns, hydroclones can be used for primary dewatering. These devices, much smaller and simpler than thickeners, are preferred where the particle size distribution is suitable. The gypsum crystals produced by lime/limestone systems with forced oxidation are usually suitable for hydrocyclones.

Secondary dewatering of FGD wastes is accomplished using a number of methods: vacuum drum filters, vacuum belt filters, solid bowl centrifuges and vertical basket centrifuges. Vacuum drum filters are the most common U.S. application, accounting for about 80% of the installations. Germany uses vacuum belt filters on more than 90% of its units.

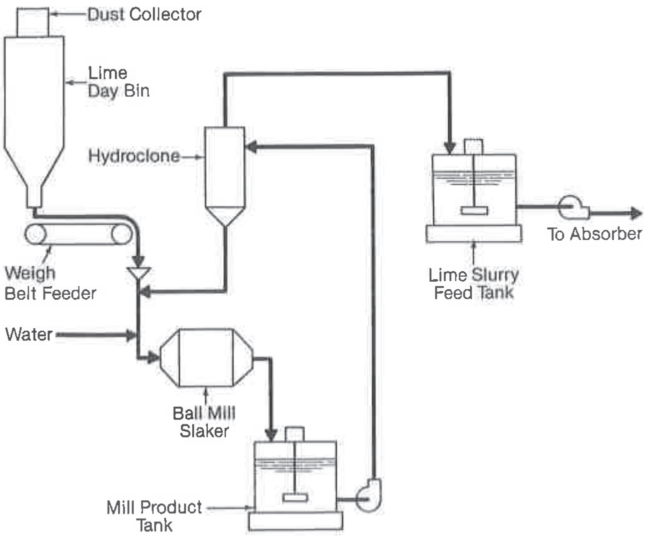


Fig. 6 Lime reagent preparation system.

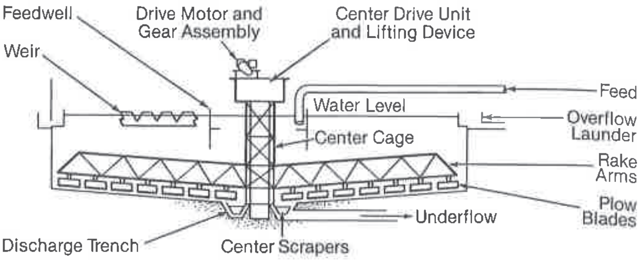


Fig. 7 Thickener system for primary dewatering of FGD scrubber effluent.

When landfilling is used for sulfite sludge disposal, additional treatment is required for sludge management at the landfill. *Sludge fixation* is used to increase the compressive strength of the sludge. Sulfite sludge is mixed with flyash and lime to yield a material suitable for landfilling. If gypsum is to be landfilled it needs no special treatment after dewatering.

Overall process flow diagrams and mass balance

All lime/limestone FGD wet scrubbers require fresh water for mist eliminator wash. This fresh water is usually combined with recycle water from the clarifier, thickener and/or vacuum filter to provide the total wash flow. Fresh water is also used for pump seals, reagent preparation and filter cake washing. Water losses from the system include evaporative losses, moisture in the waste solids, waters of crystallization and, in some cases, a controlled water purge. Careful management is required to assure adequate water supplies.

A typical limestone based wet scrubbing process using in situ forced oxidation is depicted in Fig. 8. In this example, the reagent preparation system includes a closed circuit ball mill system producing a slurry of ground limestone to a fineness of 95% minus 325 mesh (44 microns). This means that 95% by weight of the ground limestone will pass through a screen designated as a 325 mesh (44 micron) sieve. This slurry contains 30% by weight of suspended solids. The water used in the milling system is recycled from the spent slurry dewatering system. The feed slurry is pumped to the absorber reaction tank at a controlled rate to maintain the pH of the slurry in this tank at a set point of 5.5. Air is also pumped to this reaction tank and distributed by spargers located near the bottom. The oxygen in the air reacts with any sulfite present in the slurry to produce gypsum (calcium sulfate dihydrate).

The slurry is pumped from the reaction tank to the spray headers shown in Fig. 3. The slurry is sprayed countercurrently into the flue gas where it absorbs the SO_2. The slurry falls to the perforated plate tray where additional SO_2 is absorbed into the froth created by the interaction of the flue gas and slurry on the tray. The slurry then drains back to the reaction tank.

A small fraction of the slurry being pumped to the spray nozzles is diverted to the dewatering system. The spent slurry typically contains about 15% suspended solids. In this example, a hydroclone is used to concentrate the slurry. The underflow from the hydroclone is

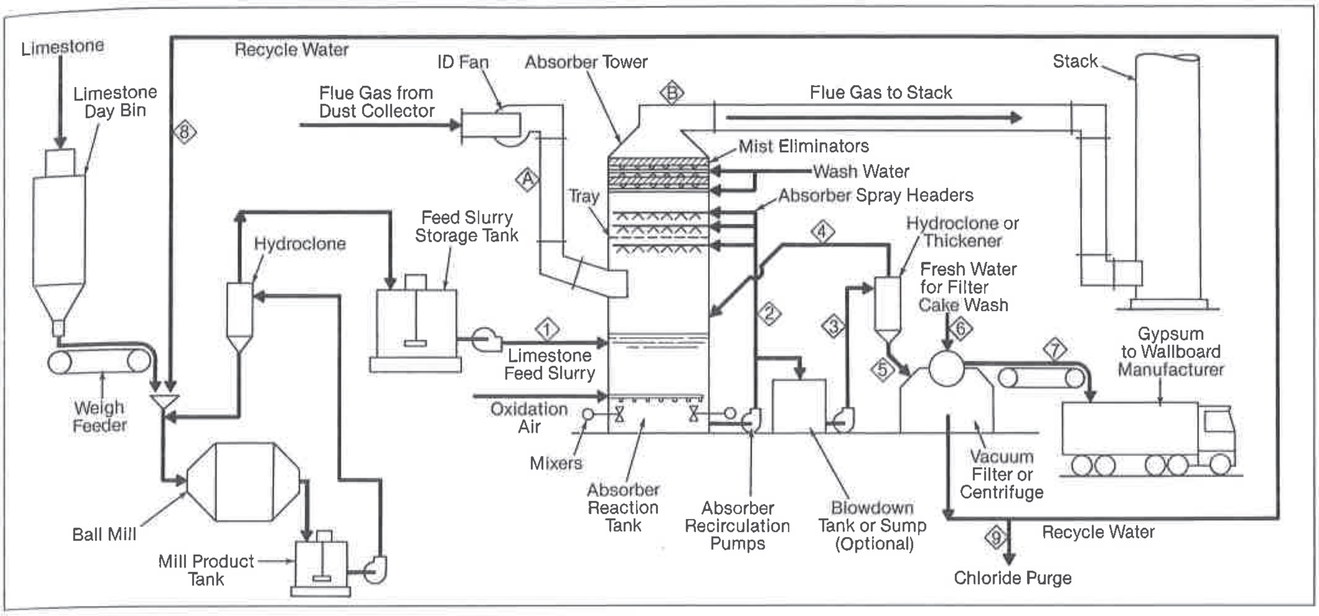


Fig. 8 Wet scrubber FGD system flow diagram (see Table 2 for material balance).

concentrated to 25% solids. The overflow containing 4% suspended solids is sent back to the absorber.

The underflow from the hydroclone is directed to a vacuum filter where the filtered solids are washed with fresh water and concentrated to form a filter cake containing about 10% free moisture. The cake is then sent by truck to a wallboard manufacturer. A mass balance for this example is presented in Table 2. A summary of the major power requirements for this limestone to gypsum process is shown in Table 3.

Fig. 9 illustrates a typical flow sheet for an FGD process using a lime produced from a dolomitic limestone. This lime contains about 5% magnesium oxide (MgO), 90% calcium oxide and 5% inerts. Within the process, the MgO is converted to $MgSO_3$, where, because of its relatively high solubility (approximately 10 g/l), the sulfite acts as a buffer to increase the SO_2 capacity of the slurry. The overall reaction is:

$$Ca(OH)_2(s) + SO_2(g) \rightarrow CaSO_3 \cdot {}^1\!/_2\, H_2O(s) + {}^1\!/_2\, H_2O(\ell) \qquad (7)$$

In this instance, a closed circuit ball mill system is used to produce a slaked lime:

Table 2
Mass Balance for The Limestone Forced Oxidation System Shown in Fig. 8

Gas side	Inlet	Exit
Stream number	A	B
Flow rate, ACFM	626,724	500,000
Total mass flow rate, lb/h	1,905,400	1,982,091
Mass flow rate of H_2O, lb/h	76,466	157,700
Mass flow rate of SO_2, lb/h	8,565	600
Mass flow rate of HCl, lb/h	344	0
Static pressure, in. wg	6	1
Temperature, F	330	123

180 MW boiler burning coal with 3.2% sulfur
Limestone stoichiometry = 1.03
L/G = 130 gal/1000 ACF
SO_2 efficiency = 93%

Liquid side	Feed Slurry	Recirc	To Hydroclone	Hydroclone Overflow	Hydroclone Underflow	Filter Wash Water	Filter Cake	Recycle Water	Chloride Purge
Stream number	1	2	3	4	5	6	7	8	9
Flow rate, GPM	59	65,260	319	236	83	26	22	51	36
Total flow rate, lb/h	38,819	37,275,000	180,196	125,136	55,060	13,215	24,471	25,732	18,072
Flow rate of sus. solids, lb/h	13,586	5,607,000	27,029	5,005	22,024	0	22,024	0	0
% suspended solids	35	15	15	4	40	0	90	0	0
Chloride conc., ppm in liquid	25,000	25,000	25,000	25,000	25,000	50	100	18,514	18,514
pH	7.8	5.7	5.7	5.7	5.7	7	7	5.7	5.7
Temperature, F	100	123	123	123	123	70	70	70	70

Table 3
Typical Power Requirements for Limestone Scrubber with Forced Oxidation

Absorber System	Avg. Power (kW)	% Power
Oxidation air blower	375	
Absorber recirc. pump #1	312	
Absorber recirc. pump #2	367	
Absorber recirc. pump #3	380	
Absorber recirc. tank agitators	60	
Mist eliminator wash water pump	19	
Misc. pumps and agitators	24	
Subtotal	1537	60.3%
Dewatering Area	**Avg. Power (kW)**	**% Power**
Vacuum pump for filter	55	
Filter wash water tank heater	16	
Reclaim water pump	14	
Hydroclone overflow pump	15	
Filter feed tank agitator	7	
Clarifier overflow sump pump	6	
Misc. pumps and agitators	13	
Subtotal	126	4.9%
Reagent Preparation	**Avg. Power (kW)**	**% Power**
Ball mill driver	220	
Mill product tank pump	5	
Limestone feed tank agitator	25	
Misc. pumps and agitators	6	
Subtotal	256	10.0%
Other Systems	**Avg. Power (kW)**	**% Power**
General-instrument air	50	2.0%
Differential induced draft fan power	580	22.8%
Subtotal	630	
Total	2549	

Notes:
180 MW boiler burning coal with 2.5% sulfur
Heating value of coal = 12,767 Btu/lb
Absorber L/G = 130 gal/1000 ACF
Total pressure drop = 5 in. wg
Parasitic power = 2.549 MW/180 MW
= 1.42%

$$CaO + H_2O \rightarrow Ca(OH)_2 + Heat \qquad (8)$$

$$MgO + H_2O \rightarrow Mg(OH)_2 \qquad (9)$$

The absorber towers used for this process are smaller than their limestone counterparts because the L/G required to achieve a comparable level of SO_2 absorption is typically only about 20% of L/G for the limestone units.

The size distribution of the particles in the spent slurry is much smaller than the gypsum particles produced in the limestone forced oxidation process described above. A hydroclone would be incapable of achieving adequate concentration. Therefore, a thickener as illustrated in Fig. 7 is used. By comparison to a hydroclone, a thickener has the advantage of producing a clear overflow. The clear overflow means that this water can be recycled to the process and used for washing mist eliminators. The space requirement for a thickener is many times greater than that required by a hydroclone, however. The underflow from the thickener is directed to a vacuum filter where the unwashed cake is filtered to 45 to 55% solids. This cake is then mixed with lime and flyash to form an aggregate suitable for landfilling.

Wet scrubber chemistry

SO_2 absorption in a wet scrubber and its subsequent reaction with alkaline earth materials such as limestone is an elementary acid-base reaction. However, the chemical processes involved are complex. SO_2 is a relatively insoluble gas in water. Calcium carbonate ($CaCO_3$) has a low solubility in water. The principal reaction products are calcium sulfite hemihydrate ($CaSO_3 \cdot {}^1\!/_2 H_2O$) and calcium sulfate dihydrate ($CaSO_4 \cdot 2\,H_2O$), or gypsum. Both of these salts also have low solubilities.

In a limestone system with inhibited oxidation, the following reaction model can be used to describe the process using the chemical species in Table 4.

In the gas-liquid contact zone:

$$SO_2(g) \leftrightarrow SO_2(aq)$$
$$\textit{Dissolving gaseous } SO_2 \qquad (10)$$

$$SO_2(aq) + H_2O \leftrightarrow HSO_3^- + H^+$$
$$\textit{Hydrolysis of } SO_2 \qquad (11)$$

$$CaCO_3(s) + H^+ \leftrightarrow Ca^{++} + HCO_3^-$$
$$\textit{Dissolution of limestone} \qquad (12)$$

$$HCO_3^- + H^+ \leftrightarrow CO_2(aq) + H_2O$$
$$\textit{Acid – base neutralization} \qquad (13)$$

$$CO_2(aq) \leftrightarrow CO_2(g)$$
$$CO_2 \textit{ stripping} \qquad (14)$$

Table 4
Chemical Species Found In Scrubber Reaction Model

SO_2	sulfur dioxide
H_2O	water
HSO_3^-	bisulfite ion
H^+	hydrogen ion
$CaCO_3$	calcium carbonate (main limestone constituent)
Ca^{++}	calcium ion
CO_2	carbon dioxide
HCO_3^-	bicarbonate ion
$CaSO_3 \cdot 1/2\ H_2O$	calcium sulfite hemihydrate
$CaSO_4 \cdot 2\ H_2O$	calcium sulfate dihydrate (gypsum)
(ℓ)	denotes liquid phase
(g)	denotes gaseous phase
(aq)	denotes dissolved specie in water
(s)	denotes solid phase

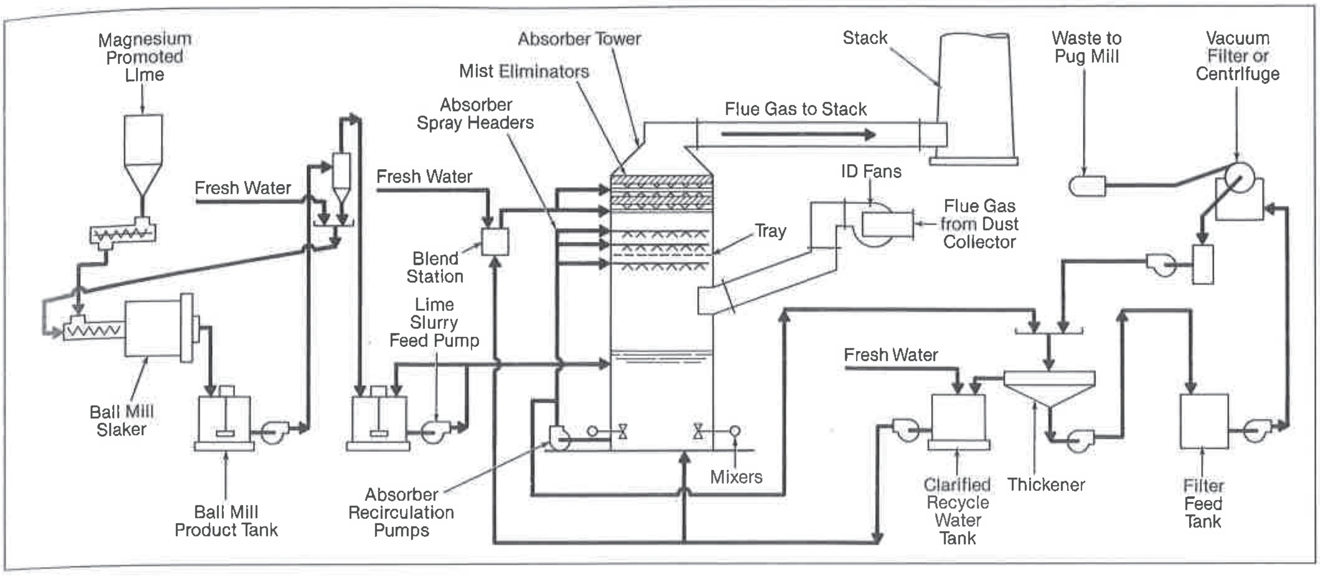


Fig. 9 Wet lime FGD system flow schematic.

