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Desulfurization and Emissions Control

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1. INTRODUCTION

Desulfurization removes elemental sulfur and its compounds from solids, liquids, and gases. Predominantly, desulfurization involves the removal of sulfur oxides from flue gases, compounds of sulfur in petroleum refining, and pyritic sulfur in coal cleaning. This chapter discusses the following topics:

4. Liquid-phase desulfurization (acid-lake restoration for H\textsubscript{2}SO\textsubscript{4} removal and groundwater decontamination for H\textsubscript{2}S removal).
5. Gas-phase desulfurization (SO\textsubscript{x} and H\textsubscript{2}S removals from air emission streams).
Special emphasis is placed on gas-phase desulfurization, introducing various technologies for the removal of SO\textsubscript{x} and H\textsubscript{2}S from air emission streams. Of these technologies, the most important is lime/limestone flue gas desulfurization (FGD). This chapter describes FGD process systems, facilities, chemistry, and technology demonstrations, design configurations, gas handling/treatments, reagent/feed preparation, waste handling/disposal, Operation and maintenance (O&M), and process control. The wet and dry scrubbing chapter of this handbook series (chapter 5, volume 1) presents additional technical information on the unit process and unit operation aspects of scrubbing/absorption (73).

1.1. Sulfur Oxides and Hydrogen Sulfide Emissions

Sulfur oxides (SO\textsubscript{x}) and hydrogen sulfide are two major sulfur-containing air pollutants. Both cause great environmental concern.

Hydrogen sulfide gases are released from sanitary landfill sites, sanitary sewer systems, wastewater-treatment plants, reverse-osmosis drinking water plants, septic tank systems, and hydrogeothermal plants (1–8). However, H\textsubscript{2}S releases are negligible in comparison with SO\textsubscript{x} releases. Accordingly, only the quantitative information of SO\textsubscript{x} emissions is presented in this section.

More than 25 million metric tons of sulfur oxides (SO\textsubscript{x}) are emitted annually in the United States, and about 65 million metric tons are annually emitted by the entire world’s industrialized nations. The US SO\textsubscript{x} emission alone represents about a quarter of the releases from human activities and natural sources throughout the world.

Major air pollutants are as follows: (a) sulfur oxides 14%, (b) nitrogen oxides 12%, (c) carbon monoxide 53%, (d) hydrocarbons 15%, and (e) suspended particulate matter (PM) 6%. Most sulfur oxides are released in the form of sulfur dioxide, which reacts in the atmosphere to sulfates. These interfere with normal breathing patterns, reduce visibility, and contribute to the formation of acid rain.

Coal combustion for power generation accounts for more than two-thirds of SO\textsubscript{x} emissions in the United States. Sulfur is a natural contaminant of coal and is almost completely converted to sulfur oxide when coal is burned. The substitution of oil and natural gas for coal reduces emissions. However, these fuels are more expensive.

In terms of SO\textsubscript{x} emission sources, the following is a statistical breakdown:

1. Industrial boilers, 8%.
2. Electric generation stations, 69%.
3. Copper smelters, 8%.
4. Petroleum refining, 5%.
5. Transportation, 5%.
6. Residential, commercial, and institutional, 5%.

1.2. SO\textsubscript{x} Emissions Control Technologies

Most SO\textsubscript{x} control systems contact a calcium-based compound with the sulfur dioxide to form calcium sulfite, CaSO\textsubscript{3}. This is oxidized to CaSO\textsubscript{4}. The first scrubbers were introduced in Great Britain in the 1920s and 1930s and demonstrated 90% removal of SO\textsubscript{2}. In the 1960s, installations followed in Japan and Europe. Under the provisions of the Clean Air Act of 1970, installations were made at new power plants in the United States. However, older plants were exempt, until the 1990 Clean Air Act
Amendments (CAAA) required controls for older plants. The major technologies include the following.

1.2.1. Dry and Semidry Sorbent Injection

In this method, particles of limestone or a quickly drying slurry of lime are injected into the economizer or flue gas. This latter is called the semidry method and it dominates sorbent injection applications.

1.2.2. Sulfuric Acid Production

Less commonly performed, the SO₂ is oxidized over a catalyst to SO₃, which is dissolved in water.

1.2.3. Conventional Wet FDG Technology

Flue gas from a particulate collector flows to the SO₂ scrubber, and the flue gas is contacted with a slurry containing particulate limestone to form calcium sulfite. The gas flux is limited to prevent entrainment, and mass transfer determines the absorber height. The calcium sulfite oxidizes to calcium sulfate, which crystallizes to gypsum (CaSO₄ • 2H₂O). A dewatering system concentrates the gypsum to 80–90% solids for disposal or fabrication of wallboard. Over its life, a 500-MWe coal-fired plant, using a conventional scrubber, produces enough gypsum sludge to fill a 500-acre pond, 40 ft deep. Early scrubber systems also had poor reliability, requiring installations of spare modules.

1.2.4. Innovative Wet FGD Technology

Innovative scrubbers incorporate better designs and materials. They are characterized by greater compactness, lower capital and operating costs, high reliability (eliminating the need for spares), and elimination of waste disposal problems by producing wallboard-quality gypsum. A number of these have been demonstrated at a commercial scale through the US Department of Energy Clean Coal Technology program. Sections 9–11 of this chapter describe these systems and summarize performance data.

2. SULFUR OXIDES AND HYDROGEN SULFIDE POLLUTION

Although SOₓ is a symbol of all oxides of sulfur (e.g., SO₂ and SO₃), about 95% of all sulfur oxides are in the form of sulfur dioxide (SO₂). It is a colorless gas that when cooled and liquefied can be used as a bleach, disinfectant, refrigerant, or preservative. In the atmosphere, however, SO₂ is a precursor of highly destructive sulfates (SO₄²⁻), formed by the chemical addition of oxygen (O₂). SO₃ is not a stable compound and may react with water (H₂O) to form sulfuric acid (H₂SO₄), a component of acid rain (9,10).

Hydrogen sulfide and organic sulfur-containing compounds cause odor pollution at low concentrations, but they cause extreme public concern when their concentrations are high. SO₂ in the atmosphere has been recognized as a major air pollution problem in the United States since the inception of clean air legislation. SOₓ emissions cause acid rain, affect public health, corrode materials, and restrict visibility.

2.1. Acid Rain

Acid rain is composed primarily of two acids: sulfuric (H₂SO₄) and nitric (HNO₃). Sulfuric acid, resulting from sulfur oxide emissions, comprises from 40% to 60% of the
acidity, depending on regional emission patterns. Acid rain is a major problem throughout the world, especially in Scandinavia, Canada, and the eastern United States.

Rain in the northeastern United States averages 10–100 times the acidity of normal rainwater. More than 90 lakes in the Adirondack Mountains of New York State no longer contain fish because the increased acidity of lake water has caused toxic metals in the lakebeds and surrounding soils to be released into the lakes. Similar effects are beginning to occur in other areas of the United States such as northern Minnesota and Wisconsin. Preliminary studies indicate that the direct effects of acids on foliage and the indirect effects resulting from the leaching of minerals from the soil can reduce the yield from some agricultural crops (11).

2.2. Public Health Effects

As the concentration of sulfur oxides in the air increases, breathing becomes more difficult, resulting in a choking effect known as pulmonary flow resistance. The degree of breathing difficulty is directly related to the amount of sulfur compounds in the air. The young, the elderly, and individuals with chronic lung or heart disease are most susceptible to the adverse effects of sulfur oxides. Sulfates and sulfur-containing acids are more toxic than sulfur dioxide gas. They interfere with normal functioning of the mucous membrane in respiratory passages, increasing susceptibility to infection. The toxicity of these compounds varies according to the nature of the metals and other chemicals that combine with sulfur oxides in the atmosphere.

H₂S and organic sulfur compounds only cause offensive odor at low concentrations (5–8). At high concentration levels, both H₂S and organic sulfur compounds are toxic. Fortunately, their offensive odors may serve as a warning sign for people to move to safety.

2.3. Materials Deterioration

Sulfur acids corrode normally durable materials, such as metals, limestone, marble, mortar, and roofing slate. As a result, acidic sulfates are destroying statuary and other archeological treasures that have resisted deterioration for thousands of years. These include such well-known structures as the Parthenon in Greece and the Taj Mahal in India, as well as lesser known bronze and stone statuary in US cities.

Corrosive destruction of statuary is most severe in areas where droplets of moisture collect sulfates and other atmospheric particles, forming a crust on the statuary that retains moisture and promotes the formation of sulfuric acid. This acid destroys the surface of the statuary, causing smooth metal sculptures to become pitted and resulting in such severe spalling of stone figures that the outlines of the features become blurred.

2.4. Visibility Restriction

Small particles suspended in a humid atmosphere are the major cause of reduced visibility in the eastern United States. Sulfates constitute 30–50% of the suspended particles.

3. US AIR QUALITY ACT AND SO₂ EMISSION CONTROL PLAN

The Air Quality Act of 1967 required that states develop ambient air quality standards for SO₂. The Clean Air Act (CAA) of 1970 mandated performance standards for new and significantly modified sources of SO₂. In 1971, the US Environmental Protection
Agency (EPA) issued the first such standards for fossil-fuel-fired boilers greater than 25 MWe. These source performance standards (NSPS) limited allowable emissions to 1.2 lb of SO₂ per million British thermal units (Btu) of heat input to a boiler, and essentially restricted operators of these boilers to two choices: use low-sulfur coal or apply FGD technology (12,13).

In accordance with the 1977 Clean Air Act Amendments, the EPA established regulations that require electric power companies and industries to take steps to reduce SO₂ emissions. In 1979, the NSPS were revised for power plants, requiring a percentage reduction of SO₂. This mandate was intended to be technology forcing, essentially requiring all new power plants to add SO₂-removal equipment to the base design (13).

In the 1980s, the US Congress began debating the need for additional SO₂ control as a means of reducing damage from acid rain, culminating in the Clean Air Act Amendments (CAAA) of 1990. Two portions of the CAAA of 1990 are important for SO₂ emissions control. These are Title I and Title IV. Title I establishes the National Ambient Air Quality Standards (NAAQS) for six criteria pollutants, including SO₂. National Ambient Air Quality standards for sulfur oxides establish a maximum safe level of the pollutant in the atmosphere. According to these standards, atmospheric concentrations of SOₓ should not exceed 0.5 part per million (ppm) during a 3-h period, or 0.14 ppm during a 24-h period. The annual mean concentration should not exceed 0.03 ppm.

Title IV, sometimes called the Acid Rain Program, sets requirements for reducing SO₂ emissions in three distinct phases:

1. Phase I targeted specific large sources to reduce SO₂ emissions by 5 million tons by January 1, 1995, using a limit of 2.5 lb/10⁶ Btu.
2. Phase II required, by January 1, 2000, reduction of all power plants to a nationwide emission level of 1.2 lb SO₂/10⁶ Btu and a sliding scale percentage reduction of 70–90%, depending on input sulfur content. The SO₂ emission levels are generally 0.3 and 0.6 lb/10⁶ Btu for low- and high-sulfur coals, respectively.
3. Phase III required that SO₂ emissions be capped beyond the year 2000.

Title IV was the first large-scale approach to regulating emissions by using marketable allowances. These can be bought and sold in units of 1 ton of SO₂ emitted (14). Until the late 1990s, prices for allowances had remained low, but then increased. This has provided the potential for a large-scale retrofit. To meet limits, especially with high-sulfur coals, requires high removal efficiencies of 90% or more. Higher efficiencies will generate salable credits. In addition, Title IV has an option whereby unregulated sources can reduce SO₂ emissions and receive credits. Regardless of credits held, Title I sets the limits for compliance. Through certification provisions, a Title IV Permit serves as the primary verification and documentation of a facility’s compliance with all applicable requirements of the Clean Air Act.

As a result of Phase I, SO₂ emissions declined by 20% from 1990 to 1997. Advanced scrubbers essentially halved the cost of conventional scrubbers (prior to the CAAA). The Clean Coal Technology (CCT) Program has supported the development of a number of options for meeting the requirements: advanced scrubbers, low-cost absorbent injection, clean fuels, and advanced power generation systems (14). Under Title IV, utilities meeting limits by repowering with advanced technologies were allowed a 4-yr extension to December 31, 2003.
4. DESULFURIZATION THROUGH COAL CLEANING

Coal contains pyritic and organic sulfur, as well as some sulfatic (sulfate) forms. Pyritic sulfur is a mineral form, whereas the organic sulfur is chemically bound in the structure of the coal. Most mineral sulfur can be removed by mechanical coal cleaning processes, but removing organic sulfur requires chemical processing (1–4,10,15–22). Illustrative values appear in Table 1 (23).

### 4.1. Conventional Coal Cleaning Technologies

Conventional coal cleaning processes are physical and mechanical processes. Coal is crushed to < 50mm in diameter and screened into coarse, intermediate, and fine particle size fractions. Crushing to a smaller size liberates ash-forming minerals and nonorganically bound sulfur (e.g., pyrites, FeS₂). The mineral matter has a higher density than organic-rich coal particles and can be separated from the coarse and intermediate particles of coal by jigs, dense-medium baths, cyclone systems, and concentrating tables (Table 2) (24).

From 40% to 90% of the total sulfur content in coal can be removed by this physical cleaning process. Physical cleaning cannot remove organically bound sulfur, which requires chemical or biological methods. Cleaning effectiveness depends on the size of

<table>
<thead>
<tr>
<th>Coal</th>
<th>Total wt%</th>
<th>Pyritic wt%</th>
<th>Sulfatic wt%</th>
<th>Organic wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Illinois</td>
<td>4.490</td>
<td>1.23</td>
<td>0.060</td>
<td>3.210</td>
</tr>
<tr>
<td>Kentucky</td>
<td>6.615</td>
<td>5.05</td>
<td>0.135</td>
<td>1.415</td>
</tr>
<tr>
<td>Martinka</td>
<td>2.200</td>
<td>1.48</td>
<td>0.120</td>
<td>0.600</td>
</tr>
<tr>
<td>Westland</td>
<td>2.600</td>
<td>1.05</td>
<td>0.070</td>
<td>1.480</td>
</tr>
<tr>
<td>Texas lignite</td>
<td>1.200</td>
<td>0.40</td>
<td>—</td>
<td>0.800</td>
</tr>
</tbody>
</table>

**Table 1**

Representative Sulfur Content of Coal: Speciation and Totals

**Table 2**

Conventional Coal Cleaning Technologies

<table>
<thead>
<tr>
<th>Technology type</th>
<th>Process</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crushing</td>
<td>Grinders pulverize coal, which is then screened into coarse (&gt;50 mm in diameter), intermediate, and fine (&lt;0.5 mm) particles. The crushing liberates the inorganic, bound mineral particles from the coal. Because these mineral particles are denser than the organically rich coal, they can be separated from the coal by further processing (see next items).</td>
</tr>
<tr>
<td>Jigs (G)</td>
<td>For coarse to intermediate particles.</td>
</tr>
<tr>
<td>Dense-medium baths (G)</td>
<td>For coarse to intermediate particles.</td>
</tr>
<tr>
<td>Cyclones (G)</td>
<td>For coarse to intermediate particles.</td>
</tr>
<tr>
<td>Froth flotation (G)</td>
<td>For fines; relies on the different surface properties of ash (hydrophilic) versus coal (hydrophobic); high potential, but current technologies do not handle the small particles efficiently.</td>
</tr>
</tbody>
</table>

*Note: G = gravity(density)-based separation.*
Desulfurization and Emissions Control

Nearly half of the sulfur in coals from eastern Kentucky, Tennessee, Georgia, and Alabama and most of the sulfur in coal from the western mountain states is in the pyritic form and is relatively easy to remove by mechanical cleaning. The combination of physical coal cleaning and partial FGD enables many generating stations to meet SO$_2$ emission standards at less expense than using FGD alone. The advantages and disadvantages of coal cleaning are summarized in Table 3.

The cost of physical cleaning varies from US$1 to US$10/ton, depending on the coal quality, the cleaning process used, and the degree of cleaning desired. In most cases, cleaning costs range from US$1 to US$5/ton (25).

4.2. Advanced Coal Cleaning Technologies

A number of advanced cleaning technologies have been developed to improve performance and economics and to exploit currently underutilized coal fines (as discussed below) (26,27). These technologies, including advanced physical, aqueous, and organic phase pretreatment and selective agglomeration, are at an earlier stage of commercialization and development with less well-established effectiveness and economics. Advanced coal cleaning technologies are listed in Table 4 (24).

