Discussion on the Mechanism of Semi-Dry Desulphurization

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Abstract: This paper discussed on the mechanism of four type of semi-dry desulphurization technics (Circulating, Fluid bed, LIFAC -limestone injection into Furnace and Activation of Calcium Oxide and Spray semi-dry desulphurization), and introduced several engineering examples of these desulphurization technics. In addition, the reaction time, operation temperature, ratio of calcium to sulfur, suitable conditions for coal and future application are also discussed.

Keywords: Semi-dry desulphurization, LIFAC, Application, Fluid bed

1 INTRODUCTION

There are four types of semi-dry technics in the desulphurization industry: Circulating, Fluid bed, LIFAC -limestone injection into Furnace and Activation of Calcium Oxide and Spray semi-dry desulphurization. This paper mainly discussed on the Circulating semi-dry desulphurization (NID) and Circulating Fluid bed semi-dry desulphurization (CFB). NID was developed by the ALSTON Company, and CFB was developed by the BESHOLF Company of Germany. There are some common characteristics of the two technics: high proportion of limestone circulation, the whole system is a dry process and the products of desulphurization need the transportation. Because the calcium did not circulate, the desulphurization efficiency of the other two technics is lower and the calcium cost is higher than that of NID and CFB.

2 COMPARISON BETWEEN THE FOUR SEMI-DRY DESULPHUR- IZATION TECHNICS

2.1 Reaction Time

The common characteristic of NID and CFB is that a limestone circulating system was used at the back of the throat part of the reactor. High proportion limestone was humidified and circulated, and the efficiency of desulphurization was improved. The Schematic diagrams of the two technics were shown in Figs. 1 and 2. The reactor of the NID is rectangle, and that of the CFB is cylinder. The velocity of the gas flow is 10 m/s–20 m/s and 3.5 m/s, respectively. C_1 and C_0 are the concentration of the active $Ca(OH)_2$ in the reactor. The pressure drop of CFB mainly at the throat and enlarge part and the total pressure drop is high (1800 Pa). While the pressure drop of NID distribution evenly and the total pressure drop is 1200 Pa.

The main difference of NID and CFB is the place of the water input. The spray nozzle of the CFB was placed on the unstable and unevenly humidified place of the reactor. For this reason, the big size limestone slurry may cause caking easily in the spray nozzle and the absorption tower. Therefore CFB can not operate stably for long. In view of NID, a special apparatus was used to spray and humidify the circulated limestone. With an even film on the surface of the limestone and large evaporation surface, the surface water can evaporated quickly. The temperature of flue gas decreased to 75 ℃ in a 1 m high reactor, and the efficiency of the desulphurization is up to 90%.

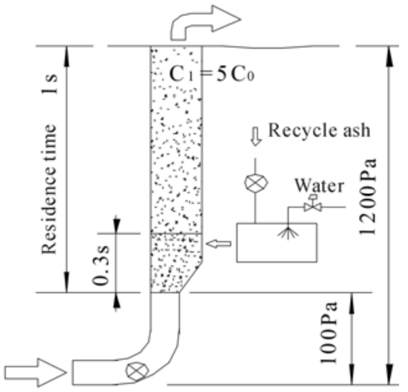

Fig.1 Schematic NID react system

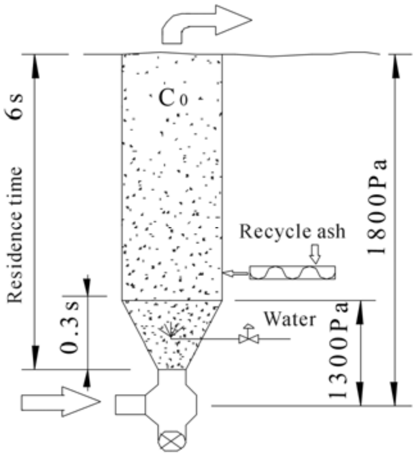

Fig. 2 Schematic CFB react system

The efficiency of desulphurization vs. the reaction time of CFB and NID was shown in Fig. 3. The desulphurization efficiency and reaction velocity of NID is six times than that of CFB. The desulphurization reaction is an elementary reaction, the effectual collision odds is direct proportion to the concentration of the reactant in the reactor, according to the collision theory.