$$CaSO_3 \cdot \tfrac{1}{2} H_2O + H^+ \leftrightarrow Ca^{++} + HSO_3^- + \tfrac{1}{2} H_2O$$

Dissolution of calcium sulfite **(15)**

In the reaction tank:

$$CaCO_3(s) + H^+ \leftrightarrow Ca^{++} + HCO_3^-$$

Dissolution of limestone **(16)**

$$HCO_3^- + H^+ \leftrightarrow CO_2(aq) + H_2O$$

Acid – base neutralization **(17)**

$$CO_2(aq) \leftrightarrow CO_2(g)$$

CO_2 *stripping* **(18)**

$$Ca^{++} + HSO_3^- + \tfrac{1}{2} H_2O \leftrightarrow CaSO_3 \cdot \tfrac{1}{2} H_2O + H^+$$

Precipitation of calcium sulfite **(19)**

Reaction 10 expresses the mass transfer rate of SO_2 from the gas phase to the liquid or aqueous phase. Its mass transfer rate can be expressed by:

$$\frac{d(Gy)}{dV} = k_g a(y - y^*) \qquad \textbf{(20a)}$$

or

$$N_g = \int \frac{dy}{y - y^*} = \int \frac{k_g a}{G} dV \qquad \textbf{(20b)}$$

where

G = molar gas flow rate, moles/s
y = mole fraction of SO_2 in flue gas
k_g = gas film mass transfer coefficient, moles/m²s
a = interfacial surface area, m²/m³
y^* = equilibrium SO_2 concentration at the gas-liquid interface
V = volume of the gas-liquid regime, m³
N_g = number of gas phase transfer units, dimensionless

Although k_g can be approximated, the interfacial surface area can not. The gas phase mass transfer rate must be determined experimentally. This involves operating the scrubber under conditions in which $y^* \rightarrow 0$. Equation 20 can then be integrated to:

$$N_g = -\ell n(1 - E) = k_g a \, V / G \qquad \textbf{(21)}$$

where

N_g = overall number of gas phase transfer units, dimensionless
E = overall SO_2 fractional efficiency

Many factors determine the number of gas phase transfer units (N_g). These include the slurry spray rate, the droplet size and spacial distributions, the gas phase residence time (height of spray zone), the liquid residence time, wall effects and the gas flow distribution.

In a limestone based wet scrubber, the rate-limiting reactions in the gas-liquid contact zone are believed to be Reactions 12 and/or 15. The reaction rate for limestone dissolution can be expressed by:

$$\frac{d[CaCO_3]}{dt} = k_c([H^+] - [H^+]_{eq}) S_{pc} [CaCO_3] \qquad \textbf{(22)}$$

where

$[CaCO_3]$ = calcium carbonate concentration in the slurry, moles/l
$[H^+]$ = hydrogen ion concentration, moles/l
$[H^+]_{eq}$ = equilibrium (H^+) at the limestone surface, moles/l
S_{pc} = specific surface area of limestone in slurry

Fig. 10 is a plot of limestone dissolution rates at various pH values and CO_2 partial pressures. The dissolution rate of calcium sulfite can be expressed in a form similar to Equation 22. The calcium sulfite will dissolve only if the H^+ concentration exceeds its equilibrium value in the gas-liquid contact zone.

The equilibrium pH for calcium sulfite is approximately 6.3 at a CO_2 partial pressure of 0.12 atm (12 kPa). Therefore, in order for Reaction 15 to proceed to the right, the pH in the gas-liquid contact zone must be below the

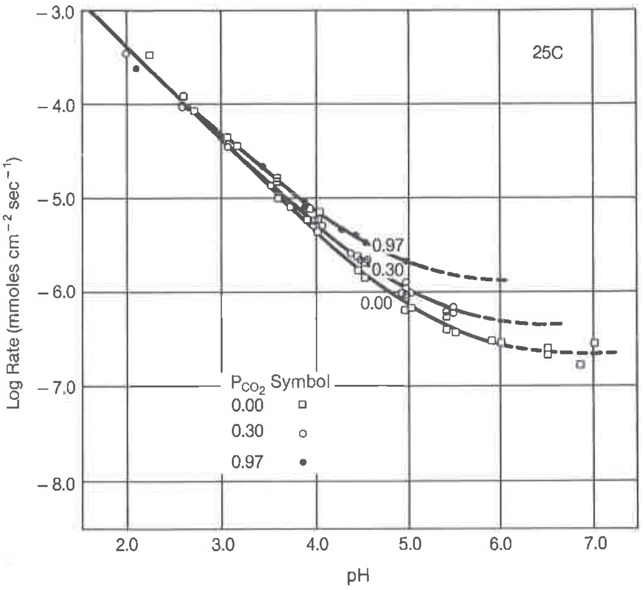


Fig. 10 Limestone dissolution rates at various pH values and CO_2 partial pressures (atm).[2]

equilibrium pH. If the pH were to stay above 6.3, then Reaction 15 would proceed to the left. This is undesirable because scaling due to sulfite precipitation in the scrubber is a likely consequence.

The reaction tank permits Reactions 16 through 19 to approach completion. In a limestone scrubber, limestone is added directly to the reaction tank. The pH of the slurry returning from the gas-liquid contact zone to the reaction tank can be as low as 3.5. The pH in the reaction tank is usually 5.2 to 6.2. Therefore, the overall reaction in the reaction tank is:

$$CaCO_3(s) + H^+ + HSO_3^- + \tfrac{1}{2}\,H_2O \rightarrow$$
$$CaSO_3 \cdot \tfrac{1}{2}H_2O(s) + CO_2(g) \qquad (23)$$

Some oxidation of sulfite to sulfate inevitably occurs in the gas-liquid contact zone of the scrubber:

$$HSO_3^- + \tfrac{1}{2}\,O_2 \rightarrow SO_4^= + H^+ \qquad (24)$$

This is called *natural oxidation* to distinguish it from *forced oxidation* in which air is sparged through the slurry. The extent of natural oxidation is typically 15 to 30%, although it may be as high as 50% or higher.

The sulfate combines with dissolved calcium and water to form calcium sulfate dihydrate, or gypsum. The reaction proceeds as follows:

$$Ca^{++} + SO_4^= + 2H_2O \leftrightarrow CaSO_4 \cdot 2H_2O \qquad (25)$$

The rate of gypsum crystallization can be expressed by:

$$\frac{d[CaSO_4 \cdot 2H_2O]}{dt} = k(R-1)Sp_g[CaSO_4 \cdot 2H_2O] \qquad (26)$$

where

$R = A_{Ca^{++}} A_{SO_4^=} / K_{Sp}$
$A_{Ca^{++}}$ = activity of Ca^{++} ion
$A_{SO_4^=}$ = activity of $SO_4^=$ ion
K_{sp} = solubility product of gypsum
Sp_g = specific surface area of gypsum

R is a measure of the level of supersaturation. If R is greater than 1, the solution is supersaturated in gypsum. If R is less than 1, the solution is subsaturated in gypsum.

The reaction tank serves a second important function in lime/limestone scrubber systems. The tank is sized to provide sufficient time for the dissolved gypsum to crystallize and precipitate. Typically, the reaction tank is designed for six to ten minutes of residence time based upon the recirculation rate.

Gypsum scaling might be more of a problem in wet scrubbers that use lime or limestone and operate in the natural oxidation mode if it were not for a phenomenon known as *co-precipitation*. The principal reaction product in these wet scrubbers is $CaSO_3 \cdot \tfrac{1}{2}H_2O$. Co-precipitation occurs when the sulfate ion ($SO_4^=$) is substituted for the sulfite ion ($SO_3^=$) in the calcium sulfite crystal lattice. This has the effect of removing sulfate from solution thereby reducing the gypsum supersaturation.

The reaction model for lime based wet scrubbers is similar to that for limestone. Two principal differences exist. First, calcium hydroxide is much more soluble than limestone, approaching 1 g/l at 77F (25C). Secondly, solid $Ca(OH)_2$ has a much higher specific surface area. For example, ground limestone has a specific surface area of about 0.2 to 0.8 m^2/g. By contrast, slaked lime typically varies from about 5 to 15 m^2/g. The equilibrium pH of $Ca(OH)_2$ at 77F (25C) is 12.4 compared to a value of 7.8 for $CaCO_3$. In many respects, lime behaves like a highly reactive limestone. The following lime reactions could be substituted for Reactions 12 and 13.

$$Ca(OH)_2(s) + H^+ \leftrightarrow CaOH^+ + H_2O \qquad (27)$$

$$CaOH^+ + H^+ \leftrightarrow Ca^{++} + H_2O \qquad (28)$$

Performance enhancing additives

The steady-state hydrogen ion concentration of the slurry in the gas-liquid contact zone is determined by the balance between the rate of H^+ generation in Reaction 11 and the rate of H^+ consumption by Reactions 12, 13 and 15. As the hydrogen ion concentration increases, i.e., as the pH drops, the equilibrium SO_2 vapor pressure increases. This equilibrium relationship can be expressed by:

$$y^* = \frac{C' \times 10^3[H^+]}{k_1(k_2 + [H^+])} \qquad (29)$$

where

k_1 = the equilibrium constant for Reaction 10, moles/l atm
k_2 = the equilibrium constant for Reaction 11, moles/l
C' = total concentration of dissolved SO_2, millimoles/l
= $[SO_2]_{aq} + [HSO_3^-]$
$[H^+]$ = steady-state hydrogen ion concentration
y^* = SO_2 vapor pressure expressed as ppm (assuming barometric pressure = 1 atm)

At 122F (50C):

k_1 = 0.4643 moles/l atm
k_2 = 7.162×10^{-3} moles/l

As the SO_2 vapor pressure rises, the rate of SO_2 absorption diminishes and approaches zero as $y^* \rightarrow y$. (See Equation 20.) If a simple means existed to reduce the hydrogen ion concentration in the gas-liquid contact zone, then the SO_2 vapor pressure could be controlled and the SO_2 absorption rate would be maximized. A buffer is a chemical specie which performs this function. A class of weak organic acids has been found suitable for use in limestone scrubbers to control pH and improve overall SO_2 removal. These buffers can be described by:

$$H^+ + A^- \leftrightarrow AH \qquad \textbf{(30)}$$

where AH is the generalized acid group. When the pH falls in the gas-liquid contact zone, Reaction 30 is driven to the right. Some organic acids which buffer in this range include adipic, formic and succinic acid. Because these are water soluble, the pH buffering is nearly instantaneous compared to the lime or limestone dissolution. Because the SO_2 vapor pressure, i.e., the equilibrium SO_2 concentration of the gas-liquid interface, is proportional to the hydrogen ion concentration, buffers minimize the rise in SO_2 vapor pressure. The buffer concentration required to achieve a given absorption depends upon SO_2 concentration and L/G ratio (the ratio of slurry flow to gas flow). Typically, the concentration of these additives which is required to achieve adequate control ranges from 3 to 30 millimoles/l.

A second additive used in wet FGD systems is magnesium oxide, which reacts with SO_2 to form magnesium sulfite. Because magnesium sulfite is highly soluble, the sulfite ion is the primary reactant in the gas-liquid interface as follows:

$$SO_3^= + H^+ \leftrightarrow HSO_3^- \qquad \textbf{(31)}$$

Sodium carbonate can also be added to the lime/limestone system for a similar benefit.

The total concentration of dissolved alkaline species such as $CO_3^=$, HCO_3^-, $SO_3^=$ and OH^- in the slurry is referred to as *dissolved alkalinity*. If the dissolved alkalinity is sufficiently high, the scrubber may become gas-phase diffusion controlled. This is illustrated in Fig. 11.[2] Under these conditions the rate of SO_2 absorption is dependent only upon the amount of interfacial surface area, i.e., the spray droplet surface area plus the tray froth surface area.

Additives for scale control

Although many scrubber additives provide performance improvements, others are used specifically for scale control. Scaling, a potential problem in all lime/limestone scrubbers, is primarily due to calcium sulfate ($CaSO_4 \cdot 2H_2O$: gypsum) precipitation onto surfaces within the gas-liquid contact zone. The large reaction tanks used in these scrubbers alleviate this condition but do not eliminate it. Sodium thiosulfate ($Na_2S_2O_3$) is a recognized oxidation inhibitor which, when added to a limestone slurry, reduces the level of natural oxidation. The effectiveness of thiosulfate is proportional to the product of its molar concentration, the calcium ion concentration, and the moles of SO_2 absorbed.

An economic alternative to using $Na_2S_2O_3$ is to add colloidal sulfur to the lime/limestone slurry. The sulfur reacts with the bisulfite in solution as follows:

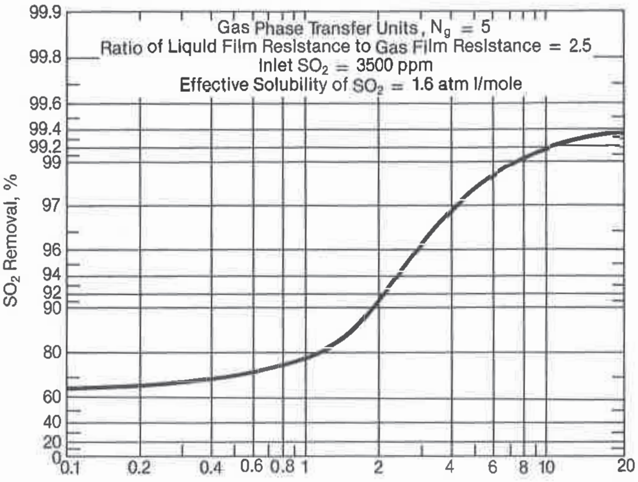


Fig. 11 Influence of dissolved alkalinity on SO_2 performance (1 milliequivalent = 50 ppm $CaCO_3$).

$$S(s) + HSO_3^- \leftrightarrow S_2O_3^= + H^+ \qquad \textbf{(32)}$$

The concentration of sulfur required ranges from 0.004 to 0.006 moles/l.

In addition to reducing scale formation in the scrubber, inhibiting sulfite oxidation permits easier removal of free water from the waste product (dewatering). Dewatering is simplified because the calcium sulfite crystal grows larger in the absence of sulfate ions.

Dry scrubbers

Dry scrubbing is the principal alternative to wet scrubbing for SO_2 control on utility boilers. Since 1980, 7200 MW of dry scrubbers have been installed at U.S. electric utilities. Dry scrubbing is also a popular choice for smaller industrial applications and for combined HCl and SO_2 control on waste-to-energy units. In the U.S., dry scrubbers have mainly been applied to units burning low sulfur fuels. Of the 43 U.S. utility dry scrubber installations, the majority lie west of the Mississippi River.

The advantages of dry scrubbing over wet scrubbing include:

1. less costly construction materials,
2. dry waste products,
3. fewer unit operations, and
4. simplicity of operation.

Dry scrubbing is sometimes referred to as spray absorption, spray drying or semi-wet scrubbing. It involves spraying a highly atomized slurry or aqueous solution of an alkaline reagent into the hot flue gas to absorb the SO_2. Fig. 12 depicts a utility size dry scrubber installation coupled with a baghouse. Unlike a wet scrubber installation, the dry scrubber is positioned before the dust collector. Flue gases leaving the air heater at a temperature of 250 to 350F (121 to 177C) enter the dry scrubber through an array of Turbo-Diffusers® as shown in Fig. 13 for a horizontal flow design. Vertical flow modules such as that shown in Fig. 14 are also supplied.