The potential for cleaning the coal fines is greater than that for the coarse and intermediate coal particles, but conventional technologies do not handle the fines efficiently. Fines <0.5 mm in diameter can be separated by froth flotation exploiting surface differences between coal and ash. Coal’s surface is hydrophobic. Ash’s surface is hydrophilic. One of the more widely commercialized flotation methods is Microcel Flotation Technology. As of the mid-1990s, there were 44 Microcel installations around the world. The process diagram appears in Fig. 1. Ash removal can reach 60%; total sulfur removal is 10–40%, increasing in tandem with a rising percentage of pyritic (mineral) sulfur in the coal. Weight recovery (the percentage of coal retained) is 60–90%, and thermal recovery (percentage of heating value retained) is 85–98% (25). The Peak Downs plant near Queensland, Australia (Fig. 2) represents the largest installation of

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Table 3
Advantages and Disadvantages of Physical Coal Cleaning

<table>
<thead>
<tr>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>10–40% lower SO$_2$</td>
<td>Coal grinding is energy intensive.</td>
</tr>
<tr>
<td>Higher pulverizer and boiler availability</td>
<td>Water-based coal cleaning methods add</td>
</tr>
<tr>
<td>(estimated: 1% improvement in availability for every 1% decrease in ash</td>
<td>moisture to the coal, which reduces boiler</td>
</tr>
<tr>
<td>content)</td>
<td>and power plant efficiency.</td>
</tr>
<tr>
<td>Lower maintenance costs (less wear and tearing.</td>
<td>A 2–15% energy loss occurs during cleaning.</td>
</tr>
<tr>
<td>on coal preparation equipment and boiler)</td>
<td></td>
</tr>
<tr>
<td>Less boiler slagging and fouling</td>
<td></td>
</tr>
<tr>
<td>Lower dust loading of ESP/bag filter</td>
<td></td>
</tr>
<tr>
<td>Lower transportation costs (applicable to cleaning at the mine only)</td>
<td></td>
</tr>
</tbody>
</table>

Pyritic sulfur particles and the proportion of sulfur in pyritic form. Thus, the larger the percentage of organically bound sulfur in the coal, the lower the percentage of sulfur that can be removed by physical methods.
Microcel coal columns in the world. Sixteen 3-m-diameter Microcel columns replaced a traditional split-feed flotation circuit. The ash content of the froth product was reduced from about 9.5% to 6%. This allowed the operating gravities in the coarse circuit to be raised, increasing total plant yield by 4% (28).

Advanced coal cleaning has found particular application for coal fines because they are already ground fine and are often an unused byproduct (waste). Thus, advanced coal cleaning provides coal and energy recovery and waste minimization. However, the treatment of fine coal is the least efficient and most costly step in coal preparation. Based on data in the literature (25), for a typical preparation plant in the eastern United

<table>
<thead>
<tr>
<th>Technology type</th>
<th>Process</th>
</tr>
</thead>
<tbody>
<tr>
<td>Advanced physical cleaning</td>
<td>Advanced froth flotation (S)</td>
</tr>
<tr>
<td></td>
<td>Electrostatic (S)</td>
</tr>
<tr>
<td></td>
<td>Heavy liquid cycloning (G)</td>
</tr>
<tr>
<td></td>
<td>Bioprocessing</td>
</tr>
<tr>
<td>Aqueous phase pretreatment</td>
<td>Hydrothermal</td>
</tr>
<tr>
<td></td>
<td>Ion exchange</td>
</tr>
<tr>
<td></td>
<td>Otisca</td>
</tr>
<tr>
<td>Selective agglomeration</td>
<td>LICADO</td>
</tr>
<tr>
<td></td>
<td>Spherical Agglomeration Aglofloat</td>
</tr>
<tr>
<td></td>
<td>Depolymerization</td>
</tr>
<tr>
<td></td>
<td>Alkylation</td>
</tr>
<tr>
<td>Organic phase pretreatment</td>
<td>Solvent swelling</td>
</tr>
<tr>
<td></td>
<td>Catalyst addition (e.g., carbonyl)</td>
</tr>
<tr>
<td></td>
<td>Organic sulfur removal</td>
</tr>
</tbody>
</table>

*Note: G = gravity(density)-based separation; S = surface-effect-based separation.*

Fig. 1. Schematic of the essential features of the Microcel Flotation Technology.
States, as particle size decreases, the ash content of the clean coal increases from 7.5% to 10.8%. Significantly, the moisture content of the fine fraction is nearly five times that of the coarse fraction (i.e., 25.1% vs 5.1%). This higher moisture content requires drying to meet increasingly stringent moisture constraints imposed by utility contracts. Field surveys at Virginia Tech suggest that the average cost to treat fine coal is three to four times higher than that for coarse coal. Consequently, the US coal producers currently discard between 27 and 36 million metric tons of fresh fine coal to refuse ponds each year. The US Department of Energy indicates that approx 1.8 billion metric tons of fine coal have been discarded in abandoned ponds and 450–725 million tons are in active ponds.

Low-ash products can be recovered from fine-coal streams using technologies such as horizontal belt filters. However, the coal has high water content, on the order of 36–42% for flotation froth (25). This restricts the use of this coal and requires further drying. Reagents have been developed that significantly improve the dewatering. Results indicate addition of 1.5 kg/ton of a novel dewatering aid can reduce filtering time by a factor of 4–5 and reduce water content by 40–60% or more, depending on time. Economic estimates show that dewatering (at US$1–5/ton) can improve profitability (25).

The economics of conventional and advanced coal cleaning for refuse pond recovery have been compared (29). Conventional circuits could not produce satisfactory ash reduction or, if they did, could not maintain profitability. The advanced fine-coal cleaning circuit, however, did achieve satisfactory ash reduction and demonstrated return on investment of 50% for both water-only and dense-medium systems, without tailings management. The dense-medium system appeared better suited to producing quality products. Tailings management was found to enhance economics. The Electric Power Research Institute has also compared economics for strategies of applying advanced coal cleaning (ACC) and FGD. Cost estimates suggested that combining ACC with FGD was more expensive than FGD alone. However, the estimates also suggested better economics.
for combining ACC and dry FGD versus ACC and wet FGD. Cleaned coal also offers other operational advantages not reflected in the estimates for desulfurization alone (27).

Several advanced processes are now available for improving the performance of fine coal cleaning and dewatering circuits. Any economic evaluation of these technologies must, however, consider the important interactions between the coarse- and fine-coal circuits on overall plant performance. A reduction in the ash and/or moisture content of the fine-coal product often allows higher cutpoints to be employed in the coarser-coal circuits without diminishing the quality of the overall plant product. This trade-off generally results in a substantial increase in total plant production. In many cases, the improved profitability can be used to justify improvements to the fine-coal circuit, although the apparent benefit to the fines circuit alone may be relatively small (25).

4.3. Innovative Hydrothermal Desulfurization for Coal Cleaning

Hydrothermal treatment removes organic sulfur (as well as inorganic), reduces the water-holding capacity, and removes other hazardous pollutants, such as mercury. It is a cleaning and upgrading treatment, particularly suited for coals with high organic sulfur or mercury, or for low-rank coals with high ash and water content. In general, it involves contacting the coal with hot water and, in some cases, at high pressure. Catalyst or inorganic reactants may be added.

An example of this technology uses supercritical water and a catalyst. The Energy and Environmental Research Center (EERC) at the University of North Dakota, Center for Air Toxic Metals (CATM) is investigating the hydrothermal pretreatment of coal to remove heavy metals. Pyritic and organic sulfur are also removed. An advantage is that it uses water to remove the sulfur and no costly or hazardous chemicals are needed for this process, such as would be needed for caustic leaching.

Raw materials include coal, water, and a cobalt/molybdenum catalyst. Estimates indicate the production of 1 million tons of product would require 1.3 million tons of raw coal and 240 gal water/ton coal. The cobalt/molybdenum catalyst has a service life of approx 6 yr.

In the first stage, crushed coal is slurried with water and pumped to system pressure, eliminating the need for a lock hopper. Supercritical water (>3200 psi and >374°C) is then forced into the bottom of the vessel and through the coal. The water removes the tars, oils, and impurities (including mercury and sulfur) from the coal. The overhead stream flows into a pair of cyclones, where the ash is removed. From the cyclones, the stream passes through a catalyst bed for further desulfurization of the tars and oils carried in the supercritical water.

The supercritical stream flows to a flash tank where the pressure is reduced. Hydrogen sulfide and some water vaporize. In an industrial system, the sour gas and sulfur-contaminated water are pumped to conventional sulfur-recovery systems. The liquid in the flash tank gravity separates into an organic layer and a water layer. The tars and oils are recombined with the cleaned product and pressed into briquettes for the finished product. The tars and oils increase the energy density of the product and serve as a binder. Feed coal and product composition are shown in Table 5.

Processing costs are estimated at US$0.57/10^6 Btu, or US$16.50/ton of clean coal. The processing cost would be partially offset by SO₂ allowances (US$12/ton coal at
US$200/ton SO$_2$ allowance), efficiency savings from moisture and ash reduction (US$2.74/ton coal). The reduced ash content should produce other savings from reduced maintenance. A rate-of-return (ROR) calculation indicated a 15% ROR could be achieved at a selling price as low as US$43/ton (US$1.48/10^6 Btu), making this product competitive for both utility and commercial applications.

The experimental work and plant design proposed have been completed. The results of the effort indicate that hydrothermal treatment of high-sulfur coals is technically and economically viable. The EERC is currently seeking funding opportunities to bring this technology through the pilot scale to demonstration (30).

5. DESULFURIZATION THROUGH VEHICULAR FUEL CLEANING

Gasoline, diesel fuel, and jet fuel all contain sulfur that is emitted in the form of sulfur oxides after combustion. Although motor vehicle emissions currently account for only about 3% of the total national sulfur oxide emissions, the EPA is concerned about them for two reasons.

First, the catalytic converter being installed in cars to control hydrocarbon and carbon monoxide emissions can convert exhaust sulfur dioxide to the more toxic compound sulfuric acid. These acid fumes could adversely affect the health of people driving in heavy traffic.

Second, diesel fuel and gasoline demand continue to rise, with projections for further increases of 1 and 2 million barrels per day, respectively, from 2002 to 2020 (DOE, 2001, EIA Annual Energy Review). As of 2002, diesel fuel is being produced with 350 ppm sulfur. Likewise, fluid catalytic cracker naphtha is a major component in blended gasoline (35% by a 1999 estimate) (31).

Major changes in vehicle fleet composition are anticipated over the next two decades: Most significantly, there will be more diesel-powered vehicles and fuel-cell-powered vehicles with onboard fuel reformers. Even with more highly fuel efficient vehicles, the US Energy Information Administration predicts that fuel demand will increase by about 50% by the year 2020 (32).

United States fuel regulations call for further reductions in sulfur content. By 2004, gasoline is to attain an average of 30 ppm, with a maximum of 80 ppm. Diesel will be required to meet the “80/20” rule, with production of 80% ultralow-sulfur diesel (ULSD)

<table>
<thead>
<tr>
<th>Moisture (wt%)</th>
<th>13.8</th>
<th>0.1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ash (wt%)</td>
<td>10.3</td>
<td>3.7</td>
</tr>
<tr>
<td>Volatile matter (wt%)</td>
<td>34.6</td>
<td>29.5</td>
</tr>
<tr>
<td>Fixed carbon, (wt%)</td>
<td>41.3</td>
<td>66.8</td>
</tr>
<tr>
<td>HHV$^a$ (Btu/lb)</td>
<td>10,778</td>
<td>14,475</td>
</tr>
<tr>
<td>Total sulfur (wt%)</td>
<td>2.9</td>
<td>0.8</td>
</tr>
<tr>
<td>Hg (ppb)</td>
<td>X</td>
<td>Y</td>
</tr>
</tbody>
</table>

$^a$Higher heating value.
with 15 ppm maximum 7–10 ppm average) and 20% 500-ppm highway diesel between June 2006 and June 2010, and a 100% requirement for ULSD after June 2010 (33).

Sulfur can be removed from diesel fuel, gasoline, and jet fuels during the refining process. When the sulfur in petroleum is exposed to hydrogen in the presence of a catalyst, hydrogen sulfide gas is formed. This compound can be commercially marketed.

Meeting the sulfur standard for gasoline only requires technologies already developed: low-pressure hydrodesulfurization (HDS) and catalytic adsorption. Capital costs have been estimated at US$8 billion, and an incremental cost estimated at US$0.045 per gallon. Adsorption technologies have been, and continue to be, developed that may improve on these cost estimates by avoiding hydrogen use costs. These adsorbents (transitional metals in some cases) preferentially remove the organic sulfur-containing compounds without removing other aromatic molecules. Sulfur-containing molecules such as benzothiophene can be altered to remove the sulfur and allow the remaining aromatic ring to continue through the process S Zorb (34).

Meeting the diesel standard will likely require all of the hydrocracked stock and the entire straight-run material to go to high-pressure, high-temperature, two-stage distillate desulfurization units. This uses proven technology, but will probably require two or more hydrogenation units in series to achieve the desired sulfur levels with heavier crude oils. Cracked stock and coker distillate will have to be diverted to other markets.

Other options for processing diesel include sulfur adsorption on zeolite and selective partial oxidation. These offer significant advantages through a lower hydrogen requirement. However, they are under pilot- and laboratory-scale development. Based on the more conventional technologies, capital costs have been estimated at US$8 billion, and an incremental cost estimated at US$0.07 to US$0.15 per gallon. The implementation time line produces scheduling conflicts that will complicate meeting the goals. One third of US diesel fuel is from cracked stock—more difficult to process to low-sulfur fuel (32).

Although not discussed here at length, sulfur content in jet fuel is also a concern. The US Air Force has proposed halving the maximum sulfur content from 3000 to 1500 ppmw. This becomes more problematic because the Air Force data suggest a trend with time of rising sulfur content in the fuels used (35).

6. DESULFURIZATION THROUGH COAL LIQUEFACTION, GASIFICATION, AND PYROLYSIS

Alternatives to combustion use thermal conversion, gasification, liquefaction, and pyrolysis of coal to produce gas, liquid, and solid fuels respectively. These fuels have much reduced sulfur content, allowing combustion with little or no emissions controls. These fuels may also be used as feedstock for other chemical processes, e.g., synthesis gas to methanol (14). In this section, we describe coal gasification, liquefaction, and pyrolytic conversion.

6.1. Coal Gasification

A very elementary process of coal gasification was designed in the late 1700s to fuel the gas lights that illuminated cities. Since that time, approx 70 different coal gasification processes have been used commercially or are currently under development.
Three basic steps are common to all coal gasification processes: coal pretreatment, gasification, and gas cleaning. Coal pretreatment includes various stages of coal washing and pulverization. Gasification produces either a low- or high-heat content gas by applying heat and pressure or using a catalyst to break down the components of coal. Coal is gasified in an atmosphere of limited oxygen. Generally, oxidation of the coal provides a gas containing carbon monoxide (CO), hydrogen (H₂), carbon dioxide (CO₂), water (H₂O), methane (CH₄), and contaminants such as hydrogen sulfide (H₂S) and char (see Fig. 3).

This “synthesis gas” is composed primarily of carbon monoxide and hydrogen. Variations in the process may increase the quantity of methane formed, producing a gas that releases more heat when it is burned.

The sulfur in coal is converted primarily to hydrogen sulfide (H₂S) during the gasification process. It exits from the gasifier with the methane and synthesis gas and is subsequently removed during the gas cleaning process. After removal, the hydrogen sulfide is then converted to elemental sulfur (S) through partial oxidation and catalytic conversion.

Four systems for gasification and combined cycle production of electricity have been demonstrated through the US DOE's Clean Coal Technology Program. These demonstration projects were performed from 1994 to 2001 and demonstrated a variety of gasifier types, cleanup systems, and applications.
PSI Energy’s Wabash River Coal Gasification Repowering Project began in 1995 and ran to 2000. It employed a two-stage entrained flow gasifier. Carbonyl sulfide was catalytically converted to hydrogen sulfide. This was removed using Methyldiethanolamine (MDEA)-based absorption/stripper columns. A Claus unit produced salable sulfur. SO\(_2\) capture was greater than 99%, with emissions consistently below 0.1 lb/10\(^6\) Btu (14).

