Performance Evaluation and Life Management of SCR Denitration Catalyst

Chao Lu*, Dong Wang, Wentao Zhu, Fengji Wang, Zhen Du and Yue Zhu
Huadian Electric Power Research Institute Co., Ltd.No. 2, Xiyuan 9th Road, Sandun Town, Xihu District, Hangzhou, Zhejiang, China
*393669435@qq.com

Abstract. A plate-type catalyst for selective catalytic reduction (SCR) denitration system of a 600MW coal-fired power plant was studied. The denitration process characteristics and physical and chemical properties of the desulfurization process at different operating times were tested and analyzed. The results show that the content of active components of the catalyst decreases, and the content of alkali metals and alkaline earth metals increases. The deposition of fly ash and the wear of the catalyst during operation are the main reasons for the denitrification performance of the catalyst. Catalyst activity decreased by 21.6m/h after installation in 2016. It was found that the catalyst in operation could not meet the operation requirements of the denitration equipment in 2018. Based on this, the catalyst replacement proposal was given, and the denitrification catalyst was replaced for the operation of the power plant. Provide a reference and use this method as a life management mode for denitrification catalysts.

1. Introduction
The use of selective catalytic reduction (SCR) to remove nitrogen oxides (NOx) is currently the most widely used denitrification technology. Catalysts are the focus of SCR denitrification technology. Catalyst performance and lifetime directly determine the environmental and economic benefits of the entire unit. Under the premise of meeting the NOx emission standards, the fundamental purpose of SCR catalyst operation management is maximizing the service life of the catalyst by detecting catalyst status and adjusting the SCR system, optimizing the catalytic replacement/installation/regeneration strategy, reducing the adverse effects on downstream equipment such as air preheaters, improving the safety and economy of the denitrification unit [1-3]. The actual performance of the catalyst the actual performance of the SCR denitrification equipment and the maintenance plan of the corresponding unit are key factors in catalyst life management [4]. The following figure 1 and figure 2 show common honeycomb and flat denitration catalysts.
2. Catalyst performance test
In this paper, a 600 MW unit SCR denitration system AB double-sided three-layer flat-type in-service catalyst is taken as an example. A2, B2, A3 and B3 is a two-stage initial catalyst in the year of 2014, and A1 B1 is a add-layered catalyst in the year of 2016. The performance parameters of the catalyst on the test platform are tested under different operating times, and the reasons for catalyst performance degradation are analyzed. Catalyst life is evaluated and catalyst management recommendations were made.

2.1 Process characteristics evaluation test
The running catalyst in the reactor on both sides of the A&B in the SCR reaction zone is retrieved from the power plant, and the catalyst prepared for the denitration performance evaluation test is loaded into the laboratory denitration reactor, and the experimental apparatus is shown in figure 3 [5].

The experimental conditions are as shown in Table 1 below:
Table 1. Test conditions

| Serial number | Parameter                     | A side(A1, A2, A3) | B side(B1, B2, B3) |
|---------------|-------------------------------|--------------------|--------------------|
| 1             | $A_V/(m/h)$                   | 6.57               | 6.57               |
| 2             | $S_V/h$                       | 1934               | 1934               |
| 3             | $NO_X/(mg/m^3)$, dry basis,6% $O_2$ | 406.3             | 406.3             |
| 4             | $SO_2/(mg/m^3)$, dry basis,6% $O_2$ | 5198.6        | 5190.6            |
| 5             | $O_2/%$, dry basis            | 4.85               | 4.85               |
| 6             | $H_2O/%$                      | 7.18               | 7.17               |
| 7             | Flue gas temperature /℃       | 350                | 350                |
| 8             | Ammonia-nitrogen molar ratio  | 0.897              | 0.899              |

2.2 Physical and chemical properties evaluation test

In this study, the NOVA 4000e automatic surface area analyzer was used to measure the specific surface size of the two samples. The main chemical components such as titanium dioxide, molybdenum trioxide, tungsten trioxide and pentoxide were measured by ZSX Primus IIX fully automatic sequential scanning X-ray fluorescence spectrometer. Divanadium, cerium oxide, etc.; Optima 8000 inductively coupled plasma atomic emission spectrometer is used to measure trace elements such as arsenic, sodium, potassium, calcium and phosphorus [6].

3. Analysis of experimental results

3.1 Process characteristic analysis

The corresponding parameter data of the catalyst was obtained by the process characteristic test. The activity of the catalyst calculated by the formula (3) is a parameter for visually characterizing the performance of the catalyst. The measurement of the activity of the catalyst requires ammonia escape data as a calculation basis, and the conversion rate of $SO_2/SO_3$ is also to some extent. The amount of active ingredient in the catalyst can be characterized. The following table 2 shows the values of catalyst denitration efficiency, ammonia slip, $SO_2/SO_3$ conversion, and calculated activity for 2019 operation after catalyst addition in 2016.

| Sample serial number | Denitration efficiency(%) | Ammonia escape(μL/L) | $SO_2/SO_3$ conversion rate(%) | Active(m/h) |
|----------------------|---------------------------|----------------------|--------------------------------|-------------|
| A three sides(2019)  | 87.8                      | 3.8                  | 0.62                           | 19.6        |
| B three sides(2019)  | 87.8                      | 4.2                  | 0.64                           | 19.3        |
| A three sides(2018)  | 87.7                      | 3.4                  | 0.65                           | 19.9        |
| B three sides(2018)  | 87.7                      | 3.7                  | 0.67                           | 19.5        |
| Add catalyst in 2016 | 89.4                      | 2.3                  | 0.68                           | 21.7        |