The quantity of water in the atomized spray is limited so that it completely evaporates in suspension. SO_2 absorp-

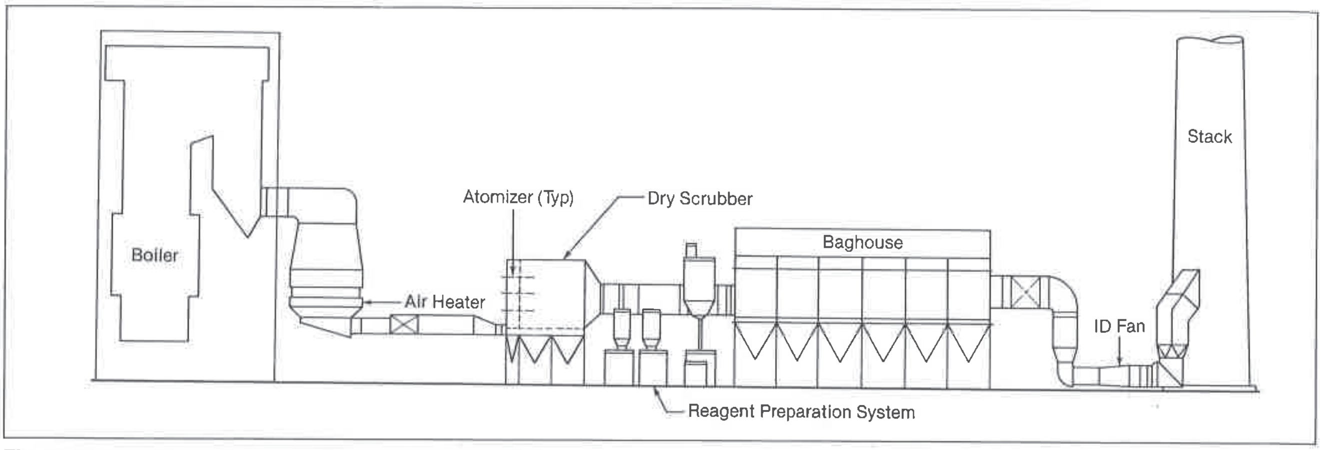


Fig. 12 Dry scrubber emissions control system configuration.

tion takes place primarily while the spray is evaporating and the flue gas is adiabatically cooled by the spray. The difference between the temperature of flue gas leaving the dry scrubber and the adiabatic saturation temperature is known as the *approach temperature*. Reagent stoichiometry and approach temperature are the two primary variables which dictate the scrubber's SO_2 removal efficiency.

The flue gas temperature leaving the dry scrubber may be too low for proper operation of the dust collector. In those instances the gases may be heated before entering the dust collector. The dust collector can be either an electrostatic precipitator (ESP) or a baghouse. The ESP is more forgiving of temperature variation but the baghouse has the advantage of being a better SO_2-lime reactor.

The predominant reagent used in dry scrubbers is slaked lime. The system shown in Fig. 15 consists of storage facilities for pebble lime (CaO), a ball mill slaking system, a system for mixing slaked lime with recycle material from the dust collector, the dry scrubber and the dust collector. Atomization of the slurry is accomplished by pneumatic or rotary atomization. A typical pneumatic atomizer is shown in Fig. 13.

Dry scrubber chemistry

SO_2 absorption in a dry scrubber is similar to that attained by wet scrubbing. The majority of the reactions take place in the aqueous phase; the SO_2 and the alkaline constituents dissolve into the liquid phase where ionic reactions produce relatively insoluble products. The reaction path can be described as follows:

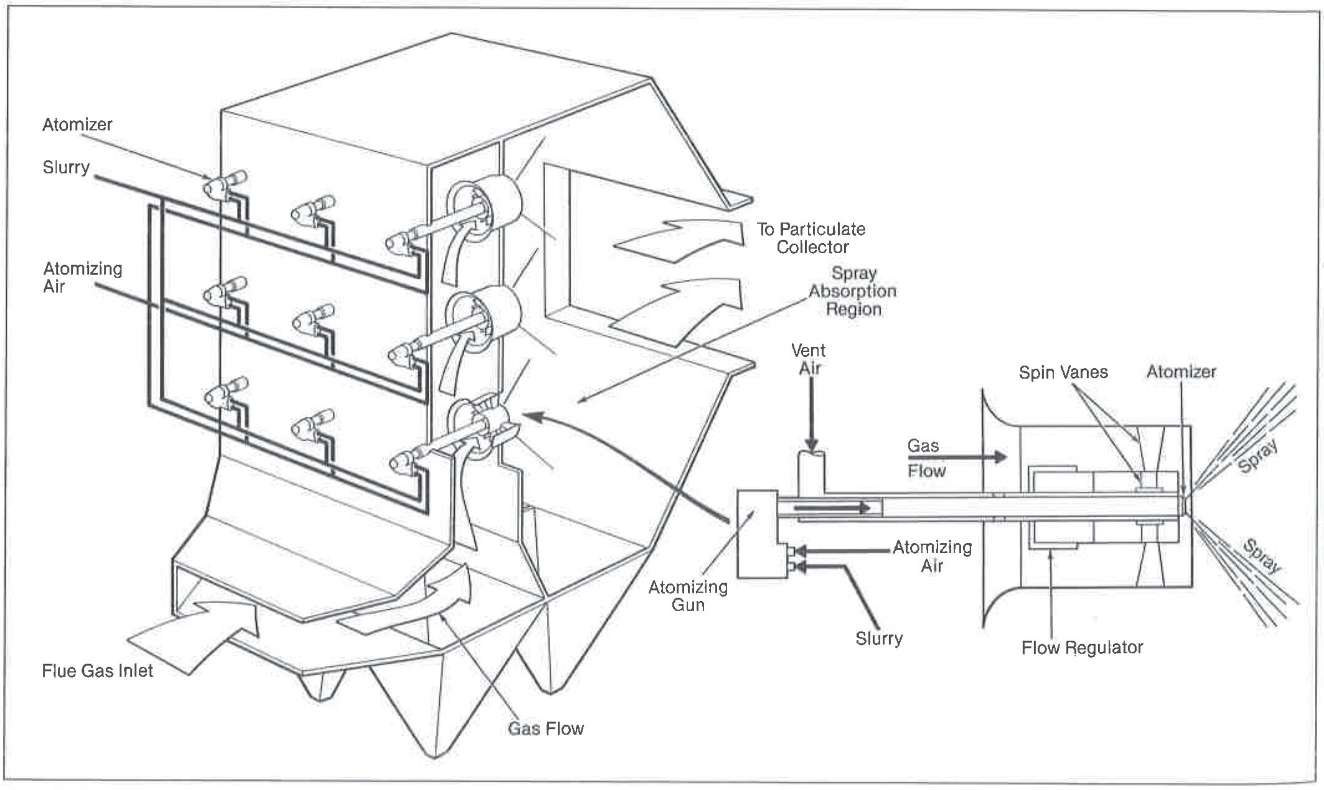


Fig. 13 Dry scrubber reactor module — horizontal flow configuration showing Turbo-Diffuser® insert.

$$SO_2(g) \leftrightarrow SO_2(aq)$$
Absorption **(33)**

$$Ca(OH)_2(s) \rightarrow Ca^{++} + 2OH^-$$
Dissolution **(34)**

$$SO_2(aq) + H_2O \leftrightarrow HSO_3^- + H^+$$
Hydrolysis **(35)**

$$SO_2(aq) + OH^- \leftrightarrow HSO_3^- \quad \textbf{(36)}$$

$$OH^- + H^+ \leftrightarrow H_2O \quad \textbf{(37)}$$

$$HSO_3^- + OH^- \leftrightarrow SO_3^= + H_2O$$
Neutralization **(38)**

$$Ca^{++} + SO_3^= + \tfrac{1}{2}\,H_2O \rightarrow CaSO_3 \cdot \tfrac{1}{2}\,H_2O\,(s)$$
Precipitation **(39)**

These dry scrubber reactions usually take place in the pH range of 10 to 12.5. The reaction scheme for wet scrubbers depicted by Equations 10 to 19 occurs below a pH of 7.0.

Dry scrubbers are normally sized for a certain gas-phase residence time, which depends on the design approach temperature and the degree of atomization. For example, if the approach temperature is 25F (14C) and the atomization system is designed for a Sauter mean diameter of 50 microns, the reactor residence time would be designed for about ten seconds.

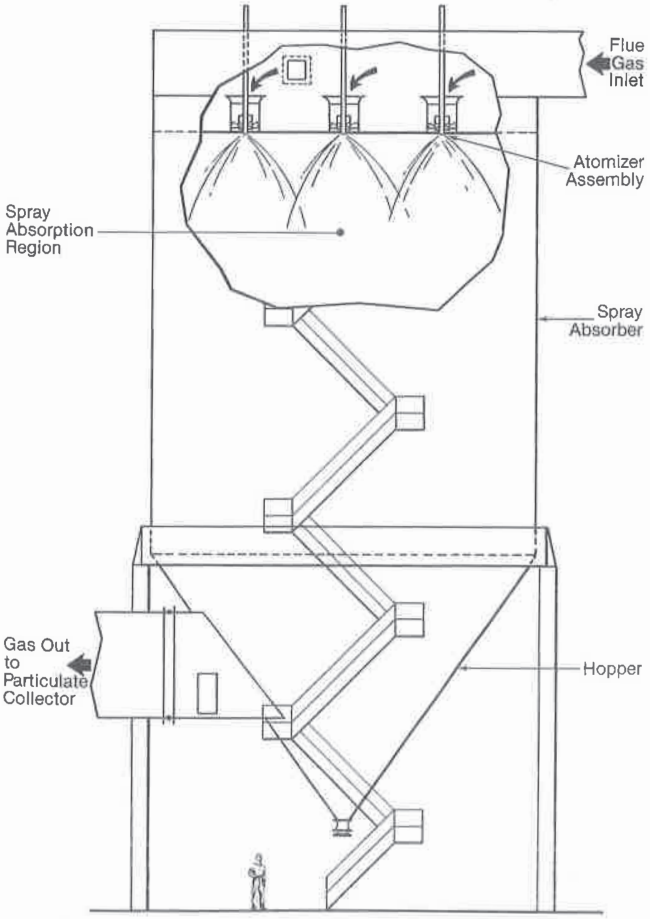


Fig. 14 Dry scrubber reactor module — vertical flow configuration.

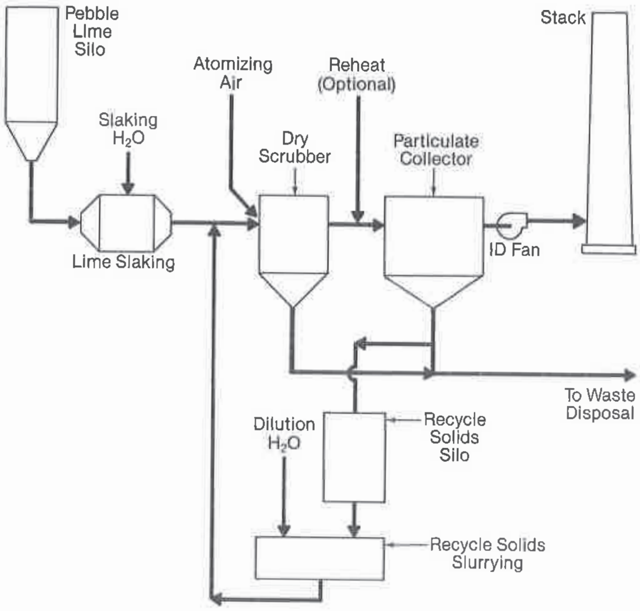


Fig. 15 Dry FGD scrubber system schematic.

The application of dry scrubbers to large electric utility boilers (see Fig. 16) is generally limited to those burning low sulfur coals. This is due primarily to the higher reagent costs for dry scrubbing. However, for smaller utility and industrial boiler applications, the simplicity and lower capital costs of dry scrubbing make it an attractive alternative.

The primary class of additives used in dry scrubbers is deliquescent salts which, when added to lime, reduce the drying rate and increase the equilibrium moisture content. SO_2 removals above 95% are possible with these additives. Of these salts, calcium chloride is the most popular. Ammonia injection upstream of a dry scrubber also increases SO_2 performance significantly.

Other commercialized technologies

A number of additional approaches and technologies are also available to control SO_2 emissions from fired processes. These range from reducing sulfur in the fuel to special combustion systems to postcombustion technology. Sulfur removal using coal cleaning processes is discussed in Chapter 11. Fluidized beds, illustrating SO_2 control during combustion, are discussed in Chapters 16 and 29. Finally, sulfur removal during coal gasification is covered in Chapter 17.

Other examples of commercialized FGD technology include:

1. furnace sorbent injection,
2. nacholite/trona injection, and
3. activated carbon.

Furnace sorbent injection has developed during the past 20 years. The technology involves the pneumatic in-

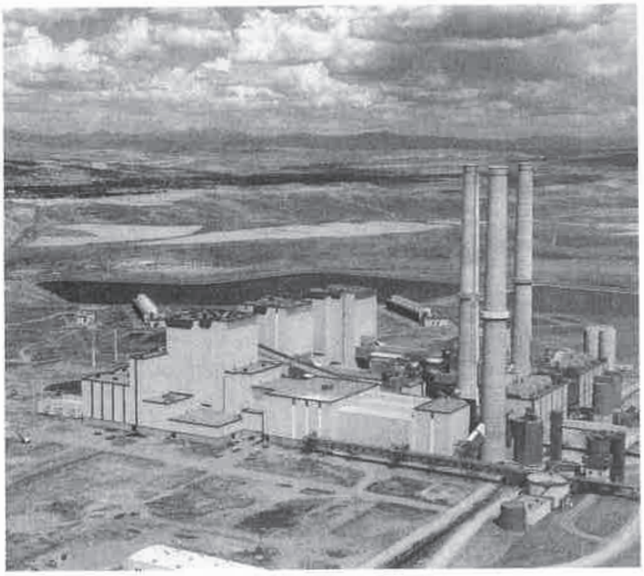


Fig. 16 470 MW utility boiler with dry scrubber and baghouse.

jection of limestone, dolomite or hydrated lime at a gas temperature of 2000 to 2300F (1093 to 1260C). Normally, the injection point is near the nose of the boiler. (See Fig. 17.) Using hydrated lime, 50 to 60% SO_2 capture is achievable with a calcium/sulfur ratio of 2.

Trona and nacholite are naturally occurring forms of sodium carbonate and bicarbonates which react with SO_2 at air heater exit temperatures. A relatively simple injection system for powdered reagent is placed between the air heater and baghouse. SO_2 reactions take place in the flue ahead of the baghouse and on the surface of the bag material. However, sodium carbonates have been observed to catalyze the oxidation of nitric oxide (NO) to nitrogen dioxide (NO_2). Whereas nitric oxide is a colorless gas, NO_2 is a brown gas which creates a visible stack plume.

Limited applications of activated carbon moving beds for SO_2 removal are seen in Germany and Japan. These beds have the added feature of low temperature SCR catalysis for the selective reduction of NO with ammonia.

Although a major worldwide effort has been expended to develop these and other alternatives, more than 97% of all SO_2 emissions control is currently accomplished by conventional wet and dry scrubbing.

Developments and trends

In addition to the commercialized FGD technologies, many new FGD processes are under development at the pilot plant scale. Some of these are at the demonstration stage on operating boilers.

The uncertainty as to which new FGD processes will make it successfully to the marketplace is great. However, it is certain that the successful processes will be those which meet the new regulations in the most economic manner. Processes which minimize capital expenses will be preferred on older power plants nearing retirement and those that are the least costly to build and operate will be preferred on newer power plants.