The Tampa Electric Integrated Gasification Combined-Cycle Project used a Texaco gasifier. Operations began in 1996. A COS hydrolysis reactor converted one of the sulfur species to a more easily removed form. The further cooled syngas then entered a conventional amine-based sulfur-removal system. SO\(_2\) emissions were kept below 0.15 lb/10\(^6\) Btu (97% reduction). In 2000, there were 10 domestic and international projects planned or under construction using the Texaco gasifier technology (14).

The Sierra Pacific Power Company Pinon Pine IGCC Power Process was operated as a demonstration from 1998 to 2001. The gasifier used dry injection of limestone with the coal, with calcium sulfate being removed with the coal ash in the form of agglomerated particles suitable for landfilling. Final traces of sulfur were removed with a metal oxide absorbent (14).

The fourth demonstration project by Kentucky Pioneer Energy was constructed in 2003. Operations will involve injection of limestone into the combustor. Conventional gas cleanup will be used to remove hydrogen sulfide emissions. SO\(_2\) emissions are expected to be less than 0.1 lb/10\(^6\) Btu (99% reduction) (14).

6.2. Coal Liquefaction

There are two basic approaches in converting coal to oil. One involves using a gasifier to convert coal to carbon monoxide, hydrogen, and methane, followed by a condensation process that converts the gases to oils. The second approach (see Fig. 4) involves using a solvent or slurry to liquefy pulverized coal and then processing this liquid into a fuel similar to heavy oil. The first approach, known as the Fischer–Tropsch process, was developed by Fischer and Tropsch in Europe in the 1930s. Tests and demonstrations of processes for producing synthetic oil from coal were initiated in the United States in the early 1960s, and a major plant was built in South Africa using the Fischer–Tropsch process.

Most recent research has involved the latter approach. Solvents and slurries used in these processes are usually produced from the coal and recycled in the system. Recently developed liquefaction processes have combined the use of solvents and distillation techniques to produce hydrocarbon gas and various hydrocarbon liquids. The Advanced Concepts for Direct Liquefaction Program was begun in 1991 by the DOE. The advanced two-stage liquefaction technology developed at Wilsonville, Alabama brought the estimated costs of liquefaction to US$33/bbl (1990 cost), with an ultimate goal of US$25 (36). Reference 36 describes research focused on improving process economics—coal cleaning, distillate hydrotreating, and dispersed catalyst development, among others. International research has continued in China, Germany, and Japan, where, in 1996, a 150 tonne/d plant was built (37).

These processes involve solvents, and slurries commonly remove sulfur from the liquefied coal by using hydrogen (H\(_2\)) to convert the sulfur to hydrogen sulfide gas. As in the gasification processes, this hydrogen sulfide is then partially oxidized to form elemental sulfur and water. More than 85% of sulfur in coal is removed during the liquefaction process. EPA research efforts currently focus on determining the sulfur content in synthetic
oils produced by different liquefaction processes and on identifying ways to improve their sulfur-removal efficiencies. EPA is also initiating programs to develop improved systems for preventing the escape of hydrogen sulfide (H₂S) and sulfur dioxide (SO₂) from the gas converter into the atmosphere.

6.3. Pyrolysis

A third approach involves thermal treatment of coal to produce a high-quality, low-sulfur fuel. Two technologies investigated under the Clean Coal Technology program, and described here, are referred to as ENCOAL and SynCoal.

The ENCOAL Mild Gasification Project was performed by the ENCOAL Corporation (a subsidiary of Bluegrass Coal Development Company) near Gillette, Wyoming using SGI International’s “Liquids-From-Coal” (LFC) process. Work was performed from 1992 to 1997. The process consists of a drying step, followed by pyrolysis at 1000°F. The solid process-derived fuel (PDF) is then cooled, rehydrated, contacted with oxygen to reduce the potential for spontaneous combustion, and mixed with a dust suppressant. The process gases are cooled to condense coal-derived liquid (CDL). The PDF had a sulfur content of 0.36% versus 0.45% for the feed coal. The CDL had a sulfur content of 0.6% versus 0.8% for No. 6 fuel oil.

The SynCoal process involves the upgrading of low-rank coal to a high-quality, low-sulfur, solid fuel. The process was demonstrated under the Clean Coal Technology
Program by Western SynCoal LLC. The project was performed at Colstrip, Montana from 1992 to 2001. High-moisture, low-rank coal is fed to a vibratory fluidized-bed dryer, where it is heated by a combustion gas. Water is driven off, and the coal is transferred to a second vibratory reactor where it is heated to nearly 600°F, driving off chemically bound water, carboxylic groups, and volatile sulfur compounds. A small amount of tar is released that seals the coal. The coal shrinks, fractures, and releases ash-forming minerals. Deep-bed stratifiers using air pressure and vibration are used to separate mineral matter, including pyrite.

SynCoal has been used by electric utilities and industries, primarily by cement and lime plants. Reduction in sulfur emissions has been demonstrated for electrical generation (14).

7. DESULFURIZATION THROUGH COAL-LIMESTONE COMBUSTION

7.1. Fluidized-Bed Combustion

Because sulfur oxides are emitted from the stacks of electrical-generating stations and industries, \( \text{SO}_x \) control efforts initially focused on flue gases. An alternative is to combine the sulfur dioxide absorbent and coal directly at the point of combustion. This is accomplished by the injection of limestone or mixing of fuel and limestone before their injection into the boiler. Fluidized-bed combustors provide the contact time needed for fuel–limestone interaction and offer other advantages. The following paragraphs describe atmospheric and pressurized fluidized-bed combustors, as well as coal–limestone pelletization.

In fluidized-bed combustion (FBC), a grid supporting a bed of crushed limestone or dolomite is set in the firebox (see Fig. 5). Air forced upward through the grid creates turbulence, causing the bed of limestone or dolomite to become suspended and move in a fluidlike motion. Natural gas is injected into the firebox, ignited, and then followed by pulverized coal. Once the coal has started to burn well, the natural gas is shut off and the fire is maintained by burning coal. Sulfur oxidized during combustion reacts with the limestone or dolomite in the firebox, forming calcium sulfate. Calcium sulfate and residual limestone or dolomite from fluidized-bed combustion can be disposed of in landfills or used in construction materials. Fluidized-bed combustion eliminates the need for FGD because the bed of limestone or dolomite can remove more than 90% of the sulfur oxides created during combustion.

Basic FBC concepts have been proven, and the US DOE and its industrial partners are now working on implementation and system design, scale-up, reliability, and control issues. Goals include achieving efficiency of 45% for high-efficiency, domestic, greenfield applications after the year 2005 (5% more than a modern pulverized coal unit with flue gas scrubbing). The target cost is US$750/kW for new FBC systems (38).

FBC in boilers can be particularly useful for high-ash coals and/or those with variable characteristics. A variation on FBC is the pressurized fluidized-bed combustor (PFBC). PFBCs have undergone significant development during the 1990s, and demonstration units have been built in Germany, Spain, and the United States.

Advantages of PFBCs include compact units, high heat transfer, potential usefulness for low-grade coals and for those coals with variable characteristics. As for atmospheric FBC, bubbling and circulating beds may be used. All commercial-scale operating units
use bubbling beds, and PFBC normally refers to pressurized bubbling bed units. A pressurized circulating FBC was also constructed for demonstration.

In the PFBC, the combustor and hot gas cyclones are all enclosed in a pressure vessel. Coal and sorbent are fed and ash removal is performed across the pressure boundary. Hard coal and limestone can be crushed together and then fed as a paste. Units operate at pressures of 1–1.5 MPa, with combustion temperatures of 800–900°C. NO\textsubscript{x} formation is less than in pulverized coal combustors (PCCs). SO\textsubscript{2} emissions are lowered by the injection of sorbent (limestone or dolomite) and its subsequent removal with the ash.

The residues consist of the original mineral matter, most of which does not melt at the combustion temperatures used. Where sorbent is added for SO\textsubscript{2} removal, there will be additional CaO/MgO, CaSO\textsubscript{4}, and CaCO\textsubscript{3} present. There may be a high free-lime content, and leachates will be strongly alkaline. Carbon-in-ash levels are higher in FBC residues than those from PCCs (39).

### 7.2. Lime–Coal Pellets

Burning pellets composed of a limestone and coal mixture is another way of eliminating the need for FGD. The US EPA's Office of Research and Development (ORD) research has shown that the combustion of these pellets in conventional stoker boilers not only reduces sulfur oxide emissions but also enhances boiler performance. The pellets are made by pulverizing coal and limestone and adding a binder material to form small cylinders. As the pellet burns, the calcium in the limestone absorbs the SO\textsubscript{2} generated from burning the coal, resulting in the formation of calcium sulfate (CaSO\textsubscript{4}).

The ability of the pellet to control sulfur emissions depends on the ratio of limestone to coal, pellet size, binder material, and types of coal and limestone used. For example, ORD has developed a binder material that enables as much as 87% of the SO\textsubscript{2} to be
absorbed by the limestone when a pellet composed of two-thirds coal and one-third limestone is used.

The expense of preparing fuel with pellets would add more than US$15 per ton to the cost of coal, which is substantially less than the cost of installing and operating wet scrubber systems for industrial boilers. In the future, fuel pellets will be developed for a greater range of coal and boiler types. This research could enable users of high-sulfur coal from eastern US mines to meet SO₂ pollution control requirements.

8. HYDROGEN SULFIDE REDUCTION BY EMERGING TECHNOLOGIES

Hydrogen sulfide emissions derive from numerous sources including petroleum hydrosulfurization, anaerobic wastewater treatment, and landfills. Major approaches to control include absorption into amine solution, catalytic oxidation to elemental sulfur, and biological oxidation. Absorbed hydrogen sulfide can be stripped from solution with steam, and sent to a Claus plant for partial oxidation to sulfur.

8.1. Innovative Wet Scrubbing Using a Nontoxic Chelated Iron Catalyst

In an innovative wet scrubber—in this case, for H₂S reduction—the process involves mass transfer from the gas to liquid phases. The offending specie, H₂S (or some other malodorous gas), is present in an emission stream or gas phase. The liquid phase is the scrubbing solution, distributed as a flowing bulk liquid into the scrubber. The scrubber is controlled by dispersing the gas phase (i.e., air emission stream with target pollutant, H₂S) as small gas bubbles into the passing liquid phase (i.e., scrubbing solution with scrubbing chemicals). The flow pattern can be either counterflow or cross-flow. The process equipment of an innovative wet scrubber resembles that for the aeration basin of an activated sludge system and is described in detail in Chapter 5, volume 1, on wet and dry scrubbing.

The innovative wet scrubber can achieve very high efficiencies (99+% ) and has very high turndown capabilities. The liquid redox system is considered by some to be the best available control technology for geothermal power plants. The process employs a nontoxic, chelated iron catalyst, which accelerates the oxidation reaction between H₂S and oxygen to form elemental sulfur (1).

The air emission stream is contacted with the aqueous, chelated iron solution, where the H₂S is absorbed and ionized into sulfide and hydrogen ions as follows:

\[
\begin{align*}
H₂S \text{ (vapor)} + H₂O & \rightarrow 2H^+ + S^{2-} \\
S^{2-} + 2Fe^{3+} & \rightarrow S \text{ (elemental sulfur)} + 2Fe^{2+} \\
0.5 O₂ \text{ (vapor)} + H₂O + 2Fe^{2+} & \rightarrow 2Fe^{3+} + 2OH^- \\
H₂S + 0.5 O₂ \rightarrow S \text{ (elemental sulfur)} + H₂O
\end{align*}
\]

where \( S^{2-} \) is the sulfide ion, \( Fe^{3+} \) is the trivalent iron ion, \( S \) is elemental sulfur, \( Fe^{2+} \) is the divalent iron ion, \( O₂ \) is oxygen vapor, \( H₂O \) is water, and \( OH^- \) is the hydroxide ion.

The final chemical reaction presented in Eq. (4) is the summary of the three chemical reactions preceding it. The nontoxic, chelated iron catalyst allows the hydrogen sulfide to be oxidized to elemental sulfur, for recovery and reuse. The readers are referred Chapter 5, volume 1 (73).
8.2. Conventional Wet Scrubbing Using Alkaline and Oxidative Scrubbing Solution

In the conventional wet scrubber, mass transfer of contaminant occurs from the gas to the liquid phase. The process is controlled by dispersing the liquid phase (i.e., scrubbing solution containing scrubbing chemicals) as liquid droplets or thin films into a passing gas phase (i.e., air emission stream with target pollutant, H₂S). The flow pattern can be either counterflow or cross-flow. The conventional wet scrubber has shown a hydrogen sulfide removal efficiency of 99.9% from a contaminated airstream at various flow rates, superficial gas velocities, liquid flux rates, tower diameters, and HTU values.

The following reactions are for a single-stage scrubbing system using 0.1% caustic and 0.3% sodium hypochlorite to control hydrogen sulfide emissions:

\[
\begin{align*}
H_2S + 2NaOH & \rightarrow Na_2S + 2H_2O \\
NaOCl + H_2O & \rightarrow HOCl + NaOH \\
4HOCl + Na_2S & \rightarrow Na_2SO_4 + 4HCl \\
HCl + NaOH & \rightarrow NaCl + H_2O
\end{align*}
\]

where H₂S is hydrogen sulfide, NaOH is caustic soda, or sodium hydroxide, Na₂S is sodium sulfide, NaOCl is sodium hypochlorite, Na₂SO₄ is sodium sulfate, HCl is hydrochloric acid, and NaCl is sodium chloride.

8.3. Scavenger Adsorption

Geothermal power plants are environmentally attractive because they employ a renewable energy source. Geothermal steam, however, contains varying amounts of noncondensible gases (NCG), such as carbon dioxide and hydrogen sulfide, which cause serious environmental, health, and safety problems (1,2). If the removal rate of hydrogen sulfide from the NCG is less than approx 140 kg/pd, it is generally economical to employ an H₂S scavenger such as Sulfur-Rite™ manufactured by US Filter/Gas Technology Products. This system is a fixed-bed process consisting of an iron-based solid material, which reacts with H₂S to form innocuous iron pyrite:

\[
H_2S + \text{Sulfur-Rite} + \text{Iron} \rightarrow H_2O + FeS_2
\]

where H₂S is hydrogen sulfide, H₂O is water, FeS₂ is iron pyrite, and Sulfur-Rite is a H₂S scavenger.

The process is a relatively simple, batch-type system consisting of a carbon steel vessel(s), which hold the iron-based media. The NCG pass through the vessel(s) until all of the iron has been converted to pyrite. The vessel is then shut down, emptied, and refilled with fresh media. A “Lead-Lag” arrangement can be employed, which permits continuous treatment of the NCG even during changeouts. In this processing scheme, the NCG flows through two Sulfur-Rite vessels in series. When the outlet H₂S concentration in the first vessel is the same as the inlet concentration, the vessel is shutin and the medium is replaced. During the changeout, the NCG is processed through the second vessel only. When the change out is complete, the flow direction is reversed.

The medium is nonregenerable, resulting in a relatively high operating cost of approx US$12.00 per kilogram of H₂S removed. However, the system is simple and noncorrosive, which results in a relatively low capital investment. The major difficulty
involved in using solid-based scavengers in Europe is disposal of the spent material. In other parts of the world, the spent material is simply landfilled in nonhazardous facilities. However, in Europe, landfilling is discouraged and expensive. Consequently, means of using the material as raw material for bricks and so forth are being investigated.

The solid-type scavengers can be replaced with liquid scavengers, which are generally triazine-based. The advantage of liquid-based scavengers is that the spent material can be injected down-hole for disposal. The disadvantage of liquid scavengers is that they are very expensive, having a relative cost of approx US$33.00 per kilogram of H₂S removed (1).

8.4. Selective Oxidation of Hydrogen Sulfide in Gasifier Synthesis Gas

In this process, oxygen is directly injected into the synthesis gas, where a selective catalytic oxidation converts the hydrogen sulfide to elemental sulfur. The process has the advantage of converting and removing the sulfur in one stage. In the case of the design for the Tampa Electric Company integrated gasification combined cycle plant, the process allowed elimination of sour gas coolers, the amine absorption unit, Claus plant, and tail gas treatment and incinerator (40,41).

8.5. Biological Oxidation of Hydrogen Sulfide

Biological oxidation has been used for odor control in hydrogen sulfide–containing airstreams. Bacteria convert the H₂S to sulfate, water, and carbon dioxide. The airstream is first humidified and warmed as needed. It then passes though a packed-bed biofilter where the H₂S is absorbed into a liquid film and oxidized there by bacteria. Collected water is removed to a sanitary drain. Hydrogen sulfide removal of 99% or greater can be achieved with inlet concentrations of up to 1000 ppm. Industrial-scale and smaller package units are in wide application (42).