$$r=K\times C_{Ca(OH)2}(l)\times C_{so2}(l)\times e^{-RT} \quad (1)$$

Because the cross section area of the NID is only 1/5 of CFB in the reaction part and no adsorbent in the throat part, the concentration of $Ca(OH)_2$ in the reactor of NID is five times than that of CFB at the same conditions. It also means that the desulphurization rate of NID is five times than that of CFB at the same conditions. Zhejiang Feida Environmental Science & Technology Company has constructed tens of NID, and the desulphur- ization efficiencies are all exceed 90% if the residence time of flue gas is 0.9–1.3 seconds in the reactor.

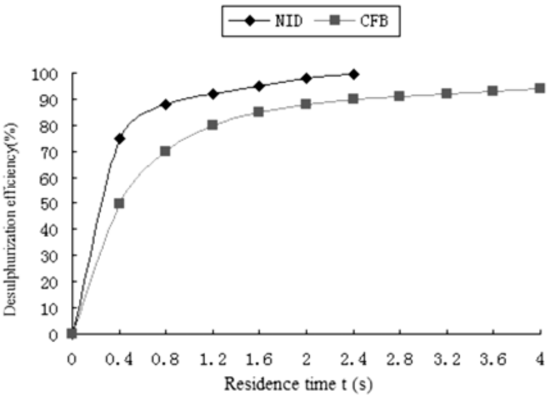

Fig. 3 Diagram of desulphurization efficiency vs. react time

The main reaction of the desulphurization as equation (2), this reaction is an exothermic reaction and low temperature can enhance the reaction. In addition, spray the $Ca(OH)_2$ (s) to be the $Ca(OH)_2$ (l) is critical and improve the velocity between the gas and solid can help the gas transfer to the liquid, see reation 3) and 4).

$$SO_2(l)+Ca(OH)_2(l)\rightarrow CaSO3\cdot 1/2H_2O(s)+1/2H_2O(l)+Q \quad (2)$$

$$SO_2(g)\rightarrow SO_2(l) \quad (3)$$

$$SO_2(l)+H_2O(l)\rightarrow H^+ + HSO_3^-(l) \quad (4)$$

In the low velocity (3 m/s–3.5 m/s) of large diameter absorption tower, the gas flow is laminar flow, and the velocity between the gas and solid is low. This is not favorable to the SO_2 (g) diffusion and dissolve to be SO_2 (l), and the refresh of the $Ca(OH)_2$ surface will be refrained. The only advantage of large diameter absorption tower is that prolong the evaporation time of the big size liquid drops, which produced in the uneven sprayed. The engineer examples of CFB project in China shows that if the wet limestone slurry can not evaporate in time, the desulphurization products would clog inevitably and the apparatus can not operate for long. The evaporation time of the slurry in the reactor was shown in Fig. 4. The limestone mist drops of 100 μm size diameter were evaporated in 12 s (lower than 3% moisture), at the temperature of 70 ℃–80 ℃. The back apparatus of ESP and fans will not clog when the limestone mist drops of 100 μm mean diameter were evaporated in 5 s. In order to operate the desulphurization apparatus of CFB and the back ESP continuously, the residence time in the reactor should larger than 8 s. But in fact, the residence time always designed to 6 s for saving the costs.

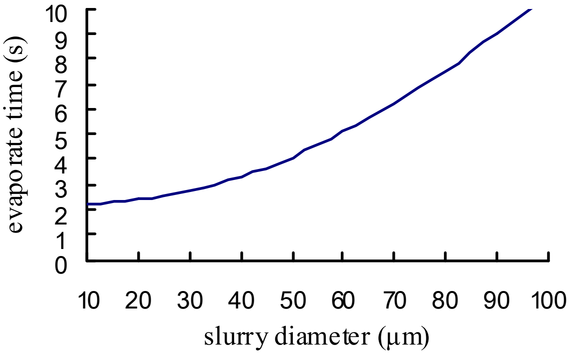

Fig. 4 Diagram of limestone slurry diameter vs. evaporate time

In view of charging semi-dry desulphurization technics, the humidity is low and the desulphurization is a slow sulfurous reaction. The reaction time is designed to 2 seconds for saving the land and costs. The efficiency of desulphurization of this techics is 50%–70%, and it was not used any more. While to the spray and LIFAC semi-dry desulphurization technics, the humidity of the desulphurization products must less 3% for operate stably. Therefore the total desulphurization time of the apparatus must exceed 8 seconds.