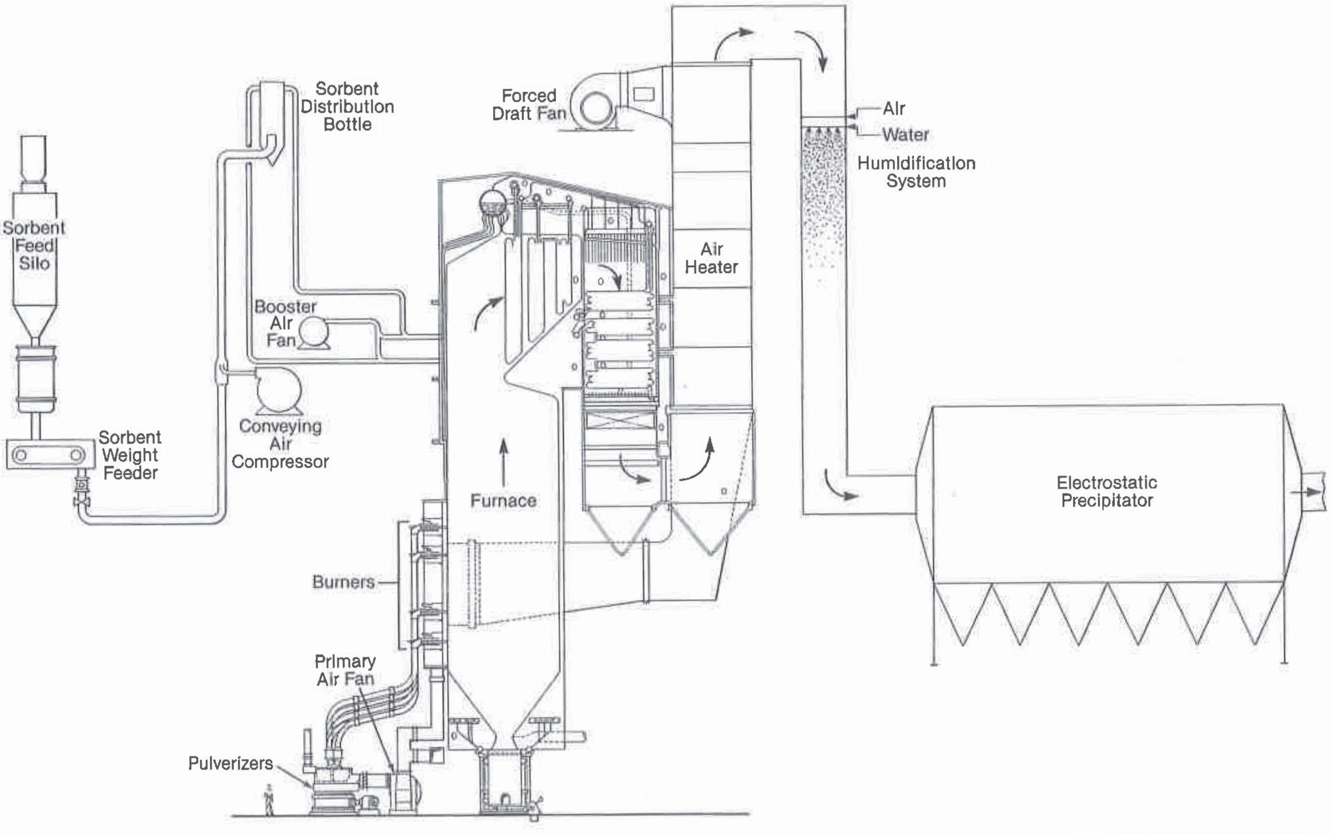
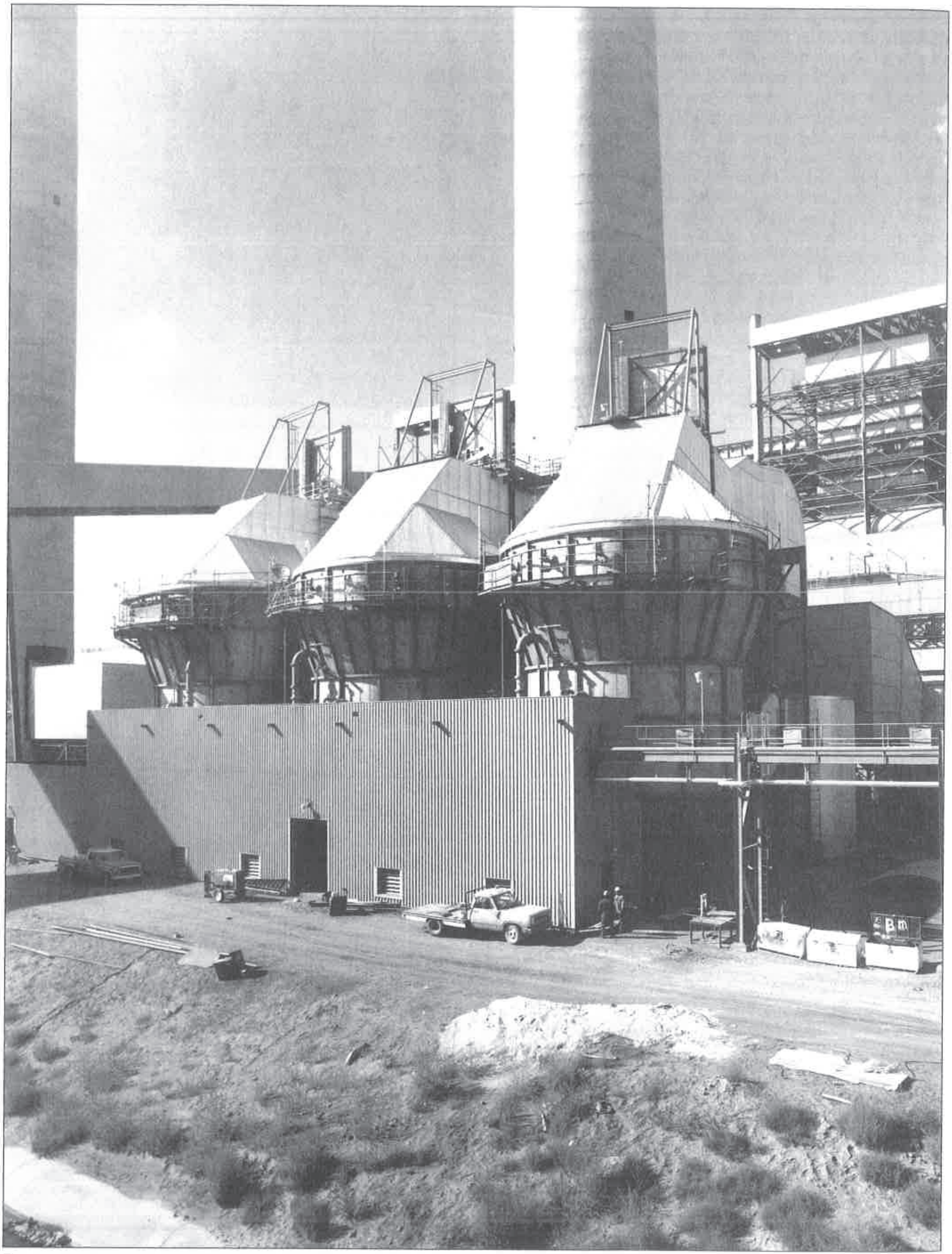


Fig. 17 Furnace sorbent injection system for SO_2 control — includes humidifier system to enhance particulate collection and SO_2 removal efficiency.

References

1. *Annual Energy Review 1990*, Report DOE/IRA 0381 (90), U.S. Energy Information Agency, Washington, D.C., 1991.

2. Plummer, L.N., Wigley, T.M.L., and Parkhurst, D.L., "The kinetics of calcite dissolution in CO_2-water systems at 5C to 60C and 0.0 to 1.0 atm CO_2," *American Journal of Science*, Vol. 278, pp. 179-216, 1978.



Flue gas desulfurization system installation in the Western U.S.

Chapter 36
Environmental Measurement

Environment related measurements at modern power plants are primarily performed to ensure compliance with government regulations. However, measurements are also necessary to monitor and optimize process performance, assess guarantees, calibrate continuous emission monitoring systems (CEMS) and verify design information. As discussed in Chapter 32, fossil fuel power plants emit air, water and solid pollutants. This chapter focuses on measurements for monitoring air pollution systems and, in particular, equipment for controlling sulfur dioxide (SO_2), nitrogen oxides (NO_x) and particulate emissions. Special emphasis is placed on measurements associated with wet SO_2 scrubbing systems which involve perhaps the most complex process.

Postcombustion emissions can be controlled by the use of one or more of the following systems: 1) particulate — electrostatic precipitators or baghouses, 2) NO_x — selective catalytic reduction (SCR) deNO_x systems or selective noncatalytic reduction (SNCR) deNO_x systems, and 3) SO_2 — wet or dry flue gas desulfurization (FGD) scrubbing systems or other forms of sorbent injection. These systems are discussed in Chapters 33, 34 and 35. In each case, the flow rate and composition must be measured for the associated gas, liquid and solid streams. In addition, the overall stack emissions are monitored and recorded.

Instrumentation

Primary measurements taken on environmental equipment include pH, liquid level, solids level, solids concentration (density), continuous emission monitoring for regulated pollutants, static and differential pressure, temperature and flow of liquid, flue gas, air and steam.

Chapter 49 discusses the measurement of pressure, temperature and fluid flow.

pH measurement

The acidic or alkaline nature of a liquid stream is monitored by measuring pH or the potential of hydrogen which is expressed as the negative log of the hydrogen ion concentration ($-\log_{10}[H^+]$). This is the most important parameter in controlling wet FGD systems. pH measurement is also important in water softening, acid neutralization, and other auxiliary processes. The alkalinity, or lack of acidity, is generally proportional to the reagent use in the FGD system. Solutions with a pH less than 7 are considered to be acidic; those having a pH greater than 7 are alkaline.

pH measurements are used to control the feed of fresh reagent slurry to the wet FGD system. (See Chapter 35.) A bleed stream of recirculation slurry is passed through one or two pH sensors. The outputs are typically combined with signals for boiler load, SO_2 level, and fresh reagent density and flow to establish the flow of fresh reagent to the FGD absorber module. An increasing pH reduces the fresh reagent feed flow and a decreasing pH increases the flow.

pH is measured by means of electrodes and a voltmeter. The electrode (Fig. 1) is an electrochemical device comparable to a battery whose voltage changes with pH. In combination electrodes, one of the half cells is the measure-

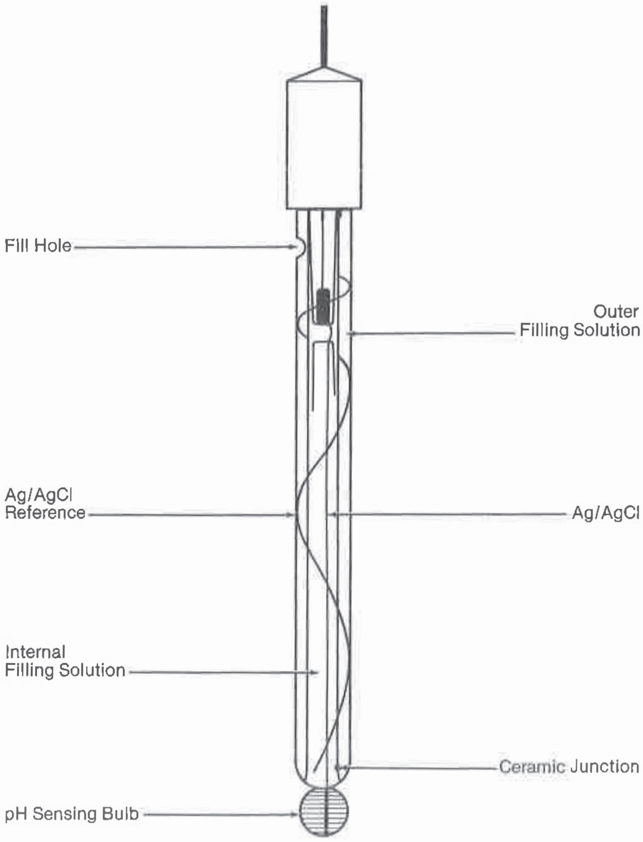


Fig. 1 Combination pH electrode (laboratory version).

ment electrode or pH sensing bulb and the other is the reference electrode or reference junction. Because the measurement electrode reacts to the pH of the solution, its potential is variable though repeatable. Theoretical electrode output varies from +414 mV at a pH of 0 to -414 mV at a pH of 14. The actual output is sensitive to the reference solution concentration at 77F (25C).

The reference electrode completes the electrical circuit and produces a comparative voltage, so changes in the overall sensor are only functions of the measuring electrode. The reference electrode is comprised of a potassium chloride (KCl) salt solution with a controlled amount of silver chloride (AgCl) dissolved in it. An Ag/AgCl electrode is placed into this electrolyte. The reference potential is a function of the KCl and AgCl concentrations. For example, a 1.0 M (molar) KCl electrolyte produces an offset (E_x), or voltage difference from theoretical, of -8 mV, while 3.3 M KCl produces a -45 mV offset (E_x). The difference, which is consistent across the entire range, is compensated for by standardization or zero adjustment.

The pH sensor is also affected by temperature. The slope (mV per pH unit) changes 1 mV per 5C (see Fig. 2). Temperature is compensated for by slope or temperature adjustment or by automatic temperature compensation.

The pH electrode used in wet FGD processes is subject to fouling and aging. This is compounded by the slurry's abrasive or scaling nature which can cause plugging of the liquid junction. This junction is the point where the KCl reference solution meets the solution being measured. The liquid junction can be a small hole or may be made of fiber, wood, porous ceramic, teflon or kynar. It holds the electrolyte in the probe and enables the electrolyte to form a salt bridge with the measured solution.

There are three types of pH sensors: dip, flow-through and insertion. The dip sensor is inserted into the tank and can be removed for maintenance and calibration. The flow-through sensor is placed in a flowing stream of process solution. The insertion sensor is a variation of the flow-through sensor, but does not require sample lines. It is inserted through packing and a valve into the flowing stream. To maintain or calibrate the insertion sensor, it is retracted through the valve, which is then closed to isolate the process.

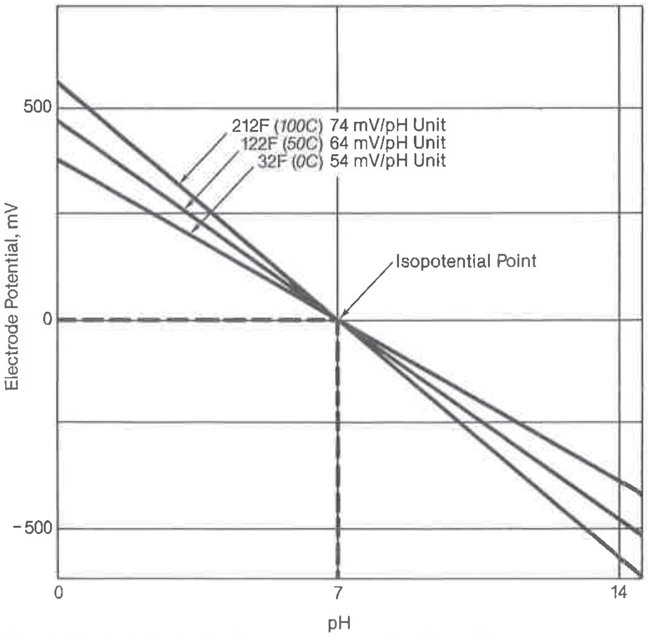


Fig. 2 Typical pH electrode response as a function of temperature.

All sensor types have advantages and disadvantages. The dip sensor is easy to maintain but prone to leakage from scrubber vessels that operate at positive pressure. Sample lines for flow-through sensors can plug. Both flow-through and insertion types are subject to high rates of erosion. All types are subject to scaling, although ultrasonic cleaning devices, which are designed to remove brittle, insoluble coatings, have been used with some success. Ultrasonic cleaners work best if used intermittently, but they can cause probe breakage.

The pH meter is a voltmeter that measures the electrode potential, converts the potential at a given temperature into pH terms, and corrects for nonideal behavior. pH meter operation depends upon proper standardization and calibration. This is best done with stable pH solutions known as buffers. Four of the best buffers, measured at 77F (25C), are pH 4.01, 6.87, 9.18 and 12.45 because they are traceable to the National Bureau of Standards. Two common buffers, pH 7 and 10, are unstable and should be avoided.

Standardization (offset or buffer adjustment) is best done at the isopotential point (pH 7). Standardization adjusts the offset so the meter reads 0.0 mV at pH 7.0. Calibration, or slope adjustment, compensates for alterations in an electrode's response to pH changes. To perform the calibration, the buffer should span the pH of the measured solution. For example, if the expected process pH is 5.4, then a buffer near pH 4 is preferred. The standardization/calibration procedure is summarized below:

1. standardize using a pH 6.87 buffer,
2 calibrate with a buffer that spans the process pH using a different adjustment than that used for standardization (calibration or slope), and
3. use the correct temperature setting, use an automatic temperature compensator or use the same temperature for the two buffers and the process.