9. "WET" FLUE GAS DESULFURIZATION USING LIME AND LIMESTONE

Flue gas desulfurization is the most commonly used method of removing sulfur oxides resulting from the combustion of fossil fuels. FGD processes result in SOₓ removal by inducing exhaust gases to react with a chemical absorbent as they move through a long vertical or horizontal chamber, known as a wet scrubber (43–54).

A typical, no-frills FGD system is shown in Fig. 6. The efforts of research engineers to bring wet FGD to commercial acceptance resulted in the following innovations researched and developed at various demonstration facilities: (1) use of high liquid-to-gas ratios (enhanced scrubber internal recirculation) to prevent scaling, (2) use of forced oxidation to avoid scaling and improve disposal/salability of solids, (3) use of thiosulfate-forming additives to inhibit scaling, and (4) use of organic acid buffers to increase SO₂ removal and improve sorbent utilization (55).

Many different FGD processes have been developed, but only a few have received widespread use. Of the systems currently in operation, 90% use lime or limestone as the chemical absorbent.
9.1. FGD Process Description

The basic lime/limestone FGD process appears schematically in Fig. 6. Some systems produce a salable byproduct (i.e., gypsum for wallboard construction), but most use the throwaway process configuration. As shown in Fig. 7, flue gas, from which fly ash has been removed in a particulate collection device such as an electrostatic precipitator (ESP) or a fabric filter, is brought into contact with the lime/limestone slurry in the absorber, where $\text{SO}_2$ is removed. The chemical reaction of lime/limestone with $\text{SO}_2$ from the flue gas produces waste solids, which must be removed continuously from the slurry loop. These waste solids are concentrated in a thickener and then dewatered in a vacuum filter to produce a filter “cake” that is mixed with fly ash. The resulting stabilized mixture is then transported to a landfill. This lime/limestone FGD system is called a “throwaway” process because it produces a waste byproduct for disposal rather than for processing to recover salable gypsum.

The principal chemical reactions for the lime/limestone FGD process are presented below according to $\text{SO}_2$ absorption, limestone dissolution, and lime dissolution.

9.2. FGD Process Chemistry

9.2.1. Sulfur Dioxide Absorption

Chemical reactions for $\text{SO}_2$ absorption in a scrubber/absorber are as follows.

$\text{SO}_2(g) \rightarrow \text{SO}_2(aq)$  \hspace{1cm} (10)

$\text{SO}_2(aq) + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_3(aq)$  \hspace{1cm} (11)

$\text{H}_2\text{SO}_3(aq) \rightarrow \text{HSO}_3^-(aq) + \text{H}^+(aq)$  \hspace{1cm} (12)
Fig. 7. Complete lime/limestone FGD process flow diagram.

\[
\text{HSO}_3^- (aq) \rightarrow \text{SO}_3^{2-} (aq) + \text{H}^+ (aq) \quad (13)
\]

\[
\text{SO}_3^{2-} (aq) + \frac{1}{2} \text{O}_2 (aq) \rightarrow \text{SO}_4^{2-} (aq) \quad (14)
\]

\[
\text{HSO}_3^- (aq) + \frac{1}{2} \text{O}_2 (aq) \rightarrow \text{SO}_4^{2-} (aq) + \text{H}^+ (aq) \quad (15)
\]

where \( g \) is the gas phase, \( \text{aq} \) is the aqueous phase, \( \text{HSO}_3^- \) is the bisulfite ion, \( \text{SO}_3^{2-} \) is the sulfite ion, \( \text{SO}_4^{2-} \) is the sulfate ion, \( \text{O}_2 \) is oxygen, \( \text{H}^+ \) is the hydrogen ion, and \( \text{SO}_2 \) is sulfur dioxide.

### 9.2.2. Lime Dissolution and Lime FGD Chemical Reaction

Chemical reactions for lime dissolution in a scrubber/absorber (see Fig. 8) are as follows:

\[
\text{CaO(s)} + \text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2 \quad (16)
\]

\[
\text{Ca(OH)}_2 (aq) \rightarrow \text{Ca}^{2+} (aq) + 2\text{OH}^- (aq) \quad (17)
\]

\[
\text{OH}^- (aq) + \text{H}^+ (aq) \rightarrow \text{H}_2\text{O} \quad (18)
\]

\[
\text{SO}_3^{2-} (aq) + \text{H}^+ (aq) \rightarrow \text{H}_2\text{SO}_3 (aq) \quad (19)
\]

\[
\text{Ca}^{2+} (aq) + \text{SO}_3^{2-} (aq) + 0.5\text{H}_2\text{O} \rightarrow \text{CaSO}_3 \cdot 0.5\text{H}_2\text{O(s)} \quad (20)
\]

\[
\text{Ca}^{2+} (aq) + \text{SO}_4^{2-} (aq) + 2\text{H}_2\text{O} \rightarrow \text{CaSO}_4 \cdot 2\text{H}_2\text{O(s)} \quad (21)
\]

where \( S \) is the Solid phase.
In the FGD system (see Figs. 6 and 7), the sulfur dioxide reacts with lime to form calcium sulfite and water, in accordance with the following overall chemical reaction:

\[ \text{SO}_x + \text{CaO} + \text{H}_2\text{O} \rightarrow \text{CaSO}_3 + \text{H}_2\text{O} \]  

where \( \text{SO}_x \) is the sulfur oxides (SO\(_2\) or SO\(_3\)), CaO is lime (calcium oxide), H\(_2\)O is water, CaSO\(_3\) is calcium sulfite, Ca(OH)\(_2\) is calcium hydroxide, Ca\(^{2+}\) is the calcium ion, OH\(^{-}\) is the hydroxide ion, H\(^{+}\) is the hydrogen ion, SO\(_3^{2-}\) is the sulfite ion, HSO\(_3^{-}\) is the bisulfite ion, CaSO\(_4\) is calcium sulfate, and SO\(_4^{2-}\) is the sulfate ion. Calcium sulfite is the final product from the scrubber.

### 9.2.3. Limestone Dissolution and Limestone FGD Chemical Reactions

Chemical reactions for limestone dissolution in a scrubber/absorber (see Fig. 8) are as follows:

\[ \text{CaCO}_3(s) \rightarrow \text{CaCO}_3(aq) \]  

\[ \text{CaCO}_3(aq) \rightarrow \text{Ca}^{2+}(aq) + \text{CO}_3^{2-}(aq) \]  

\[ \text{CO}_3^{2-}(aq) + \text{H}^{+}(aq) \rightarrow \text{HCO}_3^{-}(aq) \]  

\[ \text{SO}_3^{2-}(aq) + \text{H}^{+}(aq) \rightarrow \text{HSO}_3^{-}(aq) \]  

\[ \text{Ca}^{2+}(aq) + \text{SO}_3^{2-}(aq) + 0.5\text{H}_2\text{O} \rightarrow \text{CaSO}_3 \cdot 0.5\text{H}_2\text{O}(s) \]  

\[ \text{Ca}^{2+}(aq) + \text{SO}_4^{2-}(aq) + 2\text{H}_2\text{O} \rightarrow \text{CaSO}_4 \cdot 2\text{H}_2\text{O}(s) \]  

The use of limestone in a FGD process system (see Figs. 6 and 7) results in a similar chemical reaction, but also yields carbon dioxide:

\[ \text{SO}_2 + \text{CaCO}_3 + \text{H}_2\text{O} \rightarrow \text{CaSO}_3 + \text{H}_2\text{O} + \text{CO}_2 \]  

where SO\(_2\) is sulfur dioxide, CaCO\(_3\) is calcium carbonate (limestone), and CO\(_2\) is carbon dioxide.
Figure 8 shows that the final product from the limestone FGD chemical reactions is calcium sulfite from the scrubber/absorber.

9.2.4. Forced Oxidation Chemistry

As shown in Fig. 9, calcium sulfite is formed during the scrubbing/absorbing process. The substance presents a serious operational problem because it settles and filters poorly and can be removed from the scrubber/absorber slurry only in a semiliquid, or pastelike, form that must be stored in lined ponds. A solution to this problem involves forced oxidation in which air is blown into the tank that holds the used scrubber slurry, which is composed primarily of calcium sulfite and water. Dissolved oxygen then oxidizes the calcium sulfite to calcium sulfate (Fig. 9).

The following is the process chemistry of forced oxidation:

$$\text{CaSO}_3 + \text{H}_2\text{O} + \frac{1}{2}\text{O}_2 \rightarrow \text{CaSO}_4 + \text{H}_2\text{O}$$

where \( \text{CaSO}_3 \) is calcium sulfite and \( \text{CaSO}_4 \) is calcium sulfate.

9.3. FGD Process Design and Operation Considerations

Although not shown in the process diagrams (Figs. 6 and 7), the major equipment design difference between the lime and limestone processes is reagent feed preparation.
In the lime process, the reagent is slaked. In the limestone process, limestone is ground in a ball mill.

The basic operational factors one should be acquainted with when inspecting lime/limestone slurry FGD systems are discussed in the following Subsections. Knowing these factors and how they are interrelated with the process chemistry of each system will provide an understanding of how each process functions, in addition to providing a set of guidelines to be used during an inspection.

9.3.1. Stoichiometric Ratio

The stoichiometric ratio (SR) is defined as the ratio of the actual amount of SO₂ reagent, calcium oxide (CaO), or calcium carbonate (CaCO₃) in the lime or limestone fed to the absorber, to the theoretical amount required to neutralize the SO₂ and other acidic species absorbed from the flue gas. Theoretically, 1 mol of CaO or CaCO₃ is required per mole of SO₂ removed (SR = 1.0). In practice, however, it is usually necessary to feed more than the stoichiometric amount of reagent in order to attain the degree of SO₂ removal required. This is because of mass transfer limitations that prevent complete reaction of the absorbent.

If a high SO₂ removal efficiency is required, the absorber may not be able to achieve such removal unless extra alkalinity is provided by feeding excess reagent. The amount of excess reagent required depends on the SO₂ concentration in the inlet gas, gas flow, percentage SO₂ removal required, and absorber design. For lime reagent, the SR employed in commercial FGD systems is 1.05 for newer designs; it is up to 1.2 for older designs. For limestone reagent, a SR of 1.1 is used in newer designs, but can be as high as 1.4 in older designs (43,44).

If the reagent feed is too much in excess, the results are wasted reagent and increased sludge volume. Excessive overloading can also result in scaling in the form of CaCO₃ in the upper part of the absorber for lime systems, and calcium sulfate (CaSO₄·½H₂O), sometimes referred to as soft scale, in the lower part of the absorber for limestone systems. Excess reagent can also be carried up into the mist eliminator by entrainment, where it can accumulate, react with SO₂, and form a hard calcium sulfate (CaSO₄·2H₂O) scale (by sulfite oxidation). This is particularly a problem with limestone systems. Calcium sulfate (or gypsum) scale is especially undesirable because it is very difficult to remove. Once formed, the scale provides a site for continued precipitation. Calcium sulfite scale can generally be easily removed by reducing the operating slurry pH or rinsing manually with water.

Scale formation is usually more prominent in limestone systems than lime systems, particularly for high-sulfur coal applications. Lime systems have a greater sensitivity to pH control because lime is a more reactive reagent. The change in pH across lime systems is more pronounced than in limestone systems partly because limestone dissolves more slowly.

9.3.2. Liquid/Gas Ratio

The ratio of slurry flow in the absorber to the quenched flue gas flow, usually expressed in units of gal/1000 ft³ is termed the liquid-to-gas (L/G) ratio. Normal L/G values are typically 30–50 gal/1000 ft³ for lime systems (44) and 60–100 gal/1000 ft³ for limestone systems (49). Lime systems require lower L/G ratios because of the higher
reactivity of lime. A high L/G ratio is an effective way to achieve high SO₂ removal. This also tends to reduce the potential for scaling, because the spent slurry from the absorber is more dilute with respect to absorbed SO₂. Increasing the L/G ratio can also increase system capital and operating costs, because of greater capacity requirements of the reaction tank and associated hold tanks, dewatering equipment, greater pumping requirements, slurry preparation and storage requirements, and reagent and utility necessities.

9.3.3. Slurry pH

Commercial experience has shown that fresh slurry pH as it enters the absorber should be in the range 8.0–8.5 for lime systems and 5.5–6.0 for limestone systems (43,44,48). In both FGD processes, as the SO₂ is absorbed from the flue gas, the slurry becomes more acidic and the pH drops. The pH of the spent slurry as it leaves the absorber is in the range 6.0–6.5 for lime systems and 4.0–5.0 for limestone systems. In the reaction tank of the absorber, the acidic species react with the reagent, and the pH returns to its original fresh slurry value. Slurry pH is controlled by adjusting the feed stoichiometry. Operation of lime/limestone FGD systems at low pH levels, approaching 4.5, will improve reagent utilization but will also lower SO₂ removal efficiency and also increase the danger of hard scale (gypsum) formation because of increased oxidation at lower pH levels. Operation of lime/limestone FGD systems at high pH levels, above 8.5 and 6.0, respectively, will tend to improve removal efficiency but will also increase the danger of soft scale (calcium sulfite) formation. Hence, control of slurry pH is essential to reliable operation. The inability to maintain sensitive control of the slurry pH can lead to both lowered SO₂ removal efficiencies and hard/soft scale formation.

9.3.4. Relative Saturation

In lime/limestone FGD processes, the term “relative saturation” (RS) pertains to the degree of saturation (or approach to the solubility limit) of calcium sulfite and sulfate in the slurry. RS is important as an indicator of scaling potential, especially of hard scale, which can present severe maintenance problems. Relative saturation is defined as the ratio of the product of calcium and sulfate ion activities (measured in terms of concentrations) to the solubility product constant. The solution is subsaturated when RS is less than 1.0, saturated when RS equals 1.0, and supersaturated when RS is greater than 1.0. Generally, lime/limestone processes will operate in a scale-free mode when the RS of calcium sulfate is maintained below a level of 1.4 and the RS of calcium sulfite is maintained below a level of approx 6.0. Operation below these levels provides a margin of safety to ensure scale-free operation. This is achieved through proper design and control of process variables (e.g., L/G, pH).

9.3.5. Overall FGD System Parameters

Important overall FGD system parameters include reagent type, water loop, solids dewatering, absorber parameters, reheat, reagent preparation, and fan location. A brief summary for each FGD system consideration is provided.

9.3.5.1. Reagent Type

The gas handling and treatment subsystem, ductwork, and stack show a strong relation between lime systems and unreliability. This is probably because lime FGD systems are
predominantly used for higher-sulfur coal applications. Limestone shows a high correlation with unreliability in the slurry circuit (limestone slurry is more abrasive than lime slurry).

9.3.5.2. WATER LOOP

There are two variations: open and closed water-loop FGD systems. There are some expectations that closed water loops, higher in chloride, will be less reliable. However, open water-loop systems appear less reliable. One explanation for this observation is that virtually all of the early generation commercial lime/limestone FGD systems were originally designed for closed water-loop (no discharge) operation. Because of a variety of problems (e.g., buildup of dissolved salts), the water loop was eventually opened up as one of the first measures to relieve these problems. (In other words, the water-loop variable is an “effect” rather than a “cause.”)

9.3.5.3. SOLIDS DEWATERING

Results confirmed the expectation that FGD systems without dewatering were more reliable than systems with dewatering. They have less equipment to cause downtime and lower concentrations of dissolved salts that build up in the liquor loop.

9.3.5.4. ABSORBER PARAMETERS

Results indicated that towers with internals (packed, tray) have a high correlation with unreliability. The type of absorber exhibiting the highest unreliability is the packed tower. Spray tower absorbers exhibited the highest reliability. However, mist eliminators showed a high correlation of unreliability with spray tower absorbers. This is to be expected when considering the open structure of a spray tower, the high L/G ratio, and the upward flow of the gas without impediment or a change in direction. Absorbers with internals have been associated with a high degree of unreliability and are generally excluded from new designs. Another consideration in absorbers is the use of “prescrubbers.” Prescrubbers include upstream scrubbers, presaturators, and quench towers. A number of systems are equipped with one of these devices to remove particulates, effect initial SO₂ absorption, and/or condition the gas stream prior to the absorber. Systems without prescrubbers appear to be more reliable than systems with prescrubbers. This is an expected result because systems with prescrubbers have an additional subsystem that may fail. However, the presence of a prescrubber shows a high correlation with reliability for SO₂ absorbers in contrast to their effect on the total system. A possible explanation is that the combination of flue gas quenching and chloride, particulate, and initial SO₂ removal that occurs in a prescrubber serves to protect the SO₂ absorber from failures.