2.2 Ratio of Calcium to Sulphur (Ca/S)

At the same temperature, the factor that strongly affect the reaction velocity is the concentration of the SO_2 (l) and $Ca(OH)_2$ (l) in the reactor bed. NID and CFB technics have the same conditions that the same temperature and ratio of the circulated limestone. But the flue gas of NID is greatly higher than that of CFB, which is favorable to NID fitting to the high ratio limestone circulation. In addition, the reaction products and $Ca(OH)_2$ (s) are all wet evenly by the spray apparatus, and react with the HSO_3^- anion quickly in a comparatively small cross section of the reactor.

In the CFB process, the spry nozzle is buried in the limestone and humidified unevenly. While the $Ca(OH)_2$ (s) which did not humidified is inactive. The results of overseas studies show that the desulphur- ization efficiency of high quality $Ca(OH)_2$ (s) is about 50 % in five seconds under the charging dispersion condition. In addition, the operation temperature of CFB is high (70 ℃–85 ℃), and this can help to drying the big size limestone slurry in the reaction time of desulphurization (5 s–6 s). But, the Ca/S is higher than other technics. While the operation temperature of NID can adjust to 65 ℃–85 ℃ base on the desulphurization efficiency and costs. At the same efficiency, the Ca/S dropped 0.1. The results of three years operation in Zhejiang Juhua power plant show that the limestone saved 7 kg with the outlet temperature dropping 1 ℃.

The Ca/S of NID and CFB can be adjusted to 1.2±0.1 under the safe temperature. The Ca/S of LIFAC is 2.3–2.5, because the limestone can not be decomposed and activated completely with low residence time, and the limestone did not recycle. The Ca/S of spray semi-dry desulphurization is

1.4–1.6, at the temperature of 70 □.

2.3 Operation Temperature

The operation temperature of desulphurization is determined by the desulphurization efficiency, chlorine concentration in the coal, Ca/S and the desulphurization process. The closer to the acid dew point of the operation temperature, the longer of the water retain on the adsorbent surface. This is favorable to the anion reaction of desulphurization. To the limestone circulating desulphurization technics, the operation temperature has the larger range (65 □–85 □). When the middling sulfur concentration coal (1.5%–3.5%) was combusted, the amount of adsorbent can be saved greatly with the low operation temperature.

When the sulfur concentration coal of Zhejiang Juhua power plant NID desulphurization is 0.4%–0.8%, the outlet temperature is 75°C and the desulphurization efficiency is 90%–95%, the Cumulative mean Ca/S is about 1.2. When the sulfur concentration of the coal is 1.5%, the outlet temperature is 70 □ and the desulphurization efficiency is 90%, the Cumulative mean Ca/S is about 1.22. These results show that the operation temperature affected the desulphurization efficiency greatly. The acid dew point is decided by the concentration of SO_3, and the SO_3 almost all removed in the limestone circulating system. Therefore, the acid dew point is close to the water dew point, about 48 □-51 □. With the high sulfur coal, even the operation temperature is 65□, the apparatus would not erode.

In order to vaporized the limestone slurry, the operation of CFB is high (75 □–90 □), .and the Ca/S increase 0.1–0.2 than the NID. Therefore, the costs increased.

Because the hydrochloric acid in the flue gas can react with the $Ca(OH)_2$ (l) before the SO_x, and produce $CaCl·2H_2O$ which has strong water adsorption. The operation temperature must be higher to guarantee the apparatus operate stably.

To the LIFAC and spray semi-dry desulphurization, the operation temperature can be lower, and heat again in the outlet of the tower flue gas with the corrosion preventing facility in the adsorption tower and the flue gas pipe. By doing this, the desulphurization efficiency can be improved and save the costs.

