5B1. SOx Reduction Technology

Technology overview

1. Background

Sulfur oxides (SOx, mainly SO_2) are regulated by a "K-value" control, which uses exhaust heights and regional coefficients to limit SOx emissions. "Total amount control" is a term used in Japan to define the total emissions from the whole of a region. To comply with these regulations, flue gas desulfurizers were commercialized in 1973. Efforts to improve their performance and lower costs have been ongoing. At present, most pulverized coal-fired thermal power plants are equipped with wet limestone and gypsum-based desulfurization systems. Furthermore, a wet desulfurization process requiring no wastewater treatment is now under development.

2. Technology

(1) Wet limestone-gypsum process

Research and development: Mitsubishi Heavy Industries, Ltd.; Babcock Hitachi K.K.; Ishikawajima-Harima Heavy Industries Co., Ltd.; Chiyoda Corporation; Kawasaki Heavy Industries, Ltd.; others

Overview

There are two limestone-gypsum processes; a soot-separation process, in which a dust (cooling) tower is installed upstream for dust collection and HCl/HF removal and cooling, and a soot-mixed process without such a dust (cooling) tower. The soot-separation process is used when high-purity gypsum containing no soot or dust is desired. At present, however, more and more systems employing the soot-mixed process, which is less expensive to install, are being installed since high-performance dust collection devices, such as an advanced low-temperature electrostatic precipitator, which lowers soot/dust concentrations, have been developed.

In the absorption tower, on the other hand, a water-mixed limestone slurry is reacted with SO_2 within the exhaust gas for the recovery of sulfur contents as gypsum ($CaSO_4$-$2H_2O$).

The overall reaction is as follows:

$CaCO_3+SO_2+0.5H_2O \rightarrow CaSO_3\text{-}0.5H_2O+CO_2$

$CaSO_3\text{-}0.5H_2O+0.5O_2+1.5H_2O \rightarrow CaSO_4\text{-}2H_2O$

There are two types of absorption towers, as shown in Figure 1: a $CaSO_3$-$0.5H_2O$ separate tower oxidation system and a comprehensive single tower oxidation system. At present, single tower oxidation systems are less expensive to install and operate and their use is increasing annually. There are several methods to have recycled absorption liquid come into contact with SO_2 in the absorption tower section; the "spray method," which sprays the absorption liquid, the "grid method," which spreads absorption liquid on the surface of a grid-like pad, the "jet-bubbling method," which blows exhaust gas into the absorption liquid, and the "water-column method," in which absorption liquid flows in the absorption tower.

For developing countries, a simple desulfurizer installable in the flue gas duct or at the lower part of a smoke stack has also been commercialized.

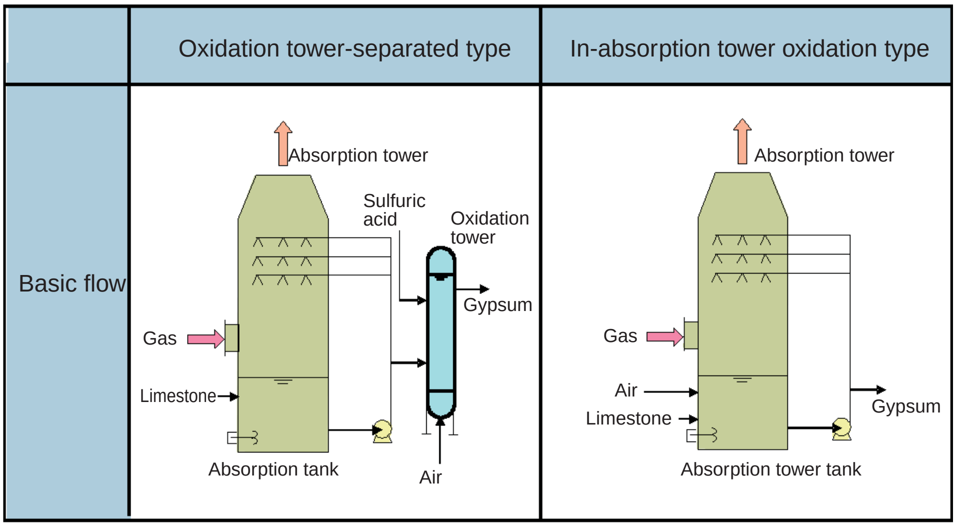

Fig. 1 Limestone-gypsum process-based desulfurizers

(2) Coal ash-based dry desulfurization process
Research and development: Hokkaido Electric Power Co., Inc.; Hitachi, Ltd.; Babcock Hitachi K.K.
Project type: Subsidized development of oil-alternative energy-related technology for commercialization
Development period: 1986-1989

Overview

The coal ash-based dry desulfurization process was one of the technologies developed to make effective use of coal ash. This is a process to produce a new absorbent from limestone, calcium hydroxide ($Ca(OH)_2$) and spent absorbent. By using the newly produced absorbent, SOx is removed from the flue gas. Figure 2 shows an outline of this process, which also includes a stage to manufacture the absorption agent. The desulfurization reaction allows $Ca(OH)_2$ to remove SO_2. Temperatures are maintained between 100-200°C, where an SOx removal efficiency of 90% or greater can be attained. The process can also remove dust and NOx, with a NOx removal efficiency of approximately 20% and a dust collection efficiency of 96% or more. By 2003, the technology had been installed at Hokkaido Electric Power's Tomatoh-Atsuma Thermal power plant No. 1 unit (350MW), where the equipment is being used to treat one-half of the flue gas.