9.3.5.5. REHEAT

The order of decreasing reliability for type of reheat is no reheat, bypass reheat, inline reheat, and indirect reheat. Figure 6 shows the position of a reheat unit; Fig. 10 shows the FGD system reheat schematic diagrams. Reheaters are described at length in Section 9.6.1.4.

9.3.5.6. REAGENT PREPARATION

Reagent preparation in a ball mill (limestone) is associated with considerably higher costs for slurry circuit equipment (e.g., pipes, valves) than is reagent preparation in a slaker (lime).
9.3.5.7. Fan Location

Fan unreliability was affected by fan location between the scrubber and the absorber. This location means that the fan operates completely wet, and more downtime is expected. There was little difference between downtime for fans located either upstream (operating on hot, particulate-cleaned gas) or downstream (operating on reheated gas) from the FGD system.

9.4. FGD Process Modifications and Additives

9.4.1. Forced Oxidation Modifications

The most important chemical consideration in lime/limestone processes is the oxidation of sulfite to sulfate. (see Fig. 9) Uncontrolled oxidation across the absorber leads to sulfate formation and resultant hard scaling problems on the absorber internals. Sulfite oxidation can occur either naturally or can be artificially promoted (i.e., forced
oxidation). Natural oxidation occurs when sulfite in the slurry reacts with dissolved oxygen \( (O_2) \), which has been absorbed either from the flue gas or from the atmosphere (e.g., during agitation in the reaction tank). With forced oxidation, air is bubbled into the absorber reaction tank to further promote oxidation. This prevents the dissolved sulfite in the slurry from returning to the absorber, which minimizes the potential for the oxidation of the sulfite to sulfate in the absorber and resultant hard scaling problems. Forced oxidation has additional advantages of reducing the total volume of waste generated because of improved dewatering characteristics of the sulfate solids and improved characteristics of the final solid-waste product. Oxidation tends to increase with decreasing slurry pH. For this reason, forced oxidation is normally employed only with limestone systems.

The process chemistry of forced oxidation has been presented above. It should be noted that the calcium sulfate formed by this reaction grows to a larger crystal size than does calcium sulfite. As a result, the calcium sulfate can easily be filtered to a much drier and more stable material that can be disposed of as landfill. In some areas, the material may be useful for cement or wallboard manufacture or as a fertilizer additive.

Another problem associated with limestone scrubbing is the clogging of equipment by calcium sulfate scale. Forced oxidation can help control scale by removing calcium sulfite from the slurry and by providing an abundance of pure gypsum (calcium sulfate) to rapidly dissipate the supersaturation normally present. The scrubber operation also requires less freshwater, which is scarce in many western locations.

### 9.4.2. Chemical Additives

#### 9.4.2.1. Adipic Acid Additive

The recent discovery that the addition of adipic solid to FGD limestone can increase the level of SO\(_2\) removal from 85% to 95–97% represented a major breakthrough in SO\(_2\) removal technology. Adipic acid, a crystalline powder derived from petroleum, is available in large quantities.

EPA experiments have shown that when limestone slurry reacts with SO\(_2\) in the scrubber, the slurry becomes very acidic. This acidity limits SO\(_2\) absorption. Dicarboxylic acids, in the form of adipic acid or dibasic acids, have been used commercially. Dibasic acids enhance SO\(_2\) removal in a special manner. Acting as buffers, they tend to neutralize acid-generated hydrogen ions \((H^+)\), which, in turn, prevents the decrease of the system pH and SO\(_2\) removal.

Adding adipic acid to the slurry slightly increases the slurry’s initial acidity, but prevents it from becoming highly acidic during the absorption of SO\(_2\). The net result is an improvement in scrubbing efficiency. Adipic acid can reduce total limestone consumption by as much as 15%. Furthermore, the additive is nontoxic (it is used as a food additive) and does not degrade calcium sulfite sludge \((\text{CaSO}_3)\) and gypsum \((\text{CaSO}_4)\), the FGD wastes. In addition, high liquid-phase calcium concentrations permitted by the dibasic acids leads to a reduced potential for scaling tendencies in the absorber (47).

#### 9.4.2.2. Magnesium Oxide Additive

In recent years, inorganic additives have been used to improve SO\(_2\) removal efficiency, increase reagent utilization, decrease solid-waste volume, and decrease scaling potential of lime/limestone FGD systems. In lime/limestone FGD systems, inorganic
additives enhance utilization by improving dissolution. This allows a lower stoichiometric ratio, which reduces limestone addition and the resulting volume of solid waste.

Magnesium oxide additives permit a higher SO$_2$ removal rate per unit volume of slurry. This is because the salts formed by the reaction of magnesium-based additives with the acid species in the slurry liquor are more soluble with respect to those of the calcium-based salts. This, in turn, increases the available alkalinity of the scrubbing liquor, which promotes a higher SO$_2$ removal rate.

9.4.3. Limestone Utilization

Adding adipic acid is one way to increase limestone utilization in the scrubber system. Researchers are studying other factors that affect SO$_2$ absorption and limestone utilization, including the limestone’s particle size, impurities, and geological structure.

Limestone used in a scrubber system is crushed into small particles to allow more calcium carbonate (CaCO$_3$) molecules on the surface of the particles to react with the sulfur dioxide (SO$_2$) gas. ORD scientists are testing two sizes of limestone particles: a coarse grind, similar to that of sugar or salt, and a fine grind, similar in consistency to flour. Various types of limestone, crushed to the same particle size, are currently being compared for their effectiveness in removing sulfur oxides from exhaust gases.

These tests have shown that different limestones of equal particle size vary in their absorption effectiveness. Impurities in the limestone account for part of this difference. Recent experiments have shown that the presence of magnesium carbonate, the main impurity in limestone, inhibits calcium carbonate from reacting with the sulfur dioxide.

The presence of such impurities, however, cannot fully account for variations in the efficiencies of various limestones. Researchers are investigating such geological factors as crystal size and pore size to determine why some kinds of limestone work better than others. These data can then be used to improve the utilization of all limestones employed in FGD systems.

9.5. Technologies for Smelters

9.5.1. Water as a Scrubbing Solution

In a copper scrubber, if an air emission stream contains a high enough concentration of SO$_x$, water alone can be used, at least at an initial stage as a scrubbing solution. The final product will be sulfuric acid, which can be reused or sold. Specifically, copper ore contains large amounts of sulfur that are converted to sulfur oxides when the ore is processed. About 2 tons of sulfur dioxide (SO$_2$) is generated for each ton of copper produced.

Smelters produce two streams of gases containing sulfur oxides: a strong stream containing a 4% or greater concentration of SO$_x$, and a weak stream normally containing less than 2% SO$_x$. The strong stream is usually treated by a chemical process that converts SO$_2$ to sulfuric acid (H$_2$SO$_4$). In this process, SO$_2$ is cleaned and converted to SO$_3$, which reacts with water, producing H$_2$SO$_4$. In 1980, 13 of the 16 copper smelters in the United States operated sulfuric acid plants (9). The sulfuric acid can be used in ore processing operations or sold to other industries.

Most of the SO$_2$ emissions from copper smelters come from reverberatory furnaces, which burn gas, oil, or coal. When copper is heated, sulfur is released and mixes with gases from the burning fuel and with large quantities of air and is converted to SO$_2$. The
concentration of SO$_2$ ranges from 0.5% to 3.5%, but rarely exceeds 2.5%. This SO$_2$ concentration is lower than the 4% or more required to process SO$_2$ into sulfuric acid (H$_2$SO$_4$), so the furnace exhaust gases are vented to the atmosphere. As of the early 1990s, none of the reverberatory furnaces operating in this country were equipped with controls for SO$_2$ emissions (45,46).

9.5.2. Wet Scrubbing Using Citrate Solution

The Industrial Environmental Laboratory in Cincinnati, Ohio investigated a citrate process for copper smelters, which concentrates SO$_2$ gas from the smelter furnace to allow the production of sulfuric acid.

In the citrate process, sulfur dioxide is dissolved in water and thus removed from the exhaust system:

$$\text{SO}_2 + \text{H}_2\text{O} \rightarrow \text{HSO}_3^- + \text{H}^+$$  \hspace{1cm} (31)

where HSO$_3^-$ is the bisulfite ion, H$^+$ is the hydrogen ion, H$_2$O is water, and SO$_2$ is sulfur dioxide.

Adding citrate to the water increases the amount of SO$_2$ that the water will absorb because the citrate ion (CIT) chemically bonds with the hydrogen ions (H$^+$). Sulfur can then be removed from the citrate solution in the form of an SO$_2$ stream strong enough to be used in the acid plant and converted to marketable sulfuric acid.

The citrate process was demonstrated in a copper smelter in Sweden and in a zinc smelter in Pennsylvania. The demonstrations have shown the citrate process to have at least 90% removal efficiency for SO$_2$ from an air emission stream.

9.5.3. Wet Scrubbing Using Magnesium Oxide Slurry

In the second SO$_x$ control process, magnesium oxide is mixed with water to form a slurry. Washing the smelter gas with this slurry causes the SO$_2$ in the gases to combine with the magnesium and form magnesium sulfite.

The magnesium sulfite is collected, dried, and heated to temperatures of from 670$^\circ$C to 1000$^\circ$C (1250$^\circ$F to 1800$^\circ$F). The heat causes the magnesium sulfite molecules to break apart, regenerating magnesium oxide that can be reused and a highly concentrated SO$_2$ gas that can be converted to sulfuric acid.

The magnesium oxide process was tested for its effectiveness in removing SO$_2$ from the exhaust gases of industrial boilers and electric generating plants (9,14). The magnesium oxide process was also demonstrated in a smelter in Japan. The process was shown to be at least 90% effective in removing SO$_2$ from exhaust systems. Adapting them to the US smelting industry would be a major step in reducing national sulfur oxide emissions (52).

9.6. FGD Process Design Configurations

This Subsection briefly describes important equipment items one is likely to encounter when inspecting a conventional lime/limestone FGD system. Descriptions and diagrams are provided for each of the equipment items discussed. Operation and maintenance considerations for the equipment described here are presented later.

The equipment is organized by three major equipment areas: (1) gas handling and treatment, (2) reagent preparation and feed, and (3) waste solids handling and disposal.
The gas handling and treatment facilities include the following:

1. Fans
2. Scrubbers/absorbers (see Figs. 6–10)
3. Mist eliminators (see Fig. 11)
4. Reheaters (see Figs. 6 and 10)
5. Ductwork and dampers
6. Stack

The reagent preparation and feed facilities include the following:

1. Reagent conveyors and storage (see Figs. 12 and 13)
2. Ball mills (see Fig. 14)
3. Slakers (see Fig. 15)
4. Tanks

The waste solids handling and disposal facilities include the following:

1. Thickeners
2. Vacuum filters
3. Centrifuges
4. Waste processing
5. Waste disposal
6. Pumps and valves

9.6.1. Gas Handling and Treatment Facilities

9.6.1.1. Fans

Fans move gas by creating a pressure differential by mechanical means. Fans are used to draw or push flue gas from the boiler furnace through the FGD system. Fans used in FGD systems are either centrifugal or axial. Most fans used in FGD systems are of the centrifugal variety. Both fan designs may be equipped with variable-pitch vanes (or blades), which provide more efficient fan operation and better gas flow control.

9.6.1.2. Scrubbers/Absorbers

Strictly speaking, the term “scrubber” (see Fig. 6) applies to first-generation systems that remove both particulate and SO₂. “Absorber” (see Figs. 7 and 10) applies to the second- and third-generation systems (see Table 6) that remove SO₂ only, although the term “scrubber” is also used by some for this application. The basic scrubber/absorber types are described in Chapter 5, Volume 1 (73). There are various gas/slurry contacting devices used in the FGD systems.
9.6.1.3. Mist Eliminators

A mist eliminator (see Fig. 11) removes entrained material introduced into the gas stream by the scrubbing slurry. These materials include liquid droplets, slurry solids, and/or condensed mist.

There are two basic types of mist eliminator used in FGD systems: the precollector and the primary collector. A precollector precedes the primary collector and is designed...
to remove the larger entrained particles from the gas stream before it passes through the primary collector. A primary collector typically sees the heaviest duty with respect to entrainment loading and required removal efficiency.

Precollectors are of the bulk separation or knockout type. Bulk separation is effected by baffle slats, perforated trays, or a gas direction change (90° to 180°). Bulk separation devices are characterized by a low potential for solids deposition, a low gas-side pressure drop, and simplicity. Knockout-type precollectors are either the wash tray or trap-out tray design. Knockout devices remove large solid and liquid particles, they also provide a means to recycle the mist eliminator wash water. By recirculating the relatively clean wash water, the flow rate of the wash water to the mist eliminator can be significantly

Fig. 13. Barge-based limestone handling and storage system.

Fig. 14. Two types of ball mill used in limestone slurry FGD systems: (a) compartmented ball mill (b) Hardinge ball mill.
increased, which allows greater flexibility in washing operations, wash water treatment, and the addition of scaling inhibitors. Despite all of these advantages, knockout-type precollectors are not used at most installations primarily because of plugging, high pressure drop (approx 3 in. H₂O), increased complexity, and operating problems.

Impingement (or inertial impaction) removes mist by collection on surfaces placed in the gas streams. Entrained mist is collected in such devices by forcing the gas to make
Table 6
Typical Characteristics of First-, Second-, and Third-Generation Lime/Limestone Slurry FGD Systems

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>First</th>
<th>Second</th>
<th>Third</th>
</tr>
</thead>
<tbody>
<tr>
<td>Duty</td>
<td>SO₂/fly ash</td>
<td>SO₂</td>
<td>SO₂</td>
</tr>
<tr>
<td>Absorber design</td>
<td>Venturi Tower</td>
<td>Tower with internals</td>
<td>Open spray tower</td>
</tr>
<tr>
<td>Chemistry</td>
<td>High stoichiometric</td>
<td>Moderate stoichiometric</td>
<td>Low stoichiometric</td>
</tr>
<tr>
<td>ratio</td>
<td>ratio</td>
<td>ratio</td>
<td>ratio</td>
</tr>
<tr>
<td>Water loop</td>
<td>Open</td>
<td>Closed</td>
<td>Closed with integrated</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>water inventory</td>
</tr>
<tr>
<td>Waste processing</td>
<td>Ponding (no</td>
<td>Primary dewatering</td>
<td>Primary and secondary</td>
</tr>
<tr>
<td></td>
<td>dewatering)</td>
<td>and waste treatment</td>
<td>dewatering and</td>
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<td></td>
<td></td>
<td>solid-waste physical/</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>chemical treatment</td>
</tr>
<tr>
<td>Redundancy</td>
<td>None&lt;sup&gt;b&lt;/sup&gt;</td>
<td>None&lt;sup&gt;b&lt;/sup&gt;</td>
<td>Sparing of a number of</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>system components</td>
</tr>
</tbody>
</table>

<sup>a</sup>Some spray towers are also included in late second-generation systems.

<sup>b</sup>Most of these systems incorporate minimal redundancy (e.g., pumps); however, spares are usually not provided for major components (e.g., absorbers).

9.6.1.4. REHEATERS

Reheaters (see Figs. 6 and 10) raise the temperature of the scrubbed gas stream in order to prevent condensation of acidic moisture and subsequent corrosion in the downstream equipment (ducts, fans, and stack). FGD systems that do not use reheaters must be equipped with specially lined stacks and exit ductwork to prevent corrosion. Such liners require special attention, and FGD systems using them must be equipped with emergency deluge sprays in the event of a temperature excursion.

The generic reheat strategies discussed in this Subsection include in-line, indirect hot air, and flue gas bypass (see Fig. 10). In-line reheate involves the use of a heat exchanger in the gas stream downstream of the mist eliminator (see Fig. 10a). The heat exchanger is a set of tube bundles through which the heating medium of steam or hot water is circulated. When steam is used, the inlet steam temperatures and pressures range from 350°F to 720°F and 115 to 200 psig, respectively. Saturated steam is preferred because the heat transfer coefficients of condensing steam are much higher than those of superheated steam. When hot water is used, inlet temperature of the hot water typically ranges from 250°F to 350°F and the temperature drop (water) over the heat exchanger is 70°F to 80°F.

