Optimized Circulation Of SCR Applied To Coal-fired Power Plant

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Abstract. As SCR(selective catalytic reduction) is comprehensivly accepted domestic for high efficiency and economy,its technical principle and process applied to coal-fired power plants are introduced,then main solutions(the adjustment of the ammonia injection grid,calalyst management and controlling NH3 slip)to optimized circulation in practical operation are put forward to make references for domestic coal-fired plants in this paper.

1. Foreword

There are mainly two kinds of de-NOx methods(selective catalytic reduction and non-selective catalytic reduction)in domestic coal-fired power plants, among which SCR has been widely used in China for its high efficiency and economy. With the further promotion of environmental protection standards, ultra-low emission retrofitting of existing de-NOx devices in thermal power plants has been rapidly carried out nationwide.Currently, many domestic coal-fired power plants have completed the ultra-low emission reform of flue gas, passed environmental protection acceptance and obtained corresponding power price subsidies.Since the NOx emission requirements for flue gas performed by ultra-low emission retrofitted units are more stringent (≤50mg/m3), the operation and control of SCR de-NOx devices in thermal power plants need to be more precise. If the NH3 injection grid, the management of the catalyst, and the control of NH3 slip are not in place, it is more likely to cause NOx emissions that are difficult to reach ultra-low requirements, too high NH3 slips, and the resulting increase in air heater preheater jams, even reduce the electrostatic precipitator dust removal efficiency. These problems finally will affect the economy and safety of the unit operation[1].

2. SCR flow and principle

The SCR system is composed of an NH3 gas supply, an air supply, an NH3/air spray system, and an SCR catalytic reactor before the economizer rear air preheater. The liquid ammonia is transported by the tank truck to the liquid ammonia storage tank. The liquid ammonia output from the liquid ammonia storage tank is vaporized into ammonia gas in an ammonia vaporizer at a temperature of about 40°C, and the ammonia is heated to room temperature and sent to the ammonia buffer slot which is reserved. The ammonia gas in the buffer tank is decompressed by the pressure regulator valve and sent to the ammonia/air mixer of each unit. After fully mixing with the air from the blower, the ammonia injection grid (AIG) is used. The nozzle is sprayed into the flue gas and mixed with the flue gas to enter the SCR catalytic reactor. When the flue gas flow passes through the catalytic layer in the SCR catalytic reactor, ammonia and NOx are catalyzed by the catalyst and the oxidation-reduction reaction takes place, reducing NOx to harmless N2 and H2O.The SCR process is used in thermal power plant units and its de-NOx efficiency can reach about 90%.
Fig. 1. SCR flow diagram

The main chemical reactions are:

\[
\begin{align*}
4 \text{NH}_3 + 4 \text{NO} + 3 \text{O}_2 & \rightarrow 4 \text{N}_2 + 6 \text{H}_2 \text{O} \\
8 \text{NH}_3 + 6 \text{NO} & \rightarrow 7 \text{N}_2 + 12 \text{H}_2 \text{O} \\
\text{NH}_3 + \text{NO}_2 + \text{N}_2 & \rightarrow 2 \text{N}_2 + 3 \text{H}_2 \text{O}
\end{align*}
\]

(1)

Possible side effects are:

\[
\begin{align*}
4 \text{NH}_3 + 3 \text{O}_2 & \rightarrow 2 \text{N}_2 + 6 \text{H}_2 \text{O} \\
2 \text{NH}_3 & \rightarrow \text{N}_2 + 3 \text{H}_2 \\
4 \text{NH}_3 + 5 \text{O}_2 & \rightarrow 4 \text{N}_2 + 6 \text{H}_2 \text{O}
\end{align*}
\]

(2)

3. SCR process optimization

After the SCR device of the thermal power plant is put into operation, the adjustment of the ammonia injection grid, the management of the catalyst and the control of NH3 slip will become the main tasks of the thermal power plant in order to maintain the efficient, economical and safe operation of the SCR device[2].

3.1 AIG adjustment

When AIG’s position is improperly selected or the distribution of flue gas flow is not uniform, the mixing of NOx and NH3 and the reaction may be insufficient, which not only results in excessive partial ammonia injection, but also causes side reactions, as well as de-NOx effects and economic operation. Therefore, during the operation of the de-NOx device, in order to avoid the generation of high NH3 slip and better distribute the ammonia in the flue, it is necessary to regularly adjust the AIG. The ammonia spray uniformity test is generally performed after the last layer of catalyst. Generally, the reserved gas holes are arranged on the flue after the last layer of the catalyst layer, and the sampling grid points (40–60 points) are uniformly arranged according to the size of the flue gas. The unevenness of the distribution of NO in each point of the de-NOx device export is controlled within 15%[3]. If the requirements are not met, the AIG can be optimized by adjusting the damper. The entire work can be completed within two working day.

3.2 Catalyst Management

The composition, activity and service life of the catalyst will have a great influence on the NO removal efficiency and the de-NOx cost. Different catalysts have different activities, stability and service life. Therefore, in actual operation, full attention should be paid to changes in the physicochemical properties and activity of the catalyst in order to ensure the economical and efficient operation of the de-NOx device.
3.2.1 The composition of the catalyst
When the catalyst activity is reduced or poisoned or replaced, the composition of the catalyst should be focused on analysis. In general, the service life of the catalyst does not exceed 24,000 hours. In practical use, catalyst needs to have considerable strength and anti-corrosion and anti-toxicity properties when it is subjected to high-temperature, dust-laden, high-velocity smoke of complex components scouring and can maintain high activity. Table 1 shows two SCR catalysts that work well in practice.

| composition | unit | WO3 as Carrier | MoO3 as Carrier |
|-------------|------|----------------|-----------------|
| SiO         | %    | 5.1            | 3.4             |
| Al2O3       | %    | 0.65           | 3.9             |
| Fe2O3       | %    | 0.01           | 0.14            |
| TiO2        | %    | 79.7           | 73.3            |
| CaO         | %    | 0.79           | 0.01            |
| MgO         | %    | 0.01           | 0.01            |
| BaO         | %    | 0.01           | 0.01            |
| Na2O        | %    | 0.01           | 0.01            |
| K2O         | %    | 0.02           | 0.02            |
| SO3         | %    | 1.1            | 3.4             |
| P2O5        | %    | 0.01           | 0.01            |
| V2O5        | %    | 0.59           | 1.6             |
| MoO3        | %    | —              | 12.9            |
| WO3         | %    | 11.0           | —               |

From the above, it can be seen that both of the catalysts are mainly TiO2. The TiO2 needs to be made into a crystal structure, such as Anata-TiO2, Ruhl-TiO2, which can effectively increase the activity of the catalyst and inhibit the corrosion of SO3. At the same time, it is also equipped with a variety of oxidant substances such as CaO, Fe2O3, etc., in order to enhance the activity of the catalyst. There are also some other substances such as glass fiber, etc., in order to improve the erosion resistance of the entire catalyst. In addition, WO3 not only enhances the effect of hardness, but also fixes arsenic in the flue gas which reduces its poisoning effect on the catalyst.

3.2.2 Catalyst activity detection
The activity of the catalyst refers to the ability to catalyze the reaction of ammonia with nitrogen oxides. If the activity of the catalyst is represented by a constant K[4], it is mainly determined by the physicochemical composition of the flue gas, the temperature of the flue gas, the flow velocity of the flue gas, and the performance of the catalyst. At present, the detection and evaluation method of catalyst activity is mainly the catalyst unit method provided by the catalyst manufacturer which can only be performed after the system is shut down, and a certain number of catalyst units must be removed, and its mathematical expression can be expressed as:

$$K = -\frac{V}{F} \ln \left(1 - \frac{\eta}{\eta_0}\right)$$

In the formula (3), $\eta_0 = \frac{NO_{before} - NO_{after}}{NO_{before}}$, $NO_{before}$, $NO_{after}$—NO concentration at inlet and outlet of a layer of catalyst (mg/m3); $V$: Flue gas velocity at the catalyst layer (m3/h); $F$: Surface area of catalyst layer (m2).

In addition, a catalyst activity test method developed by a German power plant has a good
agreement with the results of the catalyst unit method, and has the advantages of not stopping the system and making the detection simple. Its mathematical expression can be expressed as:

\[ K = - \frac{1}{V_{cat}} \cdot \frac{V_{rf}}{A} \cdot \ln\left(1 - \frac{\eta}{\alpha}\right) \quad (4) \]

In the formula (4), \( K \) — Activity coefficient; \( V_{cat} \) — Catalyst volume (m\(^3\)); \( V_{rf} \) — Flue gas flow, wet basis (m\(^3\)/h); \( A \) — Catalyst specific surface area (m\(^2\)/m\(^3\)); \( \eta \) — NO conversion rate;

\[ \alpha = \frac{NO_{after} - NO_{before}}{NH_3}, \quad \eta = \frac{NO_{before}}{NO_{after}}, \quad NO_{before}, \quad NO_{after} \] — NO concentration at Inlet and Outlet of a layer of Catalyst (mg/m\(^3\)).