2.4 Compatibility to the Coal of Various Sulfur Concentration

Circulating semi-dry desulphurization of CFB and NID has good compatibility to the coal with various sulfur concentration.

When the concentration of the sulfur in the coal is less than 2.5% or the concentration of SO_2 is less than 7000 mg/Nm^3, these technics have good performance. The desulphurization efficiency vs. inlet concentration of SO_2 was shown in Fig. 5 (NID). When the inlet concentration of SO_2 is 5000 mg/Nm^3 and operation temperature is 71 □, the desulphurization efficiency is exceed 90%. While, with the high sulfur coal, we need to take care of the SO_2 concentration of outlet, make sure it less than the new emission standard. In practical engineering, following methods are used to meet the new emission standard: 1) decreasing the operation temperature, namely increasing the reaction rate; 2) increasing limestone, namely increasing the Ca/S; 3) increasing the ratio of the circulating limestone, namely enhancing the refresh of $Ca(OH)_2$ surface that covered by the reaction products; 4) increasing the height of reactor, namely increasing the residence time; 5) using the fabric filter, the calcium dust on the filter re-desulphurization. To the LIFAC and spray semi-dry desulphurization, the limestone did not circulate, and the adsorption efficiency is low. The costs are higher than the circulating technics.

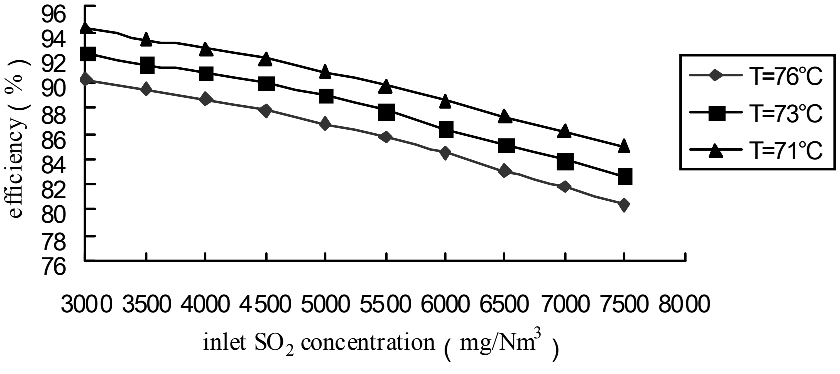

Fig. 5 Diagram of desulphurization vs. inlet SO_2 concentration

NID can be operated economically with the coal of sulfur concentration less than 2.5 %. The operation results of Zhejiang Juhua power plant (middle sulfur coal 1.5%) and Finland Huasha power plant (middle sulfur coal 3.5%) show that the desulphurization efficiency is exceeded 90%. Hubei Jingmen power plant 200 MW unit capacity used NID techic in 2005, the concentration of coal sulfur is up to 2.3%, and the highest concentration of SO_2 is 7000 mg/Nm^3.

3 APPLICATION

LIFAC and spray semi-dry desulphurization technology have been developed over thirty years, and were introduced in

China over twenty years. The spray semi-dry desulphurization technology first introduced and renovated in Sichuan Baima power plant in 1985. Shandong power plant introduced the spray semi-dry desulphurization technology from Japan in early year of 90^{th}, but no any other application later for sake of costs, unstable and low desulphurization efficiency. LIFAC was introduced to Nanjing Xiaguan power plant and Zhejiang Qianqin power plant in 1997 from Finland IVO Company. After many years of study and renovation, this technology was still used in the rebuilt industry of China.

CFB is an advanced technology, but it has no example whether it can operate continuously and stably. NID was used in Juhua power plant 70 MW, Jingmen power plant 200 MW and Taicang Jiulong paper plant 2×135 MW successfully, and get the recognition in China. This technology is also the most widely used semi-dry desulphur- ization technology in China. Zhejiang Feida Company has made this NID technology manufacture domestically in less than 300 MW unit capacity after 7 years study and renovation, and constructed about 50 NID projects such as: Baotou power plant, Jingmen power plant and Jiulong paper plant (200 MW) desulphurization projects.