Indirect hot-air reheate systems inject hot air into the gas stream (see Fig. 10b). There are two types of indirect hot-air reheate: the external heat exchanger and the boiler...
preheater design. In the external-heat-exchanger design, reheat is achieved by heating ambient air with an external heat exchanger using steam at temperatures of 350°F–450°F. The heating tubes are usually arranged in two to three banks in the heat exchanger. Hot air and flue gas may be mixed by use of a device such as a set of nozzles or a manifold in the reheater mix chamber section. In the boiler preheater design, reheat is achieved through the use of the boiler combustion air preheater to provide hot air. In this case, part of the heat that would have been used to heat the combustion air is used to reheat the stack gas. As a consequence, the temperature of the combustion air entering the boiler is lowered, thus somewhat reducing boiler efficiency.

In the bypass reheat system (see Fig. 10c) a portion of the hot flue gas from the boiler bypasses the absorber(s) and is mixed with scrubbed flue gas. Two variations of this method are "hot-side" bypass, in which the flue gas is taken upstream of the boiler air preheater, and "cold-side" bypass, in which flue gas in taken downstream of the boiler air preheater. In the former, a separate particulate-removal device (ESP or fabric filter) specifically for the bypass gas stream is required for fly ash control when an upstream (i.e., hot-side) particulate collector is not used.

9.6.1.5. DUCTWORK, DAMPERS, AND STACKS

Ductwork is used to channel the flow of gas within the FGD system. Ductwork in an FGD system in usually made of carbon steel plates \( \frac{3}{16} \) or \( \frac{1}{4} \) in thick, welded in a circular or rectangular cross section. It is supported by angle frames that are stiffened at uniform intervals. The following design factors are considered for ductwork in lime/limestone slurry systems:

1. Pressure and temperature
2. Velocity
3. Configuration (cylindrical or rectangular)
4. Flow distribution
5. Variations in operating conditions
6. Materials of construction
7. Material thicknesses
8. Pressure drop

The ductwork must be designed to withstand the pressures and temperatures that occur during normal operation and also those that occur during emergency conditions. Ductwork is subject to a variety of conditions, depending on location within the system. The following list identifies the basic variants:

1. Inlet ductwork
2. Bypass ductwork (all or part of the flue gas)
3. Outlet ductwork (with reheat and without bypass)
4. Outlet ductwork (with reheat and with bypass for start-up)
5. Outlet ductwork (without reheat and without bypass)
6. Outlet ductwork (without reheat and with bypass for startup)

Dampers are used to regulate the flow of gas through the system by control or isolation functions. The entire system or subsystems may be regulated by the use of dampers. They are mainly used at the inlet duct to the module, the outlet duct from the module, and the bypass duct. Dampers may be used individually or in combination. A variety of
damper designs are in use in lime/limestone slurry systems, including louver, guillotine, butterfly, and blanking plates.

Readers are referred to another chapter of this handbook for the stack design.

9.6.2. Reagent Preparation and Feed Facilities

9.6.2.1. Reagent Conveyors and Storage

Conveying equipment (see Fig. 12) used to transport limestone from unloading to storage includes dozing equipment, belt conveyors, and bucket elevators. Limestone is transported to feed bins by conveyors and bucket elevators. Limestone can be stored in silos, piles, or a combination of both. Short-term storage feed bins are used with both systems to feed limestone to the additive preparation system. Storage piles require more land to store a given quantity of limestone than silos. However, silos are more expensive and can experience flow problems such as plugging and jamming. Covered piles are sometimes used for limestone storage. The covers keep precipitation off the limestone pile and prevent freezing or limestone mud from developing. The primary design criterion of a limestone storage system is capacity. The storage facilities must have sufficient capacity so that the storage system does not limit the availability of the overall FGD system. There should be enough storage capacity to account for disruptions in the normal shipping schedule. Figure 13 shows an example of a limestone handling and storage system.

Conveying equipment used to transport lime can be of three basic types, as shown in Fig. 12. Most in-plant lime conveying involves simple elevation of the lime from a storage bin into a smaller feed bin. A simple combination of mechanical devices can move lime from storage at less than the initial cost and with less power consumption than a pneumatic conveyor. Mechanical conveying requires careful arrangement of bins and equipment. Alignment in a single straight row is preferable because each change of direction usually requires another conveyor.

9.6.2.2. Ball Mills

A ball mill consists of a rotating drum loaded with steel balls that crush the limestone by the action of the tumbling balls as the cylindrical chamber rotates. Ball mills used in FGD systems fall into two categories. The long drum or tube mill variety is a compartmented type (see Fig. 14a) and the Hardings ball mill is noncompartmented and somewhat conical in shape (see Fig. 14b).

9.6.2.3. Slakers

A slaker is used in lime systems to convert dry calcium oxide to calcium hydroxide. The objective of lime slaking is to produce a smooth, creamy mixture of water and very small particles of alkali. Depending on the type of slaker used, the slurry produced contains 20–50% solids. A lime slaker combines regulated streams of lime, water under agitation, and temperature conditions needed to disperse soft hydrated particles. Dispersion must be rapid enough to prevent localized overheating and rapid crystal growth of the calcium hydroxide from occurring in the exothermic reaction. However, the mixture must be held in the slaker long enough to permit complete reaction.

Three basic types of slaker are presently used in lime slurry systems: detention, paste, and batch. A simplified diagram of each type is presented in Fig. 15.
9.6.3. Waste Solids Handling and Disposal Facilities

9.6.3.1. Thickeners

The function of a thickener (see Fig. 7) is to concentrate solids in the slurry bleed stream in order to improve waste solids handling and disposal characteristics and recover clarified water. The slurry bleed stream usually enters a thickener at a solids level of about 5–15% and exits at a concentration of 25–40% solids. A thickener is a sedimentation device that concentrates the slurry by gravity. There are two basic types of thickener: gravity and plate. Only the gravity type will be described here, because plate thickeners are rarely used on utility FGD systems. A typical gravity thickener consists of a large circular holding tank with a central vertical shaft for settling and thickening of waste solids.

9.6.3.2. Vacuum Filters

Vacuum filters are widely used as secondary dewatering devices because they can be operated successfully at relatively high turndown ratios over a broad range of solids concentrations. A vacuum filter also provides more operating flexibility than other types of dewatering device as well as producing a drier product. Because a vacuum filter will not yield an acceptable filter cake if the feed solids content is too low, it is usually preceded by a thickener. A vacuum filter produces a filter cake of 45–75% solids from feed slurries containing 25–40% solids. The filtrate, typically containing 0.5–1.5% solids, is recycled to the thickener.

Two types of vacuum filter are used in conventional FGD system designs: drum and horizontal belt. Each has different characteristics and applicability. The drum type is the most widely applied.

9.6.3.3. Centrifuges

Centrifuges are used to a lesser extent than vacuum filters in solids dewatering operations. The centrifuge product is consistent and uniform and can be handled easily. Centrifuges effectively create high centrifugal forces, about 4000 times that of gravity. The equipment in relatively small and can separate bulk solids rapidly with a short residence time.

There are two types of centrifuge: those that settle and those that filter. The settling centrifuge, which is the only kind used in commercial lime/limestone slurry FGD systems, uses centrifugal force to increase the settling rate over that obtainable by gravity settling.

9.6.3.4. Waste Processing and Disposal Facilities

Readers are referred to other volumes of this handbook series and elsewhere (10) for the details of various waste processing and disposal facilities. Only the following three, the most common waste processing processes, and three disposal processes are introduced and discussed in this Subsection: (a) forced oxidation, (b) fixation, (c) stabilization, (d) ponding, (e) landfilling, and (f) stacking.

Forced oxidation supplements the natural oxidation of sulfite to sulfate by forcing air through the material. The advantages of a calcium sulfate (gypsum)—bearing material include better settling and filtering properties, less disposal space required, improved structural properties of the disposed waste, potential for utilization of the gypsum (e.g., wallboard production), and minimal chemical oxygen demand of the disposed material.
Forced oxidation, unlike fixation and stabilization, is not typically a tail-end operation; in many systems, this operation often occurs in the reaction tank.

Fixation increases the stability of the waste through chemical means. This may be accomplished by the addition of alkali, alkaline fly ash, or proprietary additives along with inert solids to produce a chemically stable solid. Examples of commercial processes of this type are those marketed by Conversion Systems, Inc. (e.g., Poz-O-Tec) and Dravo Corporation (e.g., Calcilox).

Stabilization is accomplished by the addition of nonalkaline fly ash, soil, or other dry additive. The purpose of stabilization is to enable the placement of the maximum quantity of material in a given disposal area, to improve shear strength, and to reduce permeability. Disadvantages are that the stabilized material is subject to erosion and rapid saturation and has residual leachability potential.

Waste disposal refers to operations at the disposal site for FGD waste following all handling and/or treatment stages. There are three basic FGD disposal site types: (1) ponding, (2) landfiling, and (3) stacking (10).

The most common waste disposal type is ponding. Ponds are either lined or unlined; lined ponds used for conventional FGD processes are typically clay lined. Landfilling is another waste disposal method. Wastes that have been fixated or stabilized are usually (although not always) landfilled. Stacking is only used for FGD systems designed to produce gypsum.

9.7. FGD Process O&M Practices

This section introduces the various types of operation and maintenance (O&M) practices for lime/limestone slurry FGD processes, the conditions under which the practices are implemented, and specific activities involved in each. More thorough treatment of the subject can be found elsewhere (56–59). This Subsection introduces the O&M requirements for these standard operating practices.

Increasingly stringent SO\textsubscript{2} limits require a strong commitment from the owner/operator utility to FGD operation, including adequate staffing. Operators should be assigned specifically and solely to the FGD system during each shift. FGD system operation must be coordinated with the unit’s power generation schedule and even into the purchasing of coal (i.e., sulfur, ash, and chlorine characteristics). Some of the current difficulties with lime/limestone FGD systems relate to poor operating practices, including overly complex procedures. In some cases, even properly installed equipment rapidly deteriorates and fails because of improper O&M practices. The operating characteristics of the FGD system can be established during the initial start-up period, which is also a time for finalizing operating procedures and staff training. Once steady-state operating conditions are reached, the system must be closely monitored and controlled to ensure proper performance.

During periods of changing load or variation of any system parameter, additional monitoring is required. Some standard O&M procedures (55,60) are described in the following Subsections.

9.7.1. Varying Inlet SO\textsubscript{2} and Boiler Load

As boiler load increases or decreases, modules are respectively placed in or removed from service. With each change in load, the operator must check the system to verify
that all in-service modules are operating in a balanced condition. As the SO$_2$ concentration in the inlet flue gas changes, the FGD system performance changes. To maintain proper system response, slurry recirculation pumps can be added and removed from service as the SO$_2$ concentration increases or decreases.

9.7.2. Verification of Flow Rates

The easiest method of verifying liquid flow rates is for an operator to determine the discharge pressure in the slurry recirculation spray header with a hand-held pressure gage (permanently mounted pressure gages frequently plug in slurry service). Flow in slurry piping can be checked by touching the pipe. If the piping is cold to the touch at the normal operating temperature of 125–130°F, the line may be plugged.

9.7.3. Routine Surveillance of Operation

Visual inspection of the absorbers and reaction tanks can identify scaling, corrosion, or erosion before they seriously impact the operation of the system. Visual observation can identify leaks, accumulation of liquid or scale around process piping, or discoloration on the ductwork surface resulting from inadequate or deteriorated lining material.

9.7.4. Mist Eliminators

Many techniques have been used to improve mist collection and minimize operational problems. The mist eliminator (see Fig. 11) can be washed with process makeup water or a mixture of makeup and thickener overflow water. Successful, long-term operation without mist eliminator plugging generally requires continuous operator surveillance, both to check the differential pressure across the mist eliminator section and to visually inspect the appearance of blade surface during shutdown periods.

9.7.5. Reheaters

In-line reheaters (see Figs. 6 and 10) are frequently subject to corrosion by chlorides and sulfates. Plugging and deposition can also occur, but are rarer. Usually, proper use of soot blowers prevents these problems. The reliability of various reheater configurations is discussed in Section 9.3.5.5.

9.7.6. Reagent Preparation

Operational procedures associated with handling and storage of reagent are similar to those of coal handling. Operation of pumps, valves, and piping in the slurry preparation equipment is similar to that in other slurry service.

9.7.7. Pumps, Pipes, and Valves

Operating experience has shown that pumps, pipes, and valves can be significant sources of trouble in the abrasive and corrosive environments of a lime/limestone FGD system. The flow streams of greatest concern are the reagent feed slurry, the slurry recirculation loop, and the slurry bleed streams. When equipment is temporarily removed from slurry service, it must be thoroughly flushed.

9.7.8. Thickeners

Considerable operator surveillance is required to minimize the suspended solids in the thickener (see Fig. 7) overflow so that this liquid can be recycled to the system as supplementary pump seal water, mist eliminator wash water, or slurry preparation
water. For optimum performance, the operator must maintain surveillance of such parameters as underflow slurry density, flocculent feed rate, inlet slurry characteristics, and turbidity of the overflow.

9.7.9. Waste Disposal

For untreated waste slurry disposal (see Fig. 7), operation of both the discharge to the pond and the return water equipment requires attention of the operating staff. In addition to normal operations, the pond site must be monitored periodically for proper water level, embankment damage, and security for protection of the public. Landfill disposal involves the operation of secondary dewatering equipment. Again, when any of the process equipment is temporarily removed from service, it must be flushed and cleaned to prevent deposition of waste solids. For waste treatment (stabilization or fixation), personnel are required to operate the equipment and to maintain proper process chemistry.

9.7.10. Process Instrumentation and Controls

Operation of the FGD system requires more of the operating staff than monitoring automated control loops and attention to indicator readouts on a control panel. Manual control and operator response to manual data indication may be more reliable than automatic control systems and are often needed to prevent failure of the control system. Many problems can be prevented when an operator can effectively integrate manual with automated control techniques.

10. EMERGING “WET” SULFUR OXIDE REDUCTION TECHNOLOGIES

Current efforts are directed toward further converting calcium sulfate by forced oxidation, using the limestone more efficiently, removing more SO₂ from the exhaust gas, improving equipment reliability, and altering the composition of the calcium sulfate to allow use in wallboard.

Although the meaning of “generation” is somewhat subjective, FGD systems may be distinguished in accordance with the evolution of technology per the following guidelines:

1. First generation: Designs that remove SO₂, and possibly fly ash, with gas contactors developed for or based on particulate matter scrubbing concepts. Included are lime/limestone slurry processes that use gas contactors with Venturi or packing-type internals.
2. Second generation: Designs that remove SO₂ primarily in gas contractors, developed specifically for SO₂ absorption, which utilize features to improve the chemical or physical means. Included are lime/limestone slurry processes using additives or spray towers, combination towers, or special reactors.
3. Third generation: Improved second-generation designs that encompass additional process refinements and are currently under demonstration or early commercial operation. Included are spray tower designs with spare absorbers, closed water-loop operations, and gypsum production.

Table 6 summarizes the basic characteristics of the system within the three generations.

As FGD technology evolved, more effective measures were adopted and modifications were made to earlier systems to upgrade performance.

The following Subsections summarize demonstration tests of three emerging wet FGD technologies. These have in common innovative reactor schemes for contacting flue gas with calcium-based sorbents in a slurry or solution.
10.1. Advanced Flue Gas Desulfurization Process

The Advanced Flue Gas Desulfurization (AFGD) Demonstration Project was performed by Pure Air on the Lake, L.P. (a subsidiary of Pure Air) at the North Indiana Public Service Company’s Bailey Generating Station. Operational tests ran from 1992 to 1995. The process uses one absorber vessel to perform three functions: prequenching the flue gas, absorbing $\text{SO}_2$, and oxidation of the resulting calcium sulfite to wallboard-grade gypsum. The flue gas contacts two tiers of fountainlike sprays and passes through a gas–liquid disengagement zone, over the slurry reservoir, and through a mist eliminator. Variables studied included the sulfur content of the coal, slurry recirculation rate, Ca/S ratio, and the liquid/gas ratio in the absorber.

The process achieved $\text{SO}_2$ removal efficiencies of 95% and higher at Ca/S ratios of 1.07–1.10 with coal sulfur contents of 2.25–4.5%. The system had 99.5% availability and produced wallboard-grade gypsum with an average purity of 97.2%. The system effectively captured acid gases and trace elements associated with particulates. Some boron, selenium, and mercury passed to the stack gas as vapor.