According to the relevant standards and requirements in the industry, under the premise of achieving denitration efficiency, the overall export ammonia escape of the denitration device should not exceed 3μL/L. It is obtained from the table that after the new add catalyst is installed in 2016, when the denitration device reaches the denitration efficiency of 89.4%, the ammonia slip is 2.3μL/L, and the overall catalyst activity value is calculated to be 21.7 m/h. From the data in the table, it can be
found that the catalysts on both sides of AB are decreasing year by year from 2016 to 2019, and the activity on the A side is slightly higher than that on the B side, which is related to the actual operating conditions of the power plant. The amount of side flue gas is different, resulting in slightly different actual conditions on both sides of the catalyst.

3.2 Analysis of physical and chemical properties

3.2.1 Analysis of main chemical composition

The catalyst powder was detected by an X-ray fluorescence spectrometer, and the content of the main chemical components in the catalyst was obtained by the test. The reason for the decrease in catalyst activity can be analyzed by chemical components. The table 3 show the main chemical composition A2 and B2 catalysts over the years.

Table 3. Test results of main chemical components of A2 and B2 catalysts

| Main chemical composition | A2          | B2          | Catalyst in early 2014 |
|---------------------------|-------------|-------------|------------------------|
|                           | 2015 2018 2019 | 2015 2018 2019 |                        |
| TiO₂                      | 78.02 68.47 69.48 | 78.43 70.42 66.19 | 79.80                  |
| MoO₃                      | 3.46 2.10 1.53  | 3.29 2.19 1.48  | 4.01                   |
| V₂O₅                      | 3.95 2.23 2.19  | 3.25 2.34 1.97  | 4.33                   |
| SiO₂                      | 5.88 8.94 9.54  | 6.01 9.64 9.49  | 4.86                   |
| Al₂O₃                     | 4.22 5.63 5.95  | 4.33 6.19 6.96  | 3.76                   |

A2, A3, B2, and B3 are two layers of fresh catalyst at the beginning of 2014. A1 and B1 are added fresh catalysts in 2016. The content of main chemical components was analyzed by the data in the table and they share the same trend. The content of TiO₂, MoO₃ and V₂O₅ in the three-layer catalyst samples on both sides of A and B was lower than that of fresh catalyst, and the content of SiO₂ and Al₂O₃ components increased. The Ti-Mo-V system is the catalyst active system, and its content largely determines the activity of the catalyst. The SiO₂, Al₂O₃ and other substances on the surface of the catalyst are generally introduced with dust deposition, which will cause a decrease in the specific surface area of the catalyst. The effect of alkaline earth metals such as CaO and MgO on the catalyst: it will weaken the acid site strength of the catalyst surface and inhibit the adsorption of NH₃ on the B acid site; or the alkaline earth metal and SO₃/SO₂ in the flue gas will form CaSO₄, resulting in catalyst micropores. The blockage affects the diffusion of the reactive gas to the active sites [7, 8], resulting in the physical deactivation of the catalyst.

3.2.2 Analysis of trace element

The inductively coupled plasma optical emission spectrometer was used to detect the trace element content of the catalyst. Some trace elements were incorporated in the catalyst preparation process, and more trace elements in the soot were deposited on the catalyst surface during the operation. The following table 4 show the results of A2 and B2 catalysts trace element test over the years.

Table 4. Trace element detection results of A2 and B2 catalysts

| Element | Unit | A2      | B2      | Catalyst in early 2014 |
|---------|------|---------|---------|------------------------|
|         |      | 2015 2018 2019 | 2015 2018 2019 |                        |
| As      | μg/g | ND ND ND  | ND ND ND   | ND                     |
| P       | μg/g | ND 9373 6877 | ND 9391 7729 | ND                     |
| Fe      | μg/g | 1316 1174 2660 | 1778 1593 2083 | 497                   |
| Ca      | μg/g | ND 60 78  | ND ND 77  | 92                     |
| Na      | μg/g | 3411 3881 2640 | 4381 4073 4286 | ND                     |
| K       | μg/g | 681 1093 1186 | 921 1226 1018 | ND                     |
The content of P, Fe, Na and K in the three-layer catalyst samples on both sides of A and B increased to different degrees compared with fresh catalyst. Moreover, the content of trace elements in the catalyst is increasing year by year. In the two-sided three-layer catalyst, As was not detected or was below the detection limit. As a great influence on the activity of the catalyst, the catalyst will lose its acid position, and the presence of the alkali metal will cause the acid sites of the catalyst to be occupied, resulting in deactivation of the catalyst.

3.2.3 Analysis of specific surface area. The specific surface area of the catalyst was measured using a physical adsorber, and the specific surface area of the catalyst mainly characterized the total area of the catalyst surface. The larger the total area, the greater the probability that the gas will react on the surface of the catalyst. The figure 4 and figure 5 below shows the measurement of the specific surface area of the catalyst over the years.

![Figure 4](image1.png)  
**Figure 4.** A side three layers catalysts specific surface area

![Figure 5](image2.png)  
**Figure 5.** B side three layers catalysts specