**Figure 15.5**
A limestone flue gas desulfurization unit. (This combination spray and tray tower unit treats approximately one million cfm to 85% SO_2 removal. Limestone use is about 100,000 tons per year.)

PROCESS CHEMISTRY AND OPERATIONAL FACTORS

Before proceeding to the material and energy balances necessary for process design, it is essential that the process chemistry be understood. The chemistry should be optimized to (1) maximize SO_2 removal, (2) avoid *scaling* (precipitating $CaSO_3$ and $CaSO_4$ inside the scrubber), and (3) maximize the *utilization* of the limestone. The first two objectives are met by providing two separate vessels (the scrubber and the effluent hold tank), and the third objective is met by proper pH control and by using finely ground limestone and a sufficiently high liquid/gas ratio. In this section, our discussion will be brief and limited to a few important operating considerations.

Overall, sulfur dioxide absorption is a two-step process, with the first step occurring in the tower and the second step in the effluent hold tank (see Figure 15.1). In the tower, one mole of $CaCO_3$ reacts with two moles of SO_2 as follows:

$$CaCO_3 + 2SO_2 + H_2O \rightarrow Ca^{+2} + 2HSO_3^- + CO_2 \qquad \textbf{(15.21a)}$$
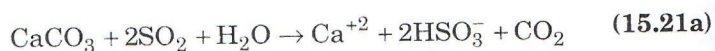
If an excessive amount of $CaCO_3$ is input, the bisulfite ion will not be stable, and $CaSO_3$ will precipitate inside the scrubber (forming scale). A high pH (6.0–6.5) is an indicator of $CaCO_3$ precipitation. However, if

the pH is too low (less than about 4.5), SO_2 absorption will be adversely affected.

In the *effluent hold tank* (EHT), more limestone is added to cause the precipitation of $CaSO_3$. The reaction is

$$CaCO_3 + 2HSO_3^- + Ca^{+2} \rightarrow 2CaSO_3 + CO_2 + H_2O \quad \textbf{(15.21b)}$$

Reaction (15.21b) requires an adequate residence time in the EHT (hence, an adequate EHT volume) and a high concentration of solids in the slurry. Reactions (15.21a) and (15.21b), when added together, portray the overall stoichiometry for SO_2 removal from flue gas. Thus, the overall stoichiometric reaction is:

$$CaCO_3 + SO_2 \rightarrow CaSO_3 + CO_2 \quad \textbf{(15.22)}$$
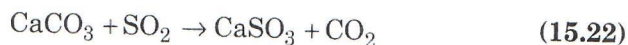
Excess oxygen in the flue gas results in oxidation of some of the $CaSO_3$ to $CaSO_4$ (gypsum). Gypsum precipitation in the scrubber can be prevented by maintaining a high liquid/gas ratio so that the pH of the solution remains fairly constant when SO_2 is absorbed. Gypsum precipitation in the EHT can be promoted by forced oxidation (introduction of additional air).

Inhibited oxidation (discussed in the previous section) is a recently developed alternative to forced oxidation, with the main objective being to prevent scaling in the scrubber. By adding a small amount of EDTA (ethylenediaminetetraacetic acid, $C_{10}H_{16}N_2O_8$) to this system, scaling is reduced even further. Inhibited oxidation is now being favored because it requires less operating power and maintenance, uses less fresh water, and generally costs less than forced oxidation (Dalton 1992).

SO_2 MASS TRANSFER

At the gas–liquid interface, we assume local equilibrium, which can be described by Henry's law as

$$\overline{P}_{SO_2(i)} = H_{SO_2} C_{SO_2(i)} \quad \textbf{(15.23)}$$

where

$\overline{P}_{SO2(i)}$ = partial pressure of SO_2 at the interface, atm

H_{SO_2} = Henry's law constant, atm/(mol/L)

$C_{SO2(i)}$ = aqueous SO_2 concentration at the interface, mol/L

The flux of SO_2 in the gas film is

$$\frac{N}{A} = k_g \left(P_{SO_2} - P_{SO_2(i)} \right) \quad \textbf{(15.24)}$$

where

$\dfrac{N}{A}$ = flux of SO_2, mol/s-cm^2

k_g = local mass transfer coefficient, $\text{mol/(s-cm}^2\text{-atm)}$

$\overline{P}_{SO_2}$ = partial pressure of SO_2 in the bulk gas, atm

The flux of SO_2 in the liquid film is

$$\frac{N}{A} = \phi k_l \left(C_{SO_2(i)} - C_{SO_2} \right) \qquad (15.25)$$

where

ϕ = an enhancement factor to account for chemical reactions that permit SO_2 to diffuse through the liquid film as bisulfite or sulfite species as well as SO_2

k_l = local mass transfer coefficient, $\text{mol/(s-cm}^2\text{-mol/L)}$

C_{SO_2} = concentration of SO_2 in the bulk liquid, mol/L

Combining Eqs. (15.23) through (15.25) to eliminate the interfacial concentrations, we obtain

$$\frac{N}{A} = K_g \left(P_{SO_2} - H_{SO_2} C_{SO_2} \right) \qquad (15.26)$$

where K_g = overall gas phase transfer coefficient

In Eq. (15.26), K_g is given by

$$\frac{1}{K_g} = \frac{1}{k_g} + \frac{H_{SO_2}}{\phi k_l} \qquad (15.27)$$

The two main enhancement reactions are those that convert SO_2 to bisulfite in the liquid film. The reactions are

$$SO_2 + H_2O \rightleftharpoons H^+ + HSO_3^- \qquad (15.28)$$

and

$$SO_2 + SO_3^{-2} + H_2O \rightleftharpoons 2HSO_3^- \qquad (15.29)$$

The enhancement factor can have a wide range of values, depending on several parameters. For enhancement factors greater than 20, the gas film resistance controls the overall mass transfer rate; for enhancement factors less than 20, both gas and liquid film resistances are important. Table 15.4 lists some chemical parameters and their effects on the enhancement factor.

The use of small amounts of chemical additives can significantly improve SO_2 scrubbing efficiency. These additives work by changing

Table 15.4   SO$_2$ Scrubber Chemical Parameters and Their Effects on
the Enhancement Factor, ϕ

Parameter	Effect on ϕ
Gas composition	ϕ decreases as SO$_2$ concentration increases; for example, at pH 5.8,
Bulk liquid sulfite and bisulfite concentrations	ϕ increases as $C_{SO_3^{-2}}$ increases; ϕ decreases as $C_{HSO_3^-}$ increases
pH	ϕ increases as pH increases. (Note: because the solution tends to be in equilibrium with CaSO$_3$ solids, $C_{HSO_3^-}$ decreases as pH increases; thus, the effect of pH is essentially that of $C_{HSO_3^-}$)
Alkali additives	ϕ increases as alkali species increase
Buffer additives (organic acids)	ϕ increases as buffer additives increase (ϕ values of 20–30 are achieved with as little as 10–15 milli-mol/L of adipic acid)

$\overline{P}_{SO_2}$, ppm	ϕ
500	10
1000	7.5
2000	5.8

the liquid phase chemistry and thus increasing the rate of SO$_2$ dissolution. Adipic acid (or adipic acid combined with succinic and glutaric acids) is very effective. For example, according to Dalton (1992), a 90% efficient limestone scrubber can be improved to 95% efficiency with as little as 200 ppm of additives, and to 99% with 500 ppm!

PHYSICAL FACTORS

In addition to the previously discussed chemical factors, there are several important physical factors that affect SO$_2$ absorption. One of the most important is the liquid/gas ratio (L/G). In general, the greater the L/G ratio, the greater the SO$_2$ absorption efficiency. However, high L/G ratios result in high operating costs because of higher pumping energy needs and the greater pressure drop in the absorber. Typically, L/G ratios range from 40 to 100 gal/1000 acf. Proper gas and liquid flow distribution is important to prevent alternating wet and dry spots, to prevent scaling, and to promote good gas–liquid contact. The limestone should be ground finely (90% passing a 325-mesh screen) for good utilization. As discussed in Chapter 13, the gas velocity affects both the scrubber diameter and the pressure drop. Loading

or flooding can be a problem in limestone scrubbers. Good pH control helps to prevent scaling; scale formation at pHs of 6 or less is only about 5% of that at pHs of 6.2 or greater (Henzel et al. 1981). The power consumption of a limestone FGD unit is large—on the order of 3–6% of the power generated by the plant.

MATERIAL AND ENERGY BALANCES

Henzel et al. (1981) have provided complete examples for performing the material balance calculations and estimating the FGD system energy usage for a typical high-sulfur coal and a typical low-sulfur coal. In this section, we will present example problems to demonstrate some of their calculations for the case with a high-sulfur coal. A simplified process flow diagram is presented in Figure 15.6. The coal contains 3.7% sulfur, and has a heating value of 11,115 Btu/lb_m. The firing rate of coal is 210 tons/hour to generate 500 MW (gross). For our example problems, we will assume that we have already performed the initial coal combustion calculations and have established the rate and composition of the flue gas entering the scrubber (see Table 15.5). Certain other data are needed and/or assumptions must be made to perform the FGD system material balances (see Table 15.6). Together, Tables 15.5 and 15.6 make up the *design basis* for the calculations. The following example problems will illustrate these calculations.

Table 15.5   Flue Gas Characteristics for FGD Design Example Problems

Parameter	Value	
Flow rate, acfm	1,615,600	
Flow rate, lb_m/hour	5,337,650	
Components	**lb_m/hr**	**Mole Percent**
Particulate matter	138	—
Carbon dioxide	942,500	11.76
Hydrogen chloride	432	0.01
Nitrogen	3,746,000	73.45
Oxygen	324,000	5.57
Sulfur dioxide	31,080	0.27
Moisture	293,500	8.94
SO_2 inlet loading	6.6 lb_m /10^6 Btu	
Particulate loading	0.03 lb_m /10^6 Btu	
Temperature	290 F	