The larger the K value, the greater the activity of the catalyst and the stronger the de-NOx ability. However, at the same time, an important side-effect of the SCR de-NOx catalyst in the high dust area is the SO2/SO3 conversion. Increasing the concentration of SO3 will cause some problems, for example, the formation of (NH4)HSO4 will block the air preheater, resulting in high pressure loss and even frequent cleaning; (NH4)HSO4 generation will also corrode the tube sheet of air preheater. Therefore, considering the choice of catalyst, the SO2/SO3 conversion rate will also be an important indicator in addition to its catalytic activity. In general, the SO2/SO3 conversion rate should be controlled below 1%.

3.2.3 Catalyst activity tracking

During the shutdown of thermal power plant units, the catalyst units in different layers are used (or on-line testing method of the catalyst activity developed by a German power plant which not need to stop) for testing activity and chemical composition of the catalyst. The analysis was performed to understand the accumulation of catalyst toxicity and the reason for the decrease in catalyst activity. At the same time, using the potential nitrogen removal index P (\( P = K/AV \), AV is the ratio of the flow velocity of flue gas to the surface area of the catalyst), the P value and the total P value of catalysts in each layer are plotted along with the running time of the system, and the changes in these data are tracked. It can make a reasonable prediction of the service life of the catalyst and enable the de-NOx device operator to better plan the replacement or regeneration of the catalyst in time to ensure that the total P value of the catalyst layer is above the minimum P value required for the normal operation of the de-NOx device, so that the de-NOx device maintains good operation.
Fig 2. Change of catalytic activity of SCR device in a coal-fired power plant

Figure 2 shows that by dynamically managing the total P value of each catalyst layer, it is ensured that the de-NOx effect and the NOx emission concentration are always met. When the P values of the first and second catalyst layers gradually decrease with the use of time, the total P value also decreases. In order to keep the total P value above 5.0, the coal-fired power plant added a third catalyst layer at the time of operation to 11129 hours. At the time of the operation to 33,610 hours, the coal-fired power plant added a fourth catalyst layer. In the subsequent operation, the first, second, and third layer catalysts were replaced according to the change in the total P value of the four catalyst layers so that the total P value was always maintained at 5.0 or more.

3.3 NH3 slip control

In the SCR process, NH3 slip control is also crucial. Because if the control is not good, this will not only increase the cost, but also lead to two main problems: the corrosion of the air preheater tube sheet and the fly ash pollution. As the excess ammonia reacts with the SO3 in the flue gas to produce (NH4)HSO4, when the flue gas temperature decreases in the subsequent flue, the (NH4)HSO4 will adhere to the air preheater surface and the fly ash particulate surface. The (NH4)HSO4 substance exists in liquid form when the smoke temperature is lower than about 150°C. It corrodes the air preheater tube sheet and changes the surface shape of the fly ash particles by reacting with the surface of the fly ash, and finally forms a large group of viscous corrosive substances, which and (NH4)HSO4 formed on the surface of the tube sheet can cause a drastic increase in pressure loss of the air preheater and frequent cleaning of the air preheater. At the same time, due to the excess ammonia, the chemical properties of fly ash have changed, making it impossible to use fly ash as a raw material for building materials, which means that power plants must pay extra costs for the disposal of fly ash.

In a sense, the SCR reactor is an ammonia reactor. Due to the existence of many factors, avoidance will inevitably lead to NH3 slip. Figure 3 shows the NH3 slip along the thermal power plant.
In general, the influencing factors of NH3 slip are the inhomogeneity of ammonia injection and the decrease of the activity of the catalyst layer. However, in the actual operation, neither of these can be found in time, and NH3 slip cannot be reflected well by the de-NOx rate. However, the long-term operation of the on-line NH3 slip meter also has inaccurate problems. At this time, it is a direct and effective method to analyze the NH3 slip of the de-NOx device by detecting the ammonia content in the fly ash (usually requiring the NH3 slip to be controlled within 3 ppm).

According to the operating experience of a foreign thermal power plants, under the normal operation of SCR, when the ammonia content in fly ash is controlled below 50mg/kg[5], which can be effectively controlled within the safe operation range.

4. Conclusion
SCR has the advantages of wide choice of catalysts and high de-NOx efficiency which dominate the flue gas de-NOx process of thermal power plants in China. When SCR technology is applied to thermal power plants, in order to achieve ultra-low emissions of flue gas, thermal power plants should ensure efficient and economical operation of SCR through daily monitoring of NH3 slip, regular inspection of ammonia injection uniformity, and long-term catalyst management.

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