Liquid level

Liquid level measurement is needed in any liquid storage tank which is not of the overflow design to control flow out of the tank. Examples in a wet FGD system (Chapter 35) include the tanks for absorber slurry recirculation, reagent storage, thickener underflow and quench recycle. Common liquid level measurement devices are listed in Table 1.

Differential pressure level transmitters are the most common for absorber recirculation tank level control because of their proven reliability. However, they are not the most accurate because of errors due to pressure above the liquid level or due to changes in slurry density.

Other liquid level devices have varying degrees of accuracy due to the tank conditions. For example, most tanks used in FGD systems contain slurry and are therefore agitated, causing waves. The liquid surface level in the absorber tower recirculation tank is also disrupted by: 1) the very high spray flow rates impinging on the surface, 2) foaming due to gas released during the reactions or entrained by the spray, and 3) oxidation air sparged into the tank. Sensors immersed in the slurry also tend to scale. Some level devices use stilling wells to reduce the effect of agitation and to shield the level probe from spray.

Table 1
Common Liquid Level Measurement Devices for Environmental Control Systems

Sensor Type	Theory of Operation	Environmental Control System Applications	Comments
Differential pressure	Measures differential static pressure with sensors or pressure taps mounted on the wall of the vessel. The sensor contacts the fluid.	Slurry tank level. This technique is often used with a ram or a flush system.	Reliable, subject to plugging in slurry application. Two types are used — flange mounted and extended diaphragm.
Ultrasonic	Emits ultrasonic pulse to the liquid surface. The transit time of the return pulse reflected from surface is converted to the liquid level.	Open tanks containing most fluids or slurries.	Sensors do not contact the liquid. Some problems result from waves, dust, vapor, foam, etc. Background noise can often be filtered electronically.
Electrical capacitance	Detects level by measuring the capacitance between the probe and the tank wall.	High/low level alarm. Discrete level capacitance probes can detect liquid surface.	Some problems with solids buildup or scale.
Float	Float moves up and down with level. The float is on an arm inserted into the vessel or within a housing.	Clean water, mill product tanks (nonscaling): high/low level alarm or constant tank volume.	Magnetic float types are available but are not considered good for scaling applications.
Radio frequency (phase tracking)	Detects an electrical signal which passes through a sensor and is reflected back at both the liquid surface and the bottom of the sensor. The signal phase shift provides a continuous indication of level.	Liquid and solids level.	Relatively new, promising technology. The electric field is much larger than the conductors.
Optical	Detects changes in light intensity.	Sludge level in thickeners.	For sludge level, the change in light intensity is measured at a fixed distance from the surface.

Solids level

Many types of sensors used for measuring liquid level are also used for solids level measurement. However, solids level measurement presents some unique problems due to the often dusty environments, the uneven level caused by bridging or normal angles of repose, or the changes in density or properties due to compaction or aeration. For environmental equipment, solids level measurement is used mainly for storage silos (ash, lime, limestone, gypsum) but is also used for hoppers on precipitators or dry scrubbers. Types of silo measurement devices include electrical capacitance, ultrasonic, and radio frequency (phase tracking) sensors. In addition, load cells or strain gauges, which measure the weight change of the silo as it fills or empties, are common. Another type of solids level device is a cable measurement system in which a weight or float is lowered from the top of the bin or silo. When the float reaches the solids surface, loss of cable tension is detected. The device then measures the distance traveled by counting electronic pulses as the float retracts. The measured level is therefore the silo maximum level less the distance traveled by the probe. This device should not be used when the silo is being filled.

A typical device used to determine high hopper level is a nuclear transmitter. When the ash level rises above the sensor, the strength of the signal from the nuclear source to the receiver is decreased. This signal is converted to a level indication.

Another high/low solids level device is the paddle wheel, which includes a motor that turns a paddle. When material is present, rotation of the paddle stops. The increased torque of the motor as it attempts to turn the stopped paddle triggers a microswitch alarm.

Finally, vibrating probes are sometimes used for single point solids level detection. The vibration of a piezoelectric transducer-driven probe inserted into the vessel is dampened by contact with material. This is detected as a voltage change, which is electronically amplified to yield a level indication.

Solids concentration (density)

The most commonly used devices for density measurement are nuclear absorption meters (see Fig. 3.) These devices measure the absorption of gamma rays from a radioactive source, and the degree of absorption is proportional to the solids content. Nuclear density meters do not contact the slurry; instead, they are installed on the outside of a slurry pipe. Some disadvantages of nuclear density meters are:

1. The signal is not linear with solids content unless a linearizer is used. If accurate chemical analysis of the slurry is available, the device can be precalibrated.
2. A nuclear license is required in the United States (U.S.) and in most other countries.
3. The device does not distinguish between suspended and dissolved solids.
4. Errors can result due to the buildup of solids or scale in the pipe.

Nuclear density meters are typically low maintenance

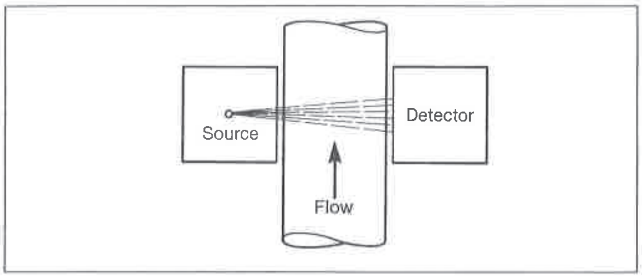


Fig. 3 Nuclear absorption meter for density measurement.

devices. The inaccuracies mentioned above are routinely verified by manual sampling and measurement.

Other devices used for density measurement include differential pressure and ultrasonic devices and vibrating reed instruments. The reed instruments electronically convert the slurry dampening effect on electrically-driven coil vibrations to a density measurement.

Pressure, flow and temperature

Pressure, pressure differential, flow and temperature measurements are common in environmental system applications. They indicate process performance, energy consumption, operational problems and ability to meet design or operating requirements. Theory, instrumentation and application for these devices are discussed in detail in Chapter 40. Selected uses in environmental systems are discussed in Chapters 33 through 35. Comments with particular importance in environmental systems include:

1. Slurries tend to be highly erosive and potentially corrosive, and provision must be made for appropriate environments.
2. The presence of solids in liquid or gas flows can lead to plugging of measuring devices. Purging systems are frequently included to ensure long term operation.
3. Temperature monitoring can be particularly important for freeze protection, crystallization prevention, thermal gradient prevention (thickeners and clarifiers), corrosion prevention (precipitators, fabric filters, dry FGD systems and flues/ducts) and general process control. Elastomeric linings and fiberglass or plastic components must be protected from high temperatures. Unlined stacks must be protected from low temperatures.

Continuous emission monitoring systems

Early power plant emission measurements focused on controlling combustion. The Orsat gas analyzer, which sampled oxygen (O_2), carbon monoxide (CO) and carbon dioxide (CO_2) flue gas concentrations, was used extensively. However, this analyzer is not a continuous monitor.

Largely due to increasing regulation, power plants have been forced to institute continuous emission measurements. In addition, continuous monitoring devices permit process control of the emissions control equipment.

During the 1980s, CEMS were used primarily to measure particulate (opacity), SO_2, NO_x and CO_2. By the early 1990s, CEMS to monitor hydrogen chloride (HCl), CO, ammonia and volatile organic compounds (VOC) were introduced for commercial combustion applications.

The common methods for continuously measuring flue gas constituents are described in Table 2 and are further detailed in Table 3. All of the analyzers are similar in that they use a measuring cell and a reference cell. They are set to zero with air or a calibration standard, the span is set with a calibration standard, and a sample is taken. The result is obtained by comparing the voltages detected across the sample, the zero standard and span standard.

There are three types of analyzers — extraction, dilution extraction and in situ.

In the extraction method (Fig. 4) a sample of flue gas is withdrawn from the process stream and directed to an external analyzer for the constituent concentration determination. This type of analyzer is typically used where there are short distances between the sample point and the analyzer. The probe and sample line are often heated to prevent condensation. Because the gas sample is typically drawn by vacuum to the external analyzer, sample line leaks can compromise the integrity of the sample.

Table 2
CEM Technologies

Technology	Operating Characteristics
Infrared radiation (IR)	An infrared beam passes through a measurement filter and is absorbed by the constitutent gas. A light detector creates a signal which is used to monitor concentrations.
Ultraviolet absorption (UV)	A split beam, with optical filters, phototubes and amplifiers, measures the difference in light beam absorption between the reference and sample.
Chemiluminescence	Ozone (O_3) is injected into the sample to react with NO_x, generating light that is measured by a photocell.
Flame ionization detection	Hydrocarbons are ionized with strong light. The signals are received by the flame ionization detector.
Transmissometer	Light is passed through the stack where it is reflected by a mirror on the opposite side. The quantity of light returning is proportional to particulate matter and aerosols in the flue gas. (See Fig. 5.)
Electrochemical cells	The voltage measured when an O_2 sample is injected into a solution with a strong base is compared to a reference voltage.
Chromatography	A sample, zero and calibration gas are eluted through a column. The output as measured by flame photometric or thermal conductivity detectors is compared.

Table 3
Continuous Emission Monitoring
(Reference Table 2 for Technologies)

Constituent	CEM Technology
Particulate matter (opacity)	Transmissometer, beta ray absorption
Sulfur dioxide (SO_2)	UV absorption, IR pulsed fluorescence
Nitrogen oxides (NO_x)	Chemiluminescence, UV spectroscopy, IR
Hydrogen chloride (HCl)	IR with gas filter
Carbon monoxide (CO)	IR
Carbon dioxide (CO_2)	IR
Oxygen (O_2)	Electrochemical cell
Volatile organic compounds (VOC)	Flame ionization detection
Other organic air toxics	Chromatography
Ammonia (NH_3)	Same as NO_x*

* NH_3 is converted to NO_x in one of two split streams. Both streams are analyzed for NO_x. NH_3 is determined as the difference.

The dilution-extraction method uses a carrier/dilution media, typically instrument air, which is supplied to the extraction probe in the flue gas process stream. Problems associated with dirty, wet and corrosive flue gases are drastically reduced by the 50 to 200 dilution ratio provided by the sample probe. Precise dilution is assured by accurately controlling the dilution air pressure which yields a constant air flow. The air flow creates a vacuum on the downstream side of a critical sample orifice. The gas sample rate, limited by sonic flow through the orifice, is therefore held constant. Furthermore, because the sample lines from the probe to the analyzer are under positive pressure, minor sample line leakage does not affect the integrity of the sample concentration as it would in a vacuum system. This method has gained wide acceptance in utility and other systems where longer sample lines are required.

In situ analyzers, such as that shown in Fig. 5, provide measurement of flue gas concentrations directly in the process stream. Several types of detection devices are available, and all are based on absorption spectroscopy. Since gas stream particulates can reduce the level of light transmission, ceramic filters are used to exclude these particles. A single in situ probe can measure several gas species and opacity. Problems with in situ analyzers generally occur in the optic or electronic components. Because a separate analyzer is required for each sample point, installations which require multiple sample points frequently find the extractive systems more cost effective.

Continuous analyzers generally require flue gas conditioning. Sample conditioning includes filtration to remove particulate (see Fig. 6), chilling to remove water, heating to maintain process temperature, and dilution (used with extractive monitor and in situ probe).

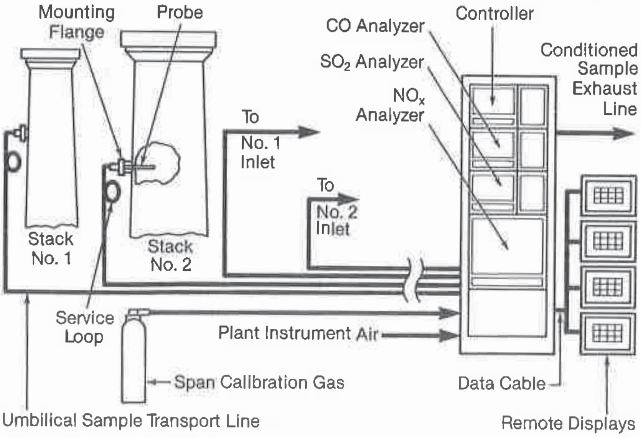


Fig. 4 Extractive stack/inlet CEM system.

The need for conditioning coupled with zero and span calibration make extractive systems complicated, costly and vulnerable to plugging, corrosion and leaking. These systems are also slow to respond due to the time lapse between sampling and analysis. In situ systems use conditioning but do not rely on long sample lines. These systems have faster response, fewer components and better availability than extractive systems. However, they are prone to interference and fouling and are less accessible for service. Extractive systems can be expanded by adding sample points as shown in Fig. 4. It is important to consider the location and ambient conditions in which CEMS equipment is placed. Many of the problems associated with CEMS can be traced to dirty conditions, excessive heat or cold, vibration, humidity, etc.

Monitoring process performance

Environmental control systems (ECS) involve physical and chemical processes. Chemical methods are used to maintain desired removal or emission levels, avoid operating problems, improve reagent utilization, improve process efficiency, troubleshoot equipment, and monitor process changes and catalyst life.

In an FGD system, the quality of the reagent and the recirculating slurry stream is monitored. Analysis is more critical for processes which produce a usable byproduct such as gypsum. In this case, the analysis extends into product purity and feed stream impurities. The quality of the reagent is normally measured extensively when

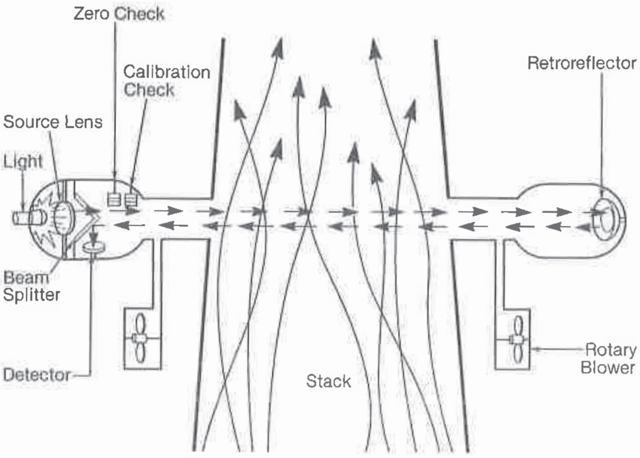


Fig. 5 In situ transmissometer system.

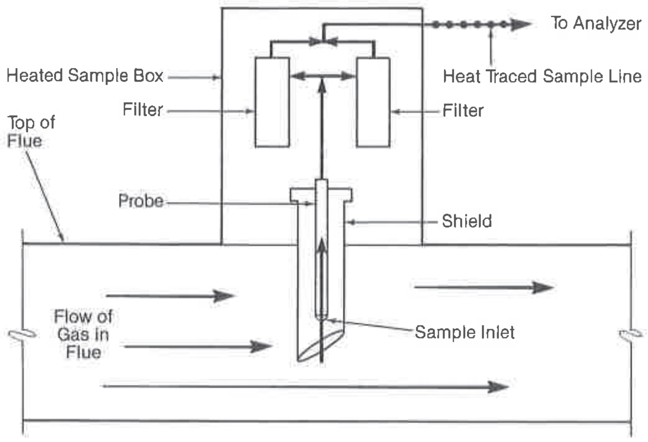


Fig. 6 Extractive sample probe with dust conditioning.

the reagent source is selected. Later it is evaluated if the source is changed or process problems occur.

Tables 4 through 7 list the important analyses for common wet scrubber FGD systems. Additional analyses are required for makeup water streams, sodium-based FGD systems, dual loop systems, regenerative systems, ex situ oxidation processes, water treatment, and sulfuric acid or SO_2 recovery processes. However, the major species and methods would be similar to those presented in Tables 4 through 7; only the concentrations would vary. Other procedures used for design or troubleshooting include relative saturation, which is determined by seed crystal procedures, and ion balance (balance of anions and cations), which is a check of the analysis accuracy.

Performance testing

As with any system, performance tests are conducted on environmental control systems to determine if the units are operating properly. A typical new environmental control system might include low NO_x burners, wet FGD scrubber modules, gypsum processing equipment, and an electrostatic precipitator. An SCR deNO_x system could also be added. The ten most common parameters measured to determine performance for such a system include:

1. system pressure drop,
2. particulate removal efficiency,
3. stack opacity,
4. NO_x emission concentration,
5. SO_2 removal efficiency,
6. makeup water requirements,
7. reagent consumption,
8. gypsum purity,
9. mist eliminator carryover, and
10. electric power consumption.