Efficient operation and high reliability eliminated the need for a spare absorber. These advantages, with compactness, reduced space requirements. Concurrent flow allowed high flue gas velocities (up to 20 ft/s). A nonpressurized slurry distribution system reduced recirculation pump power requirements by 30%. The fountainlike flow of absorber reduces mist loading by as much as 95%. Use of dry pulverized limestone eliminates the need for sorbent preparation equipment. An air rotary sparger combines agitation with oxidation to enhance performance. A novel wastewater evaporation system controls chlorides without creating a new waste stream. A compression mill system (PowerChip™) modifies the physical structure of the gypsum.

Cost estimates were made for a 500-MWe power plant firing a 3% sulfur coal and achieving 90% $\text{SO}_2$ removal. The capital costs were estimated at US$94/kW, with a 15-yr levelized cost of US$6.5mil/kWh, equivalent to US$302/ton of $\text{SO}_2$ removed. This costs is about half that for conventional wet FGD.

High efficiency, compactness, elimination or use of byproduct streams, and costs of about one-half those of a conventional wet FGD process make the system highly applicable. As of 1999, there were no sales yet, but the system remains in operation with commercial gypsum sales (14).

10.2. CT-121 FGD Process

The CT-121 FGD system was demonstrated by Southern Companies Services, Inc. at the Georgia Power Company’s Plant Yates, No.1 in Coweta County, Georgia from 1992 to 1994. The system uses a unique absorber called the Jet Bubbling reactor (JBR). In one vessel (see Fig. 16), the JBR combines limestone AFGD, forced oxidation, and gypsum crystallization. Flue gas is quenched with water injection and is bubbled into the scrubbing solution. $\text{SO}_2$ is absorbed and forms calcium sulfite. Air bubbled into the bottom of the reactor oxidizes the calcium sulfite to gypsum. The gypsum is removed from the slurry in a settling pond.

$\text{SO}_2$ removal efficiency was over 90% at $\text{SO}_2$ inlet concentrations of 1000–3500 ppm. Limestone utilization was over 97%. Particulate removal efficiencies of 97.7–99.3% were achieved. Hazardous air pollutant capture was greater than 95% for
hydrogen chloride; 80–98% for most trace metals, but less than 50% for mercury and less than 70% for selenium. The gypsum was suitable for making wallboard, although requiring washing to remove chloride.

Availability was 95–97%, eliminating the need for a spare absorber. Simultaneous SO$_2$ and particulate removal were achieved at ash loadings for which an electrostatic precipitator has marginal performance. The fiberglass-reinforced plastic equipment proved durable and eliminated the need for a flue gas prescrubber and reheater.

The technology is applicable to new construction and retrofitting. Capital costs were estimated at US$80–95/kW, with operating costs at US$34–64/ton (1994 US$) of SO$_2$ depending on specific conditions. Elimination of the need for a flue gas prescrubber, gas preheater, and a spare absorber should significantly reduce capital costs compared to conventional FGD. This technology is sold internationally (14).

10.3. Milliken Clean Coal Technology Demonstration Project

The Milliken Clean Coal Technology Demonstration Project was carried out by the New York State Electric & Gas Corporation (NYSEG) and other team members, at the NYSEG Milliken Station in Tomkins County, New York from 1995 to 1999. The demonstration used the Saarberg–Holter–Umwelttechnik (S-H-U) FGD process. This uses a space-saving concurrent/countercurrent absorber vessel. The vessel is Stebbins tile lined and constructed of reinforced concrete. The process is specifically designed to benefit from the use of formic acid to buffer the slurry to low pH, improving the rate of limestone dissolution and calcium solubility. This enhances SO$_2$ absorption efficiency and reduces limestone consumption. Energy efficiency and byproduct quality are improved. Formic acid use improved SO$_2$ removal efficiency to 98%, versus 95% without it.
Grinding the limestone finer, from 90% −325 mesh to 90% −170 mesh, improved SO₂ removal by 2.6%. The capital costs of the FGD system were estimated at US$300/kW (1998 US$), with operating costs at US$412/ton of SO₂ removed (1998 US$) (14).

11. EMERGING “DRY” SULFUR OXIDES REDUCTION TECHNOLOGIES AND OTHERS

11.1. Dry Scrubbing Using Lime or Sodium Carbonate

Chapter 5, volume 1, Wet and Dry Scrubbing, introduces the dry scrubbing process in detail. Dry scrubbing is a modification of wet scrubbing flue gas desulfurization technology. As in other FGD systems, the exhaust gases combine with a fine slurry mist of lime or sodium carbonate. This system, however, takes advantage of the heat in the exhaust gases to dry the reacted slurry into particles of calcium sulfite or sodium sulfite, depending on lime or sodium carbonate being the scrubbing slurry. The following is a chemical reaction if lime is used:

\[
\text{SO}_2 + \text{CaO} \rightarrow \text{CaSO}_3
\]  (32)

where CaO is lime and CaSO₃ is calcium sulfite.

If a fine slurry mist of sodium carbonate is used for SO₂ removal, the following will be the chemical reaction:

\[
\text{SO}_2 + \text{Na}_2\text{CO}_3 \rightarrow \text{Na}_2\text{SO}_3 + \text{CO}_2
\]  (33)

where Na₂CO₃ is sodium carbonate, Na₂SO₃ is sodium sulfite, and CO₂ is carbon dioxide.

Dry scrubbing normally removes 70% of the dioxide in an air emission stream.

11.2. LIMB and Coolside Technologies

LIMB stands for the “Lime/Limestone Injection Multistage Burners” process. The LIMB and Coolside demonstrations were performed at Ohio Edison’s Edgewater Station, Unit No. 4 during 1989 to 1992. The LIMB process (see Fig. 17) involves injection of a calcium-based sorbent into the boiler, above the burners, near a temperature of 2300°F. The sorbent calcines to calcium oxide, reacts with SO₂ and oxygen, and is removed with the fly ash in an electrostatic precipitator (ESP). The process produces particulates that are difficult to remove, but this is overcome by humidifying the stream prior to the ESP. SO₂ removal efficiencies at a Ca/S ratio of 2.0, minimal humidification, and the four sorbents tested ranged from 22% to 63%. Grinding the limestone sorbent to finer particle size ranges (100% < 44 and 10 µm) improved SO₂ removal efficiencies another 10–17%, respectively. SO₂ removal efficiencies were improved by about another 10% with humidification to a 20°F approach-to-saturation. Incorporating low-NOₓ burners reduced NOₓ emissions 40–50%. Availability was 95%, and humidifier operation in the vertical mode (versus. horizontal) was indicated to reduce floor deposits. Capital costs were US$31–102/kW (1992 US$) for plants ranging from 100 to 500 MWe, coals with 1.5–3.5% sulfur, and a 60% SO₂ reduction target. Commercialization includes sale of the LIMB technology to an independent power plant in Canada and multiple sales of the low-NOₓ burners.

In the Coolside technology, the sorbent (hydrated lime) is injected into the flue gas downstream of the air preheater. Injection is followed by humidification with a mist
containing sodium hydroxide or sodium carbonate. The sorbent reacts with SO$_2$ in the presence of the sodium compounds to desulfurize the stream. The mist cools the flue gas from about 300°F to 140–145°F, with an approach to saturation of 20–25°F, to maximize sulfur capture. The sorbent and sodium compounds retain high reactivity and are recycled with fresh hydrated lime.

Coolside technology achieved an SO$_2$ removal efficiency of 70% at a Ca/S ratio of 2.0, a Na/Ca ratio of 0.2, and a 20°F approach-to-saturation temperature, using commercial hydrated lime and a 2.8–3.0% sulfur coal. Recycling sorbent, reduced sorbent and additive usage by up to 30% and improved SO$_2$ removal efficiency by 20%.

The LIMB and Coolside technologies are applicable to most utility and industrial coal-fired units. They provide alternatives to conventional wet flue gas desulfurization, and retrofits require modest capital investment and downtime. Space requirements are also substantially less than for conventional processes (14).

11.3. Integration of Processes for Combined SO$_x$ and NO$_x$ Reduction

The reduction of SO$_x$ emissions can be integrated with measures to reduce NO$_x$ emissions. The latter can be achieved through burner design (61), natural gas injection, and reburning (62). NO$_x$ reduction using natural gas enhances SO$_2$ reduction because natural gas displaces coal and its sulfur content. Gas reburning and sorbent injection (GR-SI) were demonstrated at Illinois Power’s Hennepin No. 1 power plant, beginning in 1990. Tests indicated successful integration of the technologies. SO$_2$ emissions were reduced by 18% through displacement of coal with sulfur-free natural gas. NO$_x$ emissions
control technologies are compatible with a wide variety of SO$_2$ emissions control methods: furnace sorbent injection, dust sorbent injection, wet scrubbers, dry scrubbers, and coal switching (62). SO$_2$ emissions credits can also help defray NO$_x$ emission control costs, and in some scenarios, they could cancel that cost.

11.4. Gas Suspension Absorbent Process

The gas suspension adsorption (GSA) 10-MWe demonstration was performed at the Tennessee Valley Authority’s Shawnee Fossil Power Plant near Paducah, Kentucky from 1992 to 1995. The GSA system (see Fig. 18) can be described as a semidry FGD technology. Flue gas passes upward through a vertical reactor. Solids coated with hydrated lime are injected into the bottom of the reactor. A major feature is that about 99% of solids are recycled to the reactor by a cyclone. The heat and mass transfer characteristics are superior to those in conventional semidry technology using a lime slurry directly sprayed into a duct or spray dryer.

Two sets of tests were performed using an electrostatic precipitator (ESP) and a pulse jet baghouse (PJBH). With ESP, an SO$_2$ removal efficiency of 90% was achieved at a Ca/S ratio of 1.3–1.4 and an approach-to-saturation temperature of 8–18°F. With a PJBH, an SO$_2$ removal efficiency of 96% was achieved at a Ca/S ratio of 1.4 and an approach-to-saturation temperature of 18°F. Both methods removed 99.9%+ of particles, 98% of hydrogen chloride, 96% of hydrogen fluoride, and 99% or more of trace metals except cadmium, antimony, mercury, and selenium. GSA/PJBH removed 99+% of the selenium.

The Ca/S ratio, approach-to-saturation temperature, and chloride content significantly affected SO$_2$ removal efficiency. As the Ca/S ratio increased from 1.0 to 1.3, SO$_2$
removal increased from 76% to 93%. As the approach-to-saturation temperature
decreased from 30°F to 12°F, SO2 removal increased from 81% to 95% (at Ca/S of 1.3).
As the chloride content (percentage of lime feed) increased from 0.5% to 2.0%, the SO2
removal increased from 85% to 99%.

Lime utilization was better than for spray drying systems: with ESP, 66.1%; with PJBH,
70.5%. Because of improved heat and mass transfer, the same performance was achieved
in one-fourth to one-third the size of a spray dryer, facilitating retrofitting in space-limited
plants and reducing installation costs. The GSA system achieved lower particulate loading,
2–5 gr/ft³ versus 6–10 gr/ft³ for a spray dryer, allowing compliance with a lower ESP effi-
ciency. The direct recycling of solids eliminates the need for multiple or complex nozzles
as well as the need for abrasion-resistant materials. Thus, special steels are not required for
construction and only a single spray nozzle is needed. The system demonstrated high avail-
ability and reliability similar to that for other commercial applications.

Cost estimates using EPRI’s TAG™ method were prepared for a moderately difficult
GSA retrofit of a 300-MWe boiler burning 2.6% sulfur coal. A SO2 removal of 90% at
a Ca/S was specified. Capital and levelized costs were compared for those of a wet lime-
stone scrubber with forced oxidation, and a spray dryer (see Table 7) (14).

11.5. Specialized Processes for Smelter Emissions:
Advanced Calcium Silicate Injection Technology

The Advanced Calcium Silicate Injection (ADVACATE) technology (see Fig. 19) is
perhaps the most competitive with conventional technology, offering comparable
(90+%) SO2 control and annualized costs in comparison with the competing lime/lime-
stone forced oxidation FGD technology. ADVACATE was evaluated on a 10-MWe pro-
totype in the early 1990s, and demonstrations on a commercial scale were planned in
the United States and overseas. The ADVACATE process was codeveloped by APPCD
with the University of Texas and is currently licensed for worldwide use (63,64).

12. PRACTICAL EXAMPLES

Example 1

In FGD lime/limestone process operation for SOx removal, the inlet SO2 concentration
is largely dependent on the sulfur content of the coal fired in the boiler. To estimate SO2
emissions (in units of lb SO2/106 Btu), a field inspector usually uses the following
equation:

Table 7
Cost Estimate for Gas Suspension Adsorption of SO2

<table>
<thead>
<tr>
<th></th>
<th>Capital cost (1990 $/kW)</th>
<th>Levelized cost (mils/kWh)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GSA: three units at 50% capacity</td>
<td>149</td>
<td>10.35</td>
</tr>
<tr>
<td>WLFO</td>
<td>216</td>
<td>13.04</td>
</tr>
<tr>
<td>Spray dryer</td>
<td>172</td>
<td>—</td>
</tr>
</tbody>
</table>

Note: Assumes 90% SO2 removal at a Ca/S ratio of 1.3 and uses EPRI TAG™ method.
where $Q_{SO_2}$ is the SO$_2$ emission rate (lb SO$_2$/10$^6$ Btu), $S_{SW}$ is the percentage sulfur in coal by weight, $C_f$ is the fractional conversion of sulfur in coal to SO$_2$, and GCV is the gross caloric value (heating value of coal), (Btu/lb).

Answer the following:

1. What should an engineer do if the $C_f$ value is unknown?
2. What are the GCV numbers for various coals?

**Solution**

1. If the fractional conversion $C_f$ value is unknown, use the US EPA AP-42 emission factors that assign SO$_2$ conversion factors as follows (65):
   - $C_f = 0.97$ for bituminous coal
   - $C_f = 0.88$ for subbituminous coal
   - $C_f = 0.75$ for lignite coal

2. The following heating values, or GCV, for various coals may be assumed if the actual GCV is unknown:
   - GCV = 10,680 Btu/lb for bituminous coal
   - GCV = 11,500 Btu/lb for subbituminous coal
   - GCV = 12,000 Btu/lb for lignite coal

**Example 2**

What is the SO$_2$ emission rate (lb SO$_2$/10$^6$ Btu) if $S_{SW}$ is known to be 3.5% $S$ and $C_f$ is known to be 0.92 for a high-quality subbituminous coal?
Solution

\[ Q_{SO_2} = \left(3.5\right) \times \left(2 \times 10^4\right) \times 0.92 \div \left(11,500 \text{ Btu/lb}\right) \]
\[ = 3.5 \times 2 \times 10^4 \times 0.92 \div 11,500 \]
\[ = 5.6 \text{ lb SO}_2 \div 10^6 \text{ Btu} \]

Example 3

Derive an engineering equation for converting normal air pollutant concentrations (lb/ft\(^3\)) to the US government required units (lb/10\(^6\) Btu) for coal-fired electrical generation plants.

Solution

\[ F_W = \frac{10^6 \left[ 5.56(\%H) + 1.53(\%C) + 0.57(\%S) + 0.14(\%N) - 0.46(\%O_2) + 0.21(\%H_2O) \right]}{\text{GCV}} \]  
\[ E = C_{WS} F_W \frac{20.9}{20.9 \left(1 - B_{WA}\right) - \%O_{2W}} \]  

where \( F_W \) is the coal analysis factor on a wet basis (std. ft\(^3\)/10\(^6\)Btu), GCV (gross caloric value) is the high heating value of coal (Btu/lb), \( E \) is the pollutant emission rate (lb/10\(^6\) Btu), \( C_{WS} \) is the pollutant concentration given as a wet basis as a std. ft\(^3\)/10\(^6\) Btu, \( B_{WA} \) is the ambient air moisture fraction, and \( O_{2W} \) is the percent oxygen in flue gas on a wet basis. The standard GCV for coal is given in Example 1.