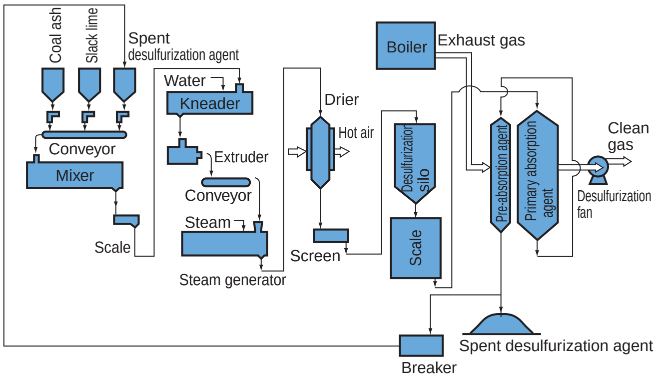

Fig. 2 Coal ash-based dry desulfurization process

(3) Spray dryer process
Research and development: The Electric Power Development Company; Mitsubishi Heavy Industries, Ltd.; Hokkaido Electric Power Co., Inc.
Project type: Voluntary under the Green Aid Plan

Overview

The spray dryer process is a so-called "semi-dry process," where water is added to burned lime (CaO) to make a slack lime ($Ca(OH)_2$) slurry, which is sprayed into a spray dryer, causing the SO_2 in the flue gas to react with $Ca(OH)_2$, and to be removed. Within the dryer, the desulfurization reaction and limestone drying take place simultaneously, giving a particle mixture of gypsum ($CaSO_4$-H_2O) and calcium sulfite ($CaSO_3$-$0.5H_2O$). These particles are recovered at a down-stream precipitator. Since this process is not adequate for good-quality gypsum and, moreover, ash remains in the mix, desulfurized particles are disposed of as waste. J-POWER, as part of the "Green Aid Plan," installed a spray dryer desulfurizer with an exhaust gas treatment capacity of $300Km^3N/h$ (one-half of total exhaust) at the Huangdao power plant No. 4 unit (210MW) in Qingdao, China. It is currently in operation and attained a 70% desulfurization rate in verification tests (Oct. 1994 through Oct. 1997).

(4) Furnace desulfurization process
Research and development: Hokkaido Electric Power Co., Inc.; Kyushu Electric Power Co., Inc.; J-POWER; Chugoku Electric Power Co., Inc.; Mitsubishi Heavy Industries, Ltd.; Ishikawajima-Harima Heavy Industries Co., Ltd.; Kawasaki Heavy Industries, Ltd.
Project type: Voluntary

Overview

The furnace desulfurization process is used for fluidized-bed boilers. Limestone to be used for desulfurization is mixed and combusted with the coal, causing the following reaction to remove SO_2 at a furnace temperature of 760-860°C:

$CaCO_3 \rightarrow CaO+CO_2$ $CaO+SO_2 \rightarrow CaSO_3$

At present, this process is employed at J-POWER's Takehara thermal power plant No. 2 unit normal-pressure fluidized-bed boilers as well as the pressurized fluidized-bed boilers of Hokkaido Electric Power's Tomatoh-Atsuma thermal power plant, Kyushu Electric Power's New Kanda thermal power plant, and Chugoku Electric Power's Osaki thermal power plant. In pressurized fluidized-bed boilers, limestone does not breakdown into CaO due to the high partial pressure of CO_2, but SO_2 is removed in accordance with the following reaction:

$CaCO_3+SO_2 \rightarrow CaSO_3+CO_2$

References

1) "Introductory Course: Environmental Preservation Technology/Equipment for Thermal Power Plants IV Desulfurization Equipment," Thermal/Electronic Power Generation Vol. 41 No. 7, 911, 1990.
2) Kudo et al., "Coal Ash-Based Dry Desulfurizer Development," Thermal/Electronic Power Generation, Vol. 41, No. 7, 911, 1990.
3) "Coal Ash-Based Dry Flue Gas Desulfurizer" pamphlet, Hokkaido Electric Power.
4) General View of Thermal Power Generation, Institute of Electric Engineers, 2002.