Other performance parameters that would be measured depend on the type of system. Performance testing is usually extensive. It is common for a new ECS to have two performance tests. The first test is scheduled soon after installation and the final test is performed after one year of operation.

Sample location selection

The first step in the performance test is often done before the ECS is built — selecting the sample locations. Outlet sampling is not difficult if it is done in the stack. However, the inlet and intermediate samples are more difficult to obtain. In Fig. 7, the system inlet at the far left is a section of flue followed by an immediate upward bend. The precipitator outlet is at the induced draft (ID) fan inlet. Fig. 7 also shows test ports in the downward flue section after the absorber tower and at the stack entrance. Test port locations are selected to give the best flow profile within the plant layout limitations.

The number and location of traverse points are selected by Environmental Protection Agency (EPA) Method 1. Application of Method 1 is illustrated in Fig. 8. The distance downstream from the flow disturbance,

Table 4
Lime Quality Analysis

Parameter	Suggested Method*	Suggested Frequency	Use of Data
Slaking rate	ASTM Method C-110-76a	Duplicate analysis on all candidate limes	Temperature rise rate is related to reactivity and lime quality.
Grit	Acid dissolution	Duplicate analysis on all candidate limes	High grit levels indicate poor lime quality.
Weight loss on ignition	Gravimetric	Duplicate analysis on all candidate limes	Weight loss is an indirect measure of lime quality via carbonate and hydroxide content.
Available lime index	Rapid sugar test	Duplicate analysis on all candidate limes	Lime quality
Calcium/ magnesium	Atomic absorption (AA) EDTA titration or Ion Chromatograph (IC)	Duplicate analysis on on all candidate limes then as needed to check reagent quality	Analysis is required for processes producing a usable byproduct or high magnesium lime systems.
Lime slurry solids content, % by wt	Gravimetric	Daily	Check density meter calibration and indicate slaker performance.

* Many methods have been standardized through the American Society of Testing and Materials, Philadelphia, Pennsylvania.

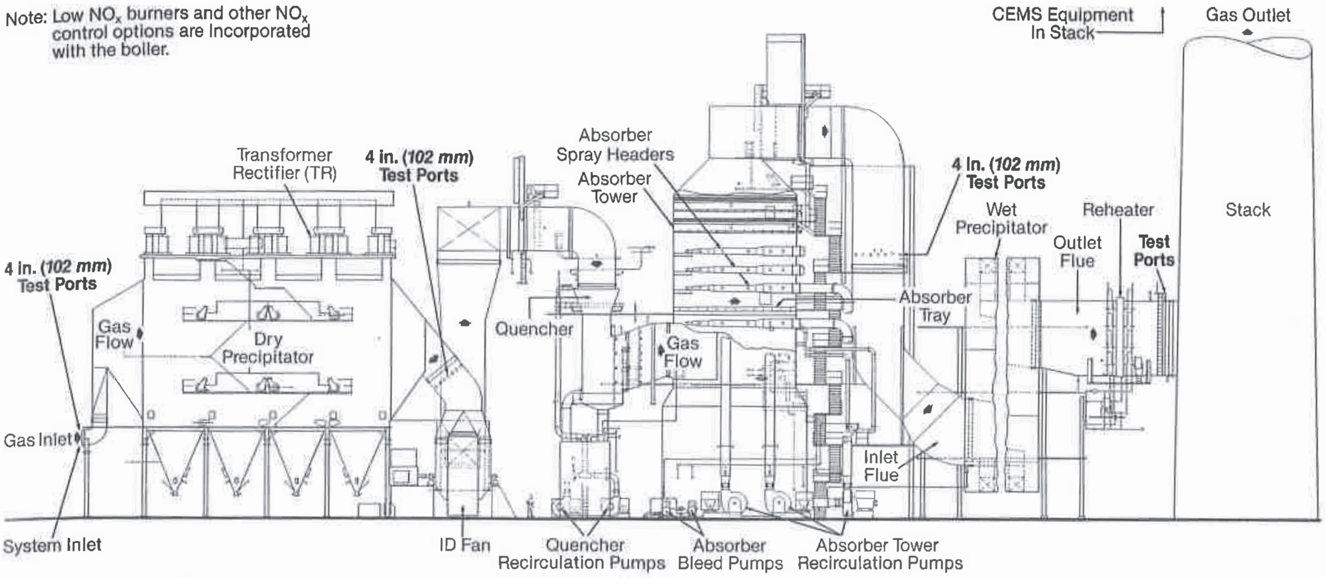


Fig. 7 Typical test port locations indicating compromises made in measurement due to equipment arrangement.

which in this case is the stack inlet, is 138 ft (42.1 m). This is more than eight diameters (138/16 = 8.6). The upstream distance to the stack exit is 5 diameters. Therefore, 12 traverse points are required by Method 1. For rectangular flues, Method 1 is applied by first determining an effective or equivalent diameter which is calculated as follows:

$$DC = \frac{2LW}{(L+W)} \qquad (1)$$

where

DC = equivalent diameter
L = length
W = width

Then a matrix layout is used for sample location selection. The cross-section is divided into as many equal rectangular areas as there are traverse points, and the sample is taken at the centroid of each area.

Gas side measurements

For a performance test of an ECS, a combination of EPA Methods 5 and 8 is the most often used procedure to simultaneously measure particulate, SO_2, and SO_3 or acid mist (H_2SO_4) levels. The Method 5 sampling train, shown in Fig. 9, is used with Method 8 impingers shown in this figure. The data obtained from this traverse also represent Methods 1 through 4. Results include gas velocity by S-type pitot tube (Fig. 10) and CO_2, O_2, moisture, SO_2, particulate, and SO_3 or H_2SO_4 levels. The following calculations are used:

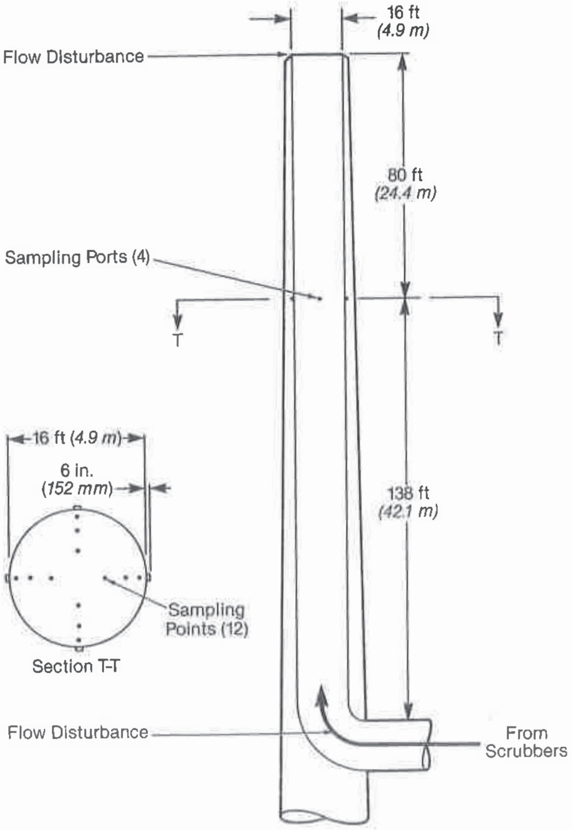


Fig. 8 Stack dimensions and sampling port locations for EPA Method 1.

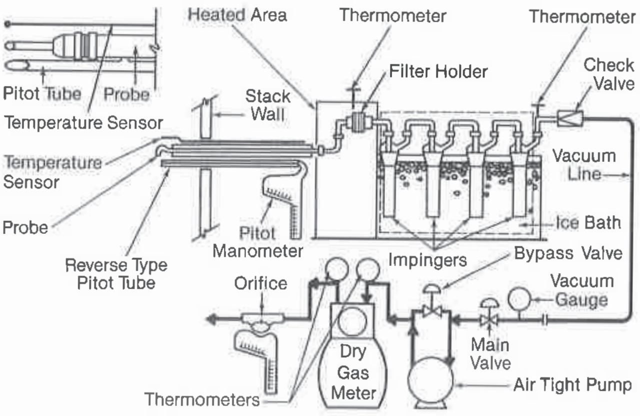


Fig. 9 EPA Method 5 particulate and SO_2 emissions sampling train.

Determination of moisture content in stack gas

$$B_w = \frac{(MWC)\ (1.339)}{[(MWC)\ (1.339)] + \dfrac{(DGV)\ (P_m)}{T_m}\ (499.9)} \qquad (2)$$

where

B_w = moisture fraction
MWC = impinger weight gain, g
DGV = sampled dry gas volume at meter conditions, ft^3
P_m = pressure at meter, in. Hg
T_m = temperature at meter, R
1.339 = constant for converting grams of H_2O to liters of H_2O vapor at standard conditions, l/g
499.9 = conversion of cubic feet at meter conditions to liters at standard conditions, l R/ft^3/in. Hg

Determination of flue gas molecular weight — dry basis

$$M_d = [(44)(\%\ CO_2\ \text{dry}) + (32)(\%\ O_2\ \text{dry}) + (28)(\%\ N_2\ \text{dry})] \times 0.01 \qquad (3)$$

where

M_d = molecular weight of gas on dry basis, lb/lb-mole
44 = molecular weight of CO_2, lb/lb-mole
32 = molecular weight of O_2, lb/lb-mole
28 = molecular weight of N_2, lb/lb-mole

Determination of flue gas molecular weight — wet basis

$$M_w = M_d(1 - B_w) + 18B_w \qquad (4)$$

where

M_w = molecular weight of gas on wet basis, lb/lb-mole
M_d = molecular weight of gas on dry basis, lb/lb-mole
B_w = moisture fraction, lb-mole H_2O/lb-mole wet gas
18 = molecular weight of H_2O, lb/lb-mole

Determination of gas humidity

$$H = \frac{18B_w}{M_d(1 - B_w)} \qquad (5)$$

where

H = gas humidity, lb H_2O/lb dry gas
B_w = moisture fraction, lb-mole H_2O/lb-mole wet gas
M_d = molecular weight of dry gas, lb/lb-mole
18 = molecular weight of H_2O, lb/lb-mole

Determination of stack gas velocity

$$V_s = 85.48\ C_p \left(\frac{T_s\ \Delta P}{P_s\ M_w} \right)^{1/2} \qquad (6)$$

where

85.48 = pitot tube constant in the following units:

$$\frac{\text{ft}}{\text{s}} \left(\frac{(\text{lb / lb-mole})\ (\text{in. Hg})}{(\text{R})\ (\text{in. } H_2O)} \right)^{1/2}$$

V_s = velocity of the flue gas, ft/s
ΔP = average differential pressure measured by S-type pitot tube, in. H_2O
T_s = average gas temperature in duct, R
P_s = absolute duct pressure, in. Hg

Table 5
Limestone Quality Analysis

Parameter	Suggested Method*	Suggested Frequency	Use of Data
Reactivity	pH stat test followed by particle size measurement	Duplicate analysis of candidate limestones	Compared to reference to determine acceptability.
Grindability (Bond Work Index)	Laboratory ball mill test	Duplicate analysis of candidate limestones	Limited by specification of wet milling system design.
Particle size of limestone as delivered	Sieve method	Duplicate analysis of candidate limestones then monitor monthly	Limited by specification of wet milling system design.
Inerts	Acid dissolution	Duplicate analysis of candidate limestones then monitor weekly for gypsum systems	Quality indicator; important for gypsum systems.
Carbonate	CO_2 evolution, $Ba(OH)_2$ absorption, alkalinity titration	Duplicate analysis of candidate limestones then monitor weekly for gypsum systems	Check reagent quality; important for gypsum systems.
Calcium and magnesium	AA, IR, EDTA titration	Duplicate analysis of candidate limestones then monitor weekly for gypsum systems	Check reagent quality.
Limestone slurry solids content, % by wt	Gravimetric	Daily	Check density meter and indicate problems in milling circuit.
Limestone slurry particle size	Wet sieve	Daily	Troubleshooting problems in milling circuit or process such as low utilization or poor gypsum quality.

* Many methods have been standardized through the American Society of Testing and Materials, Philadelphia, Pennsylvania.

Table 6
Recirculation Slurry/Blowdown Analysis

Parameter	Suggested Method*	Suggested Frequency	Use of Data
pH	2-buffer method calibration or grab sample	Once per shift by grab sample, daily by buffer method	Troubleshoot pH meter and maintain process efficiency.
Slurry suspended solids content	Gravimetric	Weekly	Calibrate density meter and maintain process efficiency.
Cations: Ca^{++} and Mg^{++} primary; K^+ and Na^+ secondary	IC, AA or wet chemistry methods	Daily for Ca^{++} and Mg^{++} in calcium-based systems	To calculate stoichiometry and monitor process chemistry.
Anions: $SO_3^=$, $CO_3^=$, $SO_4^=$ and Cl^- primary; F^- and NO_3^- secondary	IC or wet chemistry methods	Daily for $SO_3^=$, $CO_3^=$, $SO_4^=$, Cl^-	To calculate stoichiometry, measure chloride concentration, and monitor process performance and gypsum production.
Dissolved metals: Fe, Mn, Al, etc.	AA	Infrequently	Process troubleshooting.
Additives: adipic acid, dibasic acid, formate, thiosulfate, scale inhibitors, etc.	IC or wet chemistry methods	Daily	Determine or correct dosage.
TDS (total dissolved solids)	Gravimetric	Weekly	Calibrate density meter for suspended solids; important for mag-lime, high chloride or suspended solids.
Dissolved alkalinity	Acid-base titration	Weekly	Measure alkali loss in filter cake of mag-lime process; important for mag-lime or sodium systems.
Settling tests	Graduated cylinder	Weekly	Predict thickener performance and assist process troubleshooting.
Filter leaf test	Filter and weight	During startup	Predict filter cake properties.
Particle size distribution	Coulter counter	During startup	Determine settling or dewatering characteristics; important for gypsum systems.

* Many methods have been standardized through the American Society of Testing and Materials, Philadelphia, Pennsylvania.

M_w = wet gas molecular weight, lb/lb-mole
C_p = S-type pitot tube correction factor (normally 0.84)

Volumetric flow rate — actual conditions

$$Q_{ac} = 60\, V_s A \tag{7}$$

where

Q_{ac} = actual volumetric flow rate, ACFM
V_s = velocity of the flue gas, ft/s
A = cross-sectional area of the duct, ft^2
60 = conversion factor, s/min

Volumetric flow rate — dry standard conditions

$$Q_{sd} = \frac{528\ Q_{ac}\, P_s\ (1 - B_w)}{29.92\ T_s} \tag{8}$$

where

Q_{sd} = dry volumetric flow rate at standard conditions, DSCFM
Q_{ac} = actual volumetric flow rate, ACFM
B_w = moisture fraction, lb-mole H_2O/lb-mole wet gas
528 = standard temperature, R
T_s = average gas temperature in duct, R
29.92 = standard pressure, in. Hg
P_s = absolute duct pressure, in. Hg

Total particulate and H_2SO_4 — grains/ACF

$$C_a = \frac{(0.001)\ (15.43)\ (528)\ (1 - B_w)\ P_s M_n}{29.92\ V_d\ T_s} \tag{9}$$

where

C_a = concentration of specie in the flue gas at duct conditions, grains/ACF
M_n = mass of specie collected, mg
V_d = dry gas volume sampled at standard conditions, DSCF
T_s = average gas temperature in duct, R
P_s = absolute duct pressure, in. Hg
B_w = moisture fraction of gas, lb-mole H_2O/lb-mole wet gas
0.001 = conversion of milligrams to grams, g/mg
15.43 = conversion of grams to grains, grains/g
528 = standard temperature, R
29.92 = standard pressure, in. Hg

Table 7
Dewatering System Analysis

Parameter	Suggested Method*	Suggested Frequency	Use of Data
Thickener or hydroclone underflow solids, %	Gravimetric	Daily	Troubleshoot process and calibrated lime density meters
Clarified water, water analysis (anions, cations, suspended solids)	See Table 6	Weekly	Monitor thickener performance
Supernatent, filtrant solids content, % by wt	Gravimetric	Daily	Monitor filter cloth status
		Gypsum Quality Analysis	
Ca^{++}, Mg^{++}, Na^+, K^+, Fe_2O_3, R_2O_3, SiO_2	AA	Weekly	Product purity and properties
Cl^-, $SO_4^=$	IC	Daily	Product purity and properties
$SO_3^=$, $CaSO_3 \cdot \frac{1}{2}\ H_2O$	Iodimetric titration	Daily	Product purity and properties
Moisture content	Gravimetric	Daily	Important for salable gypsum and monitoring dewatering system performance.
Surface area	BET analysis (sub-sieve sizer)	Startup or process change	N_2 gas is condensed on surface and absorbed; N_2 corresponds to surface area.
Combined water	Heat to 482F (250C)	Weekly	Gypsum purity
Mean particle size	Coulter counter, Sedigraph plus sieve analysis	Startup or process change	Product purity and properties
Aspect ratio	Scanning electron microscope	Startup or process change as required by end users	Product purity and properties
Total water soluble salts	Sum $(Na^+ + K^+ + Mg^{++})$	As needed	Product purity and properties
Flyash	Determined as acid insoluble	Daily	Determined as acid insolubles along with silica (SiO_2) and other impurities.
pH	Electrode	Daily	Product purity and properties

* Many methods have been standardized through the American Society of Testing and Materials, Philadelphia, Pennsylvania.