Example 4

Energy consumption of a FGD system using lime or limestone is presented in this example. FGD energy consumption is attributed to reheat, flue gas flow, slurry preparation, and slurry recirculation. Other energy-consuming operations include slurry transfer (pumping), tank agitation, solids dewatering (thickeners, vacuum filters, centrifuges), steam tracing, electrical instrumentation, and air supply. An increase in energy consumption in any of these areas usually indicates a problem. Please answer the following:

1. Why is reheating one of the three major energy-consuming items in an FGD lime/limestone process system? What is a quick approximation method to determine the reheat energy consumption?
2. Why is forcing flue gas through the FGD one of the three major energy-consuming items in an FGD lime/limestone process system? What are the quick approximation methods to determine the forced draft energy consumption?
3. How important is the slurry preparation and recirculation system? How can the slurry recirculation pumping requirements be determined?

Solution

1. Reheating the saturated flue gas consumes more energy than any other part of the FGD system (assuming reheat is used). Reheat provides buoyancy to the flue gas, reducing nearby ground-level concentrations of pollutants. Reheat also prevents condensation of acidic, saturated gas from the absorber in the induced draft fan, outlet ductwork, or stack. Further 2 more, reheat minimizes the settling of mist droplets (as localized fallout) and the formation of a heavy steam plume with resultant high opacity. An increase in reheater energy consumption is generally indicative of plugged or scaled in-line reheat tube bundles. Energy consumption is increased because the
heat transfer efficiency of the reheater tubes is lowered. The following equation provides a quick approximation method to determine reheat energy consumption:

\[ H_e = 0.01757 Q_{\text{air}} C_p \Delta T \]  \hspace{1cm} (37)

where: \( H_e \) is heat energy (Btu), \( Q_{\text{air}} \) is the air flow rate at the inlet of reheat sections (lb/min), \( C_p \) is the specific heat [Btu/(lb)(\(^\circ\)F)], and \( \Delta T \) is the degree of reheat (\(^\circ\)F).

2. Forcing flue gas through the FGD system consumes energy. Forced or induced draft fans use energy to overcome the gas-side pressure drop of the FGD system. An increase in fan energy consumption usually indicates either a mechanical problem with the fan and/or an increase in the pressure drop somewhere in the FGD system. The following equation provides a quick approximation method to determine FGD fan power requirements.

\[ \text{Fig. 20. Fan power requirements.} \]
power requirements. Figure 20 provides a quick determination method if only plant size and gas-side pressure drop are known.

\[ P = 0.0002617(\Delta P)Q_s \]  

(assuming 80% fan efficiency), where \( P \) is power required [kw (for fan)], \( \Delta P \) is the pressure drop through the FGD system (in. H\(_2\)O), and, \( Q_s \) is the gas flow rate at the outlet of scrubber/absorber (scfm).

3. Grinding limestone and slaking lime consume relatively small amounts of energy, as compared to other energy-consuming equipment. Any increases are usually the result of poor quality makeup water or mechanical problems with the slaker or ball mill.

Fig. 21. Recirculation pump power requirements.
Energy is mainly consumed to recirculate the slurry to the absorber, to transfer water and slurry streams to various parts of the FGD system, and to treat and dispose of the solid-waste material. An increase in pumping energy consumption usually indicates either a mechanical problem or an increase in slurry side pressure drop in the system. The following equation provides a quick approximation method to determine recirculation pumping requirements. Figure 21 provides a quick determination for slurry recirculation pumping requirements if the plant size and $L/G$ are known.

\[
P = 0.000269 \times H_5 \times \left(\frac{L}{G}\right) \times \frac{Q_s}{1000}
\]

(assuming 90% pump efficiency), where $P$ is the power required (KW) (for slurry recirculation pumps), $Q_s$ is the gas flow rate at the outlet of scrubber/absorber (scfm), $H_5$ is the head (ft), and $L/G$ is the ratio of slurry flow to flue gas rate (gal/1000 scf, or gal/1000 scfm) at the outlet of the scrubber/absorber.

**Example 5**

A graphical representation of specific gravity as a function of the solids content of the slurry in lime/limestone FGD systems is presented in Fig. 22. What is the specific gravity of the recirculating slurry for the lime/limestone FGD system if the slurry’s percentage solid (by weight) is 20%? Discuss its feasibility for the FGD system.

**Solution**

From Fig. 22, the slurry specific gravity should be equal to 1.14 if the slurry’s solid content weight is 20%. Operation at consistent solids content in the various slurry process streams can improve the reliability of the absorber and slurry-handling equipment and improve process control. Specific gravity is a commonly used measure for determining...
The design specific gravity of the recirculating slurry for lime/limestone FGD systems is usually between 1.05 and 1.14 (approx 7–20% solids).

**Example 6**

What are the three most common reagents for the lime/limestone FGD process? Show how to calculate approximate reagent requirements (ton reagent/day-MW)?

**Solution**

1. The three most common reagents for the lime/limestone FGD process are limestone (CaCO₃), lime (CaO), and magnesium lime (MgO). Dolomite (dolomitic lime or dolomitic limestone) is a crystallized mineral consisting of calcium magnesium carbonate, CaMg(CO₃)₂.

2. Reagent consumption is set by the stoichiometry of the process. As noted previously, it is necessary to feed more than the stoichiometric amount of reagent in order to attain the degree of SO₂ removal required (stoichiometric ratio). However, excessive reagent can lead to several operating problems, including wasted reagent, scale formation, and erosion of slurry-handling equipment. Figure 23 is a graphic representation of reagent consumption as a function of the SO₂ emission limitation and boiler size (i.e., equivalent FGD capacity in megawatts). This figure can be used by the field inspector to estimate reagent feed rates.

3. The megawatt is a unit used to describe gross or net power generation of a facility. One watt equals one joule per second (1 MW = 10⁶ W).

**Example 7**

The solid-waste (sludge) production rate is one of the most important operational parameters for a lime/limestone FGD process system.
1. Discuss the importance of solid-waste (sludge) production rate.

2. How does one convert between dry and wet sludge production?

**Solution**

1. Solid-waste (sludge) production will vary as a function of the inlet flue gas characteristics and FGD system design and operating characteristics. The constituents usually include solid-phase $\text{SO}_2$ reaction products, unreacted reagent, fly ash, and adherent liquor.
Increases in solid waste increase the burden on solids handling and disposal. This can mean higher energy consumption, possible deviation from closed water-loop operation because of excessive amounts of wastewater effluent, and reduced land area available for disposal. Variations in the quality of the slurry bleed stream to the thickener can either overload (high or “rich” solids content) or underutilize (low or “lean” solids content) the primary dewatering subsystem. The ratio of sulfite to sulfate contained in the spent slurry stream is also important because of the size differences between gypsum (1–100 µm in length) and calcium sulfite crystals (0.5–2.0 µm in length). These differences can have a significant impact on the dewatering of the solid-waste material. Generally, as the ratio of sulfite to sulfate increases, the liquor content of the dewatered solid waste also increases.

Example 8

Acid rain is caused by SO\textsubscript{4} and NO\textsubscript{x} emissions release. Discuss possible engineering solutions to lake restoration assuming that the damage is done.

Solution

Both SO\textsubscript{4} and NO\textsubscript{x} emissions pollute lakes, usually at high elevations. SO\textsubscript{4} and NO\textsubscript{x} mix with normal rains, producing acid rain, in turn acidifying the lake water. In serious situations, the pH of lake water is too low to be habitable to many species of aquatic animals or plants.

Lakes polluted by acid rains (caused by SO\textsubscript{4} and NO\textsubscript{x} dissolution) can usually be restored by a neutralization process. Although any kind of alkaline chemicals can be used as a neutralizing agent, usually inexpensive lime is used.

In the above case of lime treatment, calcium in lime will react with sulfate ions in lake water, forming calcium sulfate. Calcium sulfate will precipitate from the lake water only when it exceeds its solubility. Most of sulfate ions will still remain in lake water.

It has been known that the ion-exchange process is technically feasible for removing sulfate ions from lake water, but it is not economically feasible.

Example 9

Removal of hydrogen sulfide from the gas phase has been introduced extensively in this chapter. It has been shown that sometimes the condensate (i.e., liquid phase) may contain high concentrations of H\textsubscript{2}S at geothermal power plants (1). Introduce and discuss the engineering solutions to this case.

Solution

1. **First Solution: Gas Stripping.** The easiest process method for removing H\textsubscript{2}S from condensate (i.e., a liquid phase) is simply to direct the condensate to the cooling tower where the H\textsubscript{2}S will be stripped from the condensate and be exhausted with the effluent air from the cooling tower. In this situation, the cooling tower becomes a stripping tower for removing H\textsubscript{2}S from condensate. This is an inexpensive process method but will create an odor nuisance or even a hazardous situation when H\textsubscript{2}S reaches high concentration levels.

2. **Second Solution: EDTA Treatment and Filtration.** A safer process method of treating H\textsubscript{2}S is to direct the condensate to the cooling tower but add chelated iron upstream of the cooling tower. The chelator is usually ethylenediaminetetraacetic acid (EDTA), whose only purpose is to increase the solubility of iron in water. The iron reacts with the dissolved H\textsubscript{2}S as follows:
Desulfurization and Emissions Control

$$2\text{Fe}^{3+} + \text{H}_2\text{S} \rightarrow 2\text{Fe}^{2+} + \text{S}^0 + 2\text{H}^+ \quad (40)$$

where $\text{Fe}^{3+}$ is the chelated trivalent ferric ion, $\text{H}_2\text{S}$ is the target S-containing pollutant, $\text{Fe}^{2+}$ is the divalent ferrous ion, $\text{S}^0$ is the insoluble elemental sulfur, and $\text{H}^+$ is the hydrogen ion.

$\text{Fe}^{2+}$ is not very effective for reacting with $\text{H}_2\text{S}$, so it must be reoxidized to $\text{Fe}^{3+}$ to be reused. This is accomplished when the cooling water is circulated in the cooling tower and comes into contact with oxygen (air) as follows:

$$2\text{Fe}^{2+} + 0.5\text{O}_2 + 2\text{H}^+ \rightarrow 2\text{Fe}^{3+} + \text{H}_2\text{O} \quad (41)$$

where $\text{O}_2$ is oxygen. The insoluble element sulfur, $\text{S}^0$, can be filtered out from the system in order to accomplish the goal of desulfurization.

3. **Third Solution: Combined EDTA and Sodium Sulfite Treatment.** The element sulfur, which is formed in Eq. (43), must be removed by filtration. The insoluble solid sulfur, left as is, will eventually plug the cooling tower. Instead of filtration removal of sulfur, sodium sulfite may be added to the cooling tower for dissolution of sulfur, forming soluble sodium thiosulfate, which can be reinjected into the geothermal formation:

$$\text{S}^0 + \text{Na}_2\text{SO}_3 \rightarrow \text{Na}_2\text{S}_2\text{O}_3 \quad (42)$$

where $\text{Na}_2\text{SO}_3$ is sodium sulfite and $\text{Na}_2\text{S}_2\text{O}_3$ is sodium thiosulfate.

13. **SUMMARY**

A recent perspective (66) summarizes energy use and emissions trends as well as key issues and developments for control of $\text{SO}_x$, $\text{NO}_x$, and particulate emissions. First, world energy use is projected to increase 50% by 2020 (67). Coal represents 80% of the world’s fossil fuel proven recoverable reserves. The chief concerns for coal use involve emissions of $\text{SO}_x$, $\text{NO}_x$, particulates, and carbon dioxide. As noted earlier, the Clean Air Act and its amendments have lead to significant decreases in emission. From 1980 to 1999, $\text{SO}_2$ emissions have been reduced from 17.3 to 13.5 million tons. From 1970 to 1996, particulate matter emissions ($<10 \mu \text{m}$) have been reduced from 1.6 million tons to 260,000 tons. In the US State Implementation Plan, the goal is to reduce $\text{NO}_x$ emissions 85% from 1990 levels.

Strategies for reducing $\text{SO}_x$ emissions include fuel switching, blending, coal cleaning, and postcombustion FGD. Only about 25% of US power plants have FGD equipment, but this is expected to rise as existing plants retrofit.

In the above sections, we reviewed the two main technologies for FGD using calcium-based absorbents (wet and dry, using respectively, a lime/limestone slurry or a dry/semidry sorbent injection). The wet systems can achieve greater than 95% $\text{SO}_x$ removal, but require ancillary equipment that can amount to 20% of overall plant costs. Dry methods involve injection of sorbent into the ductwork after the boiler, or injection directly into the furnace [furnace sorbent injection (FSI)]. The lime or limestone (CaCO$_3$) calcines, and sulfation reactions occur rapidly at the high temperatures. Injection of dry/semidry sorbents offers advantages of simplicity and ease of retrofit to existing plants. A concern relates to rate and percentage utilization of the sorbent because of the buildup of calcium sulfate that blocks pores and reduces transport and reaction. Recent research addresses this concern by producing a highly reactive absorbent by synthesis of CaCO$_3$. 
particles in aqueous slurry in the presence of small quantities of anionic surfactants or surface modifiers (68). This sorbent achieves more than 70% sulfation within 500 ms, in contrast to 20% for unmodified calcium carbonate. The sorbent can be regenerated to ultimately achieve almost complete sorbent utilization. The process, named “OSCAR,” is being demonstrated at the Ohio McCracken Power Plant on the campus of Ohio State University.

Although this chapter focuses on SO\textsubscript{2} and H\textsubscript{2}S emissions control, the technologies discussed have important implications for other pollutants. For example, Ca-based sorbents, injected in the FSI process, can capture significant amounts of trace elements such as mercury, arsenic, and selenium.

Future research should be directed at the urgent needs: novel and efficient pollution control technologies, improved efficiency, advanced pulverized combustors, pressurized fluidized-bed combustors, and integrated gasification combined cycle systems. Future work will also see investigation of CO\textsubscript{2} sequestration technologies (eg., using the sorbent from the OSCAR process) (69). Hydrogen sulfide gas from different sources (1–7, 70) can also be effectively removed by many FGD processes introduced in this chapter. It should also be noted that many systems are commercially available for flue gas conditioning, flue gas desulfurization, odor control (H\textsubscript{2}S), waste disposal, process monitoring, and emission analyses (71–73).

**NOMENCLATURE**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
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<tbody>
<tr>
<td>B\textsubscript{WA}</td>
<td>Ambient air moisture fraction</td>
</tr>
<tr>
<td>C\textsubscript{f}</td>
<td>Fractional conversion of sulfur in coal to SO\textsubscript{2}</td>
</tr>
<tr>
<td>C\textsubscript{p}</td>
<td>Specific heat [Btu/(lb)(ºF)]</td>
</tr>
<tr>
<td>C\textsubscript{WS}</td>
<td>Pollutant concentration given as a wet basis (lb/ft\textsuperscript{3})</td>
</tr>
<tr>
<td>E</td>
<td>Pollutant emission rate (lb/10\textsuperscript{6} Btu)</td>
</tr>
<tr>
<td>F\textsubscript{w}</td>
<td>Coal analysis factor on a wet basis (std. ft\textsuperscript{3}/10\textsuperscript{6}Btu)</td>
</tr>
<tr>
<td>GCV</td>
<td>Gross caloric value (heating value of coal) (Btu/lb)</td>
</tr>
<tr>
<td>H\textsubscript{T}</td>
<td>Heat energy (Btu)</td>
</tr>
<tr>
<td>H\textsubscript{s}</td>
<td>Head (ft)</td>
</tr>
<tr>
<td>L/G</td>
<td>Ratio of slurry flow to flue gas rate, gal/1000 scf (or gal/1000 scfm) at the outlet of the scrubber/absorber</td>
</tr>
<tr>
<td>O\textsubscript{2W}</td>
<td>Percent oxygen in flue gas on a wet basis</td>
</tr>
<tr>
<td>P</td>
<td>Power required (KW)</td>
</tr>
<tr>
<td>ΔP</td>
<td>Pressure drop through the FGD system (in. H\textsubscript{2}O)</td>
</tr>
<tr>
<td>Q\textsubscript{air}</td>
<td>Airflow rate at the inlet of reheat sections (lb/min)</td>
</tr>
<tr>
<td>Q\textsubscript{s}</td>
<td>Gas flow rate at the outlet of scrubber/absorber (scfm)</td>
</tr>
<tr>
<td>Q\textsubscript{SO\textsubscript{2}}</td>
<td>SO\textsubscript{2} emission rate (lb SO\textsubscript{2}/10\textsuperscript{6} Btu)</td>
</tr>
<tr>
<td>S\textsubscript{SW}</td>
<td>Percentage sulfur in coal by weight</td>
</tr>
<tr>
<td>ΔT</td>
<td>Degree of reheat (ºF)</td>
</tr>
</tbody>
</table>

**REFERENCES**


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