Total particulate, H_2SO_4, condensible total particulate and condensible H_2SO_4

$$C_s = \frac{(0.001)\ (15.43)\ M_n}{V_d} \qquad (10)$$

where

C_s = concentration of specie in the flue gas at dry conditions, grains/DSCF
M_n = mass of specie collected, mg
V_d = dry gas volume sampled at standard conditions, DSCF
0.001 = conversion of milligrams to grams, g/mg
15.43 = conversion of grams to grains, grains/g

Total particulate, H_2SO_4, NO_x and SO_2 — lb/h

$$C_m = C_s (1.428 \times 10^{-4})(60)(Q_{sd}) \qquad (11)$$

where

C_m = mass flow rate of specie in the flue gas, lb/h
C_s = concentration of specie in the flue gas at dry standard conditions, grains/DSCF
Q_{sd} = dry volumetric flow rate at standard conditions, DSCFM
60 = conversion of minutes to hours, min/h
1.428×10^{-4} = conversion of grains to pounds, lb/grain

Total particulate, H_2SO_4, NO_x and SO_2

$$E = \frac{20.9\ C_m F_d}{60\ Q_{sd}\ (20.9 - \%\, O_{2ds})} \qquad (12)$$

where

E = emission rate on a dry basis at 0% O_2, lb/10^6 Btu
C_m = mass flow rate of specie in the flue gas, lb/h
Q_{sd} = dry volumetric gas flow rate at standard conditions, DSCFM
$\%\, O_{2ds}$ = O_2 in the gas on a dry basis, %
F_d = dry F-factor at 0% O_2, determined from fuel analysis, DSCF/10^6 Btu (see Equation 17)
20.9 = O_2 in air, used with % O_2 in the gas to correct to 0% O_2, %
60 = conversion of minutes to hours, min/h

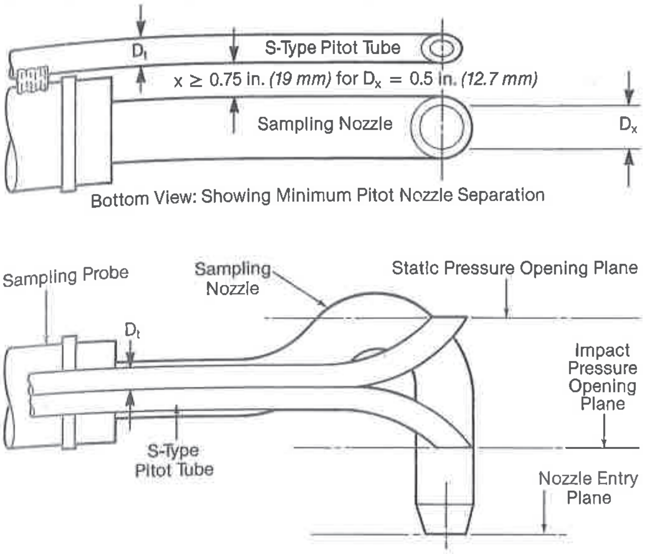


Fig. 10 S-type pitot tube with sampling probe.

SO_2 — parts per million (ppm) wet

$$C_{ppm,w} = \frac{(8.48 \times 10^{-4})\ (10^6)\ V_s C_i\ (1 - B_w)}{V_d} \qquad (13)$$

where

$C_{ppm,w}$ = gas SO_2 concentration on a wet basis, ppm wet
V_s = total volume of H_2O_2 impinger solution
C_i = SO_2 concentration in the impinger solution, mg/liter
V_d = gas volume sampled at dry standard conditions, DSCF
B_w = gas moisture fraction, lb-mole H_2O/lb-mole wet gas
8.48×10^{-4} = conversion of millimoles to standard cubic feet, SCF/mM
10^6 = conversion from fraction to ppm

SO_2 — ppm dry

$$C_{ppm,d} = \frac{20.9\ C_{ppm,w}}{(1 - B_w)\ (20.9 - \%\,O_{2ds})} \qquad (14)$$

where

$C_{ppm,d}$ = gas specie (SO_2) concentration on a dry basis, corrected to 0% O_2, ppm dry
$C_{ppm,w}$ = gas specie (SO_2) concentration on a wet basis, ppm wet
B_w = moisture fraction of the gas, lb-mole H_2O/lb-mole wet gas
$\%\,O_{2ds}$ = O_2 in the gas on a dry basis, %
20.9 = O_2 in air, used with % O_2 in the gas to correct to 0% O_2, %

NO_x — ppm dry and ppm wet

NO_x is evaluated directly by monitoring systems as parts per million, dry basis. It can be converted to ppm wet if needed by solving Equation 14 for $C_{ppm,w}$.

Collection/removal efficiency — total particulate, H_2SO_4 and SO_2

$$C_{eff} = \left[(C_{in} - C_{out}) / C_{in}\right] \times 100 \qquad (15)$$

where

C_{eff} = collection/removal efficiency, %
C_{in} = concentration of matter at inlet, lb/10^6 Btu
C_{out} = concentration of matter at stack, lb/10^6 Btu

Percent isokinetic

$$\%\,I = (V_n\ / V_s) \times 100 \qquad (16)$$

where

$$V_n = \frac{V_m T_s P_m}{60\ t A_n T_m\ P_s (1 - B_w)}$$

and where

$\%\,I$ = % isokinetic
V_s = average flue gas velocity in duct during sampling, ft/s
V_n = average sample gas velocity through the nozzle during sampling, ft/s
V_m = dry gas volume sampled at meter conditions, ft^3
t = elapsed sampling time, min
A_n = cross-sectional area of nozzles, ft^2
B_w = gas moisture fraction, lb-mole H_2O/lb-mole wet gas
T_s = flue gas temperature in the duct, R
T_m = average gas temperature at meter, R
P_m = absolute pressure at the meter, in. Hg
P_s = absolute pressure in the duct, in. Hg
60 = conversion from minutes to seconds, min/s

F-factor

The F-factor used in making emissions rate calculations was developed from chemical and combustion analyses of the fuel. This factor is the ratio of the theoretical volume of dry gases at 0% excess air (O_2) given off by complete combustion of a known amount of fuel, to the gross caloric value of the burned fuel. The data generated from the ultimate analysis of the fuel are used to calculate the F-factor as follows:

$$F_d = (10^6)\,\frac{3.64(H) + 1.53(C) + 0.57(S) + 0.14(N) - 0.46(O)}{HHV} \qquad (17)$$

where

F_d = dry F-factor at 0% O_2, DSCF/10^6 Btu
HHV = higher heating value, Btu/lb
H = hydrogen in the fuel, % by wt
C = carbon in the fuel, % by wt
S = sulfur in the fuel, % by wt
N = nitrogen in the fuel, % by wt
O = oxygen in the fuel, % by wt

F-factors are constant for a given fuel category (within ± 3%). Average values are:

Fuel	DSCF/10^6 Btu
Bituminous coal	9820
Oil	9220
Gas	8740
Wood bark	9640
Wood chips	9280

Particulate and SO_2 removal efficiencies

The SO_2 and particulate removal efficiencies are determined by inlet and outlet sampling using Equations 12 and 15.

Stack opacity

Stack opacity is determined by the installed transmissometer or by EPA Method 9.

NO_x concentration

NO_x concentration is determined by EPA Method 7. This measurement is taken in the stack on a composite sample. NO_x concentration may be adjusted to design conditions from actual test conditions.

Makeup water requirements

Makeup water requirements are measured at the appropriate terminal point with a certified flow meter. Adjustments from test conditions may be necessary due to variations in gas volume or temperature or other process deviations from design conditions.

Reagent consumption

There are two common ways to measure reagent consumption. The first method is to measure the solid reagent flow (for lime/limestone systems) using a calibrated weight belt feeder. The measurement is time averaged. This mass flow method is cumbersome because the initial and final storage tank volumes and densities must also be measured. This method is best done over a period of at least 24 hours. The second and preferred method is chemical analysis. The reagent consumption is calculated from the stoichiometric ratio, limestone (or reagent) analysis, and gas side measurements by the following equation:

$$LS = \frac{100\ (SR)\ (SO_2)}{64\ (CaCO_3)} \qquad \textbf{(18)}$$

where

LS = limestone consumption, lb/h
SR = stoichiometric ratio (see Chapter 35)
SO_2 = SO_2 removed, lb/h
64 = molecular weight of SO_2, lb/lb-mole
100 = molecular weight of $CaCO_3$, lb/lb-mole
$CaCO_3$ = available $CaCO_3$ in limestone (wt fraction: lb available $CaCO_3$/lb limestone)

Reagent consumption may be adjusted for deviations from SO_2 removal rate and mass flow (or concentration) design conditions.

Gypsum purity

A composite sample of gypsum, taken over the test period, is analyzed as outlined in Table 7. Adjustments may be necessary for flyash contamination, chloride concentration, and inerts if the inlet levels to the FGD system substantially deviate from design.

Other test methods

There are numerous procedures for measuring ECS parameters. The example in this chapter is a formal performance test; other methods could be used. For example, SO_2 can be measured with a CEMS or by other temporary instrument methods. Particulate level is measured by EPA Method 5 or 17 or alternate methods such as the probe shown in Fig. 11.

The future of environmental measurement

Advances in environmental measurement techniques will certainly continue. Technologies such as fiber optics, video imaging and Fourier transform infrared analysis (FTIR), which have been used successfully in the laboratory, are expected to move into the plant. Measurement will be extended to include other air and water pollutants, and air toxics monitoring will become increasingly important.

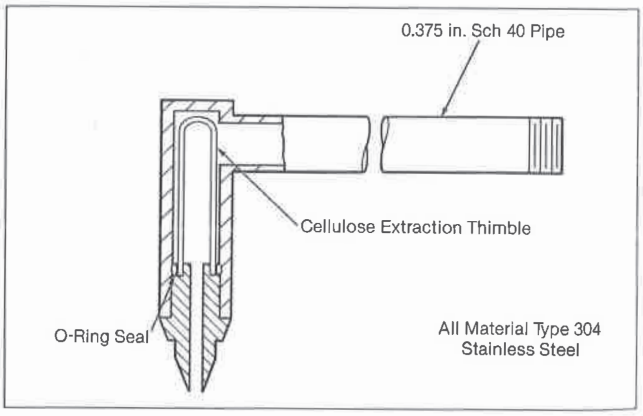


Fig. 11 Probe detail, isokinetic dust sampling.

Bibliography

ASME Performance Test Codes: PTC 1 on General Instructions, PTC 2 on Definitions and Values, and PTC 3.2 on Solid Fuels.

ASME PTC Supplements on Instruments and Apparatus: PTC 19.2 on Pressure Measurement, PTC 19.3 on Temperature Measurement, PTC 19.6 on Electrical Measurements (IEEE Standard 120), and PTC 19.10 on Flue and Exhaust Gas Analyses.

United States Code of Federal Regulations, CFR 40, parts 53 to 80.

Continuous Emission Monitoring Guidelines: Update, Report CS-5998, Electric Power Research Institute, Palo Alto, California, September 1988.

FGD Chemistry and Analytical Methods Handbook, Report CS-3612, Vols. 1 and 2, Electric Power Research Institute, Palo Alto, California, July 1984.

Handbook of Electrode Technology, Orion Research, Cambridge, Massachusetts, 1982.

Liptak, B.G., ed., *Instrument Engineers Handbook*, Chilton, Radnor, Pennsylvania, 1982.

Performance Test Code Committee No. 40, Flue Gas Desulfurization Units, Draft VII, The American Society of Mechanical Engineers, New York, October 1989.

Elliot, T.C., "Monitoring pollution," *Power*, pp. 51-56, September 1986.

Elliot, T.C., "Level monitoring," *Power*, pp. 41-58, September 1990.

Gilbert, G., "Three ways to measure flow in power plant ducts," *Power*, pp. 63-72, June 1987.

Kiser, J.V.L., "Continuous emissions monitoring: a primer," *Waste Age*, pp. 64-68, May 1988.

Kiser, J.V.L., "More on continuous emissions monitoring," *Waste Age*, pp. 119-122, June 1988.

FGD Manual, The McIlvaine Company, Northbrook, Illinois, August 1989.

Robertson, R.L., "Continuous emission monitoring and quality assurance requirements for new power plants," appearing in *Continuous Emission Monitoring Systems for Power Plants — The State-of-the-Art*, The American Society of Mechanical Engineers, pp. 13-15, New York, 1988.

Rothstein, F., and Fisher, J.E., "pH measurement: the meter," *American Laboratory*, September 1985.

Spriggs, D., "Calibration and troubleshooting of pH loops," presented to American Water Works Association Ohio Section Northeast District Meeting, Painesville, Ohio, July 20, 1989.

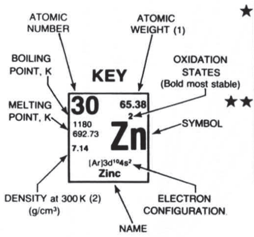
Table 3.2
Periodic Table of the Elements

GROUP IA	IIA	IIIA	IVA	VA	VIA	VIIA	VIIIA	VIIIA	VIIIA	IB	IIB	IIIB	IVB	VB	VIB	VIIB	VIII
1 1.0079 1 20.268 14.025 0.0899* **H** $1s^1$ Hydrogen																	2 4.00260 4.215 0.95 (at 26 atm) 0.1787* **He** $1s^2$ Helium
3 6.941 1 1615 453.7 0.53 **Li** $1s^22s^1$ Lithium	4 9.01218 2 2745 1560 1.85 **Be** $1s^22s^2$ Beryllium											5 10.81 3 4275 2300 2.34 **B** $1s^22s^2p^1$ Boron	6 12.011 ±4,2 4470* 4100* 2.62 **C** $1s^22s^2p^2$ Carbon	7 14.0067 ±3,5,4,2 77.35 63.14 1.251* **N** $1s^22s^2p^3$ Nitrogen	8 15.9994 −2 90.18 50.35 1.429* **O** $1s^22s^2p^4$ Oxygen	9 18.998403 −1 84.95 53.48 1.696* **F** $1s^22s^2p^5$ Fluorine	10 20.179 27.096 24.553 0.901* **Ne** $1s^22s^2p^6$ Neon
11 22.98977 1 1156 371.0 0.97 **Na** $[Ne]3s^1$ Sodium	12 24.305 2 1363 922 1.74 **Mg** $[Ne]3s^2$ Magnesium											13 26.98154 3 2793 933.25 2.70 **Al** $[Ne]3s^2p^1$ Aluminum	14 28.0855 4 3540 1685 2.33 **Si** $[Ne]3s^2p^2$ Silicon	15 30.97376 ±3,5,4 550 317.30 1.82 **P** $[Ne]3s^2p^3$ Phosphorus	16 32.06 ±2,4,6 717.75 388.36 2.07 **S** $[Ne]3s^2p^4$ Sulfur	17 35.453 ±1,3,5,7 239.1 172.16 3.17* **Cl** $[Ne]3s^2p^5$ Chlorine	18 39.948 87.30 83.81 1.784* **Ar** $[Ne]3s^2p^6$ Argon
19 39.0983 1 1032 336.35 0.86 **K** $[Ar]\ 4s^1$ Potassium	20 40.08 2 1757 1112 1.55 **Ca** $[Ar]4s^2$ Calcium	21 44.9559 3 3104 1812 3.0 **Sc** $[Ar]3d^14s^2$ Scandium	22 47.90 4,3 3562 1943 4.50 **Ti** $[Ar]3d^24s^2$ Titanium	23 50.9415 5,4,3,2 3682 2175 5.8 **V** $[Ar]3d^34s^2$ Vanadium	24 51.996 6,3,2 2945 2130 7.19 **Cr** $[Ar]3d^54s^1$ Chromium	25 54.9380 7,6,4,2,3 2335 1517 7.43 **Mn** $[Ar]3d^54s^2$ Manganese	26 55.847 2,3 3135 1809 7.86 **Fe** $[Ar]3d^64s^2$ Iron	27 58.9332 2,3 3201 1768 8.90 **Co** $[Ar]3d^74s^2$ Cobalt	28 58.70 2,3 3187 1726 8.90 **Ni** $[Ar]3d^84s^2$ Nickel	29 63.546 2,1 2836 1357.6 8.96 **Cu** $[Ar]3d^{10}4s^1$ Copper	30 65.38 2 1180 692.73 7.14 **Zn** $[Ar]3d^{10}4s^2$ Zinc	31 69.72 3 2478 302.90 5.91 **Ga** $[Ar]3d^{10}4s^2p^1$ Gallium	32 72.59 4 3107 1210.4 5.32 **Ge** $[Ar]3d^{10}4s^2p^2$ Germanium	33 74.9216 ±3,5 876 (subl.) 1081 (28 atm) 5.72 **As** $[Ar]3d^{10}4s^2p^3$ Arsenic	34 78.96 −2,4,6 958 494 4.80 **Se** $[Ar]3d^{10}4s^2p^4$ Selenium	35 79.904 ±1,5 332.25 265.90 3.12 **Br** $[Ar]3d^{10}4s^2p^5$ Bromine	36 83.80 119.80 115.78 3.74* **Kr** $[Ar]3d^{10}4s^2p^6$ Krypton
37 85.4678 1 961 312.64 1.53 **Rb** $[Kr]5s^1$ Rubidium	38 87.62 2 1650 1041 2.6 **Sr** $[Kr]5s^2$ Strontium	39 88.9059 3 3611 1799 4.5 **Y** $[Kr]4d^15s^2$ Yttrium	40 91.22 4 4682 2125 6.49 **Zr** $[Kr]4d^25s^2$ Zirconium	41 92.9064 5,3 5017 2740 8.55 **Nb** $[Kr]4d^45s^1$ Niobium	42 95.94 6,5,4,3,2 4912 2890 10.2 **Mo** $[Kr]4d^55s^1$ Molybdenum	43 (98) 7 4538 2473 11.5 **Tc** $[Kr]4d^55s^2$ Technetium	44 101.07 2,3,4,6,8 4423 2523 12.2 **Ru** $[Kr]\ 4d^75s^1$ Ruthenium	45 102.9055 2,3,4 3970 2236 12.4 **Rh** $[Kr]4d^85s^1$ Rhodium	46 106.4 2,4 3237 1825 12.0 **Pd** $[Kr]4d^{10}$ Palladium	47 107.868 1 2436 1234 10.5 **Ag** $[Kr]4d^{10}5s^1$ Silver	48 112.41 2 1040 594.18 8.65 **Cd** $[Kr]4d^{10}5s^2$ Cadmium	49 114.82 3 2346 429.76 7.31 **In** $[Kr]4d^{10}5s^2p^1$ Indium	50 118.69 4,2 2876 505.06 7.30 **Sn** $[Kr]4d^{10}5s^2p^2$ Tin	51 121.75 ±3,5 1860 904 6.68 **Sb** $[Kr]4d^{10}5s^2p^3$ Antimony	52 127.60 −2,4,6 1261 722.65 6.24 **Te** $[Kr]4d^{10}5s^2p^4$ Tellurium	53 126.9045 ±1,5,7 458.4 386.7 4.92 **I** $[Kr]4d^{10}5s^2p^5$ Iodine	54 131.30 165.03 161.36 5.89* **Xe** $[Kr]4d^{10}5s^2p^6$ Xenon
55 132.9054 1 944 301.55 1.87 **Cs** $[Xe]6s^1$ Cesium	56 137.33 2 2171 1002 3.5 **Ba** $[Xe]6s^2$ Barium	57 138.9055 3 3730 1193 6.7 **La** ★ $[Xe]5d^16s^2$ Lanthanum	72 178.49 4 4876 2500 13.1 **Hf** $[Xe]4f^{14}5d^26s^2$ Hafnium	73 180.9479 5 5731 3287 16.6 **Ta** $[Xe]4f^{14}5d^36s^2$ Tantalum	74 183.85 6,5,4,3,2 5828 3680 19.3 **W** $[Xe]4f^{14}5d^46s^2$ Tungsten	75 186.207 7,6,4,2,−1 5869 3453 21.0 **Re** $[Xe]4f^{14}5d^56s^2$ Rhenium	76 190.2 2,3,4,6,8 5285 3300 22.4 **Os** $[Xe]4f^{14}5d^66s^2$ Osmium	77 192.22 2,3,4,6 4701 2716 22.5 **Ir** $[Xe]4f^{14}5d^76s^2$ Iridium	78 195.09 2,4 4100 2045 21.4 **Pt** $[Xe]4f^{14}5d^96s^1$ Platinum	79 196.9665 3,1 3130 1337.58 19.3 **Au** $[Xe]\ 4f^{14}5d^{10}6s^1$ Gold	80 200.59 2,1 630 234.28 13.53 **Hg** $[Xe]4f^{14}5d^{10}6s^2$ Mercury	81 204.37 3,1 1746 577 11.85 **Tl** $[Xe]4f^{14}5d^{10}6s^2p^1$ Thallium	82 207.2 4,2 2023 600.6 11.4 **Pb** $[Xe]4f^{14}5d^{10}6s^2p^2$ Lead	83 208.9804 3,5 1837 544.52 9.8 **Bi** $[Xe]4f^{14}5d^{10}6s^2p^3$ Bismuth	84 (209) 4,2 1235 527 9.4 **Po** $[Xe]4f^{14}5d^{10}6s^2p^4$ Polonium	85 (210) ±1,3,5,7 610 575 — **At** $[Xe]4f^{14}5d^{10}6s^2p^5$ Astatine	86 (222) 211 202 9.91* **Rn** $[Xe]4f^{14}5d^{10}6s^2p^6$ Radon
87 (223) 1 950 300 — **Fr** $[Rn]7s^1$ Francium	88 226.0254 2 1809 973 5 **Ra** $[Rn]7s^2$ Radium	89 227.0278 3 3473 1323 10.07 **Ac** ★★ $[Rn]6d^17s^2$ Actinium	104 (261) — — — — **Unq** $[Rn]5f^{14}6d^27s^2$ † (Unnilquadium)	105 (262) — — — **Unp** $[Rn]5f^{14}6d^37s^2$ † (Unnilpentium)	106 (263) — — — **Unh** $[Rn]5f^{14}6d^47s^2$ † (Unnilhexium)												

† The names and symbols of elements 104 - 106 are those recommended by IUPAC as systematic alternatives to those suggested by the purported discoverers. Berkeley (USA) researchers have proposed Rutherfordium, Rf, for element 104 and Hahnium, Ha, for element 105. Dubna (USSR) researchers, who also claim the discovery of these elements have proposed different names (and symbols).

The A & B subgroup designations, applicable to elements in rows 4, 5, 6, and 7, are those recommended by the International Union of Pure and Applied Chemistry. It should be noted that some authors and organizations use the opposite convention in distinguishing these subgroups.

* Estimated Values



★	58 140.12 3,4 3699 1071 6.78 **Ce** $[Xe]4f^15d^16s^2$ Cerium	59 140.9077 3,4 3785 1204 6.77 **Pr** $[Xe]4f^36s^2$ Praseodymium	60 144.24 3 3341 1289 7.00 **Nd** $[Xe]4f^46s^2$ Neodymium	61 (145) 3 3785 1204 6.475 **Pm** $[Xe]4f^56s^2$ Promethium	62 150.4 3,2 2064 1345 7.54 **Sm** $[Xe]4f^66s^2$ Samarium	63 151.96 3,2 1870 1090 5.26 **Eu** $[Xe]4f^76s^2$ Europium	64 157.25 3 3539 1585 7.89 **Gd** $[Xe]4f^75d^16s^2$ Gadolinium	65 158.9254 3,4 3496 1630 8.27 **Tb** $[Xe]4f^96s^2$ Terbium	66 162.50 3 2835 1682 8.54 **Dy** $[Xe]4f^{10}6s^2$ Dysprosium	67 164.9304 3 2968 1743 8.80 **Ho** $[Xe]4f^{11}6s^2$ Holmium	68 167.26 3 3136 1795 9.05 **Er** $[Xe]4f^{12}6s^2$ Erbium	69 168.9342 3,2 2220 1818 9.33 **Tm** $[Xe]4f^{13}6s^2$ Thulium	70 173.04 3,2 1467 1097 6.98 **Yb** $[Xe]4f^{14}6s^2$ Ytterbium	71 174.967 3 3668 1936 9.84 **Lu** $[Xe]\ 4f^{14}5d^16s^2$ Lutetium
★★	90 232.0381 4 5061 2028 11.7 **Th** $[Rn]6d^27s^2$ Thorium	91 231.0359 5,4 — — 15.4 **Pa** $[Rn]5f^26d^17s^2$ Protactinium	92 238.029 6,5,4,3 4407 1405 18.90 **U** $[Rn]5f^36d^17s^2$ Uranium	93 237.0482 6,5,4,3 — 910 20.4 **Np** $[Rn]5f^46d^17s^2$ Neptunium	94 (244) 6,5,4,3 3503 913 19.8 **Pu** $[Rn]5f^67s^2$ Plutonium	95 (243) 6,5,4,3 2880 1268 13.6 **Am** $[Rn]5f^77s^2$ Americium	96 (247) 3 — 1340 13.511 **Cm** $[Rn]5f^76d^17s^2$ Curium	97 (247) 4,3 — — — **Bk** $[Rn]5f^97s^2$ Berkelium	98 (251) 3 — 900 — **Cf** $[Rn]5f^{10}7s^2$ Californium	99 (252) — — — — **Es** $[Rn]5f^{11}7s^2$ Einsteinium	100 (257) — — — — **Fm** $[Rn]5f^{12}7s^2$ Fermium	101 (258) — — — — **Md** $[Rn]5f^{13}7s^2$ Mendelevium	102 (259) — — — — **No** $[Rn]5f^{14}7s^2$ Nobelium	103 (260) — — — — **Lr** $[Rn]5f^{14}6d^17s^2$ Lawrencium

NOTES:
(1) Based upon carbon-12. ( ) indicates most stable or best known isotope.
(2) Entries marked with asterisks refer to the gaseous state at 273 K and 1 atm and are given in units of g/l.

Catalog Number S-18806

NSRDS

SARGENT-WELCH SCIENTIFIC COMPANY
7300 NORTH LINDER AVENUE, SKOKIE, ILLINOIS 60077

Table 4.1
Coal and Ash Analysis, An Example of a High Sulfur Bituminous Coal

Proximate Analysis, %		Ultimate Analysis, %		Sulfur Forms, %	
Moisture	12.0	Moisture	12.0	Pyritic	2.0
VM	35.7	Carbon	60.6	Organic	2.0
FC	40.3	Hydrogen	4.1	Sulfate	0.1
Ash	12.0	Nitrogen	1.2		4.1
		Sulfur	4.1		
		Oxygen	6.0		
		Ash	12.0		

Ash Fusion Temperatures, F (Reducing Atmosphere)	
Initial Deformation	1950
Softening	2030
Hemispherical	2100
Fluid	2150

Other

Btu/lb = 10,950 as received
Grindability = 56 HGI
Theoretical air = 7.6 lb/10,000 Btu

Ash Analysis, %	
Si as SiO_2	45.0
Al as Al_2O_3	20.0
Fe as Fe_2O_3	18.0
Ti as TiO_2	1.0
Ca as CaO	7.0
Mg as MgO	1.0
Na as Na_2O	0.6
K as K_2O	1.9
S as SO_3	3.5
P as P_2O_5	0.2

Table 4.2
Mechanical Equipment
500 MW PC-Fired Plant

Steam Generator
Balanced draft, direct-fired, pulverized coal

Pulverizers
Six, roller-mill, 50 t/h each

Main Steam		Reheat Steam	
Flow	3.625 x 10^6 lb/h	Flow	3.336 x 10^6 lb/h
Temp	1005F	Temp	1000F
Pressure	2415 psi	Pressure	532 psi

Turbine/Generator
Tandem-compound, four-flow, 3600 rpm, 640,000 kVa at 24 kV, 3 phase, 60 Hz.

Fans
FD: 2 motor-driven, total 4,000,000 lb/h
PA: 2 motor-driven, total 710,000 lb/h
ID: 4 motor-driven, total 5,174,000 lb/h

Fan Horsepower Requirements
FD: 2400 HP based on static rise from -0.5 to 14 in. wg
PA: 1700 HP based on static rise from -0.5 to 16 in. wg
ID: 3800 HP based on static rise from -16 to -1 in. wg and 200F gas inlet.

Fan data assumes 8% air heater leakage and 87% fan/motor efficiency.

Feedwater Pumps

Main:	2 turbine-driven, 50% capacity, 5000 GPM each, TDH: 7200 ft
Booster:	2 turbine-driven, 50% capacity, 4800 GPM each, TDH: 1280 ft
Condensate:	2 motor-driven, 100% capacity, 1400 hp, 7000 GPM each, TDH: 630 ft

Table 4.3
Environmental Equipment
500 MW PC-Fired Plant

Wet Limestone Scrubber (full load)

Limestone usage rate:	30.5 t/h
Fixed sludge waste:	106 t/h
SO_2 at scrubber inlet:	36,568 lb/h
SO_2 at scrubber outlet:	3,657 lb/h
Required SO_2 removal:	90%

Particulate Control

Type:	Electrostatic precipitator
Emissions:	0.03 lb/10^6 Btu
Specific collector area:	350 ft^2/1000 SCFM

Table 4.4
Plant Performance Summary
500 MW PC-Fired Plant

Turbine Steam Conditions	
Pressure	2400psig
Temperature	1000F
Reheat temperature	1000F

Fuel Input

Coal feed 223 t/h
BTU input 4.88 x 10^9 Btu/h

Ash Flow Rates	t/h
Furnace bottom ash	5.1
Economizer ash	2.2
Fly ash	20.7
Total through unit	28.0
Mill rejects (pyrites)	0.5

Heat Rates at Full Load	
Steam cycle	7880 Btu/kWh
Gross	8985 Btu/kWh
Net	9725 Btu/kWh

Rated Output Power Production	
Total gross	536 MW
Total Net	502 MW

Thermal Discharge	10^6 Btu/h
Cooling towers	2500
Stack	587

Controlled Emissions	lb/h
$S0_2$	3700
$N0_x$ as $N0_2$	2900*
Particulate	146

Efficiencies	
Boiler (coal to steam)	88%
Plant (coal to busbar)	35%

Untreated Flue Gas Characteristics

Component	Volume % Dry	Volume % Wet
Nitrogen	81.07	73.47
Carbon dioxide	15.28	13.84
Oxygen	3.26	2.95
Water	---	9.39
Sulfur dioxide	0.39	0.35
	100.00	100.00

Flue Gas Molecular Weight
30.85 (dry basis)
29.64 (wet basis)

Excess air leaving economizer 17.9%

Mass Flows	lb/10,000 Btu
Actual dry air	8.888
Wet gas from fuel	0.800
Moisture in air	0.116
Wet gas weight	9.804
Water from fuel	0.444
Water in wet gas	0.560
Dry gas weight	9.244

Water in wet gas (as%) 5.711%

Losses	%
Dry gas loss	4.659
Water from fuel	5.056
Moisture in air	0.116
Unburned Combustibles	0.500
Radiation	0.170
Unaccounted for Manufacturer's Margin	1.500
	12.001

*Federal Standard. Current technology can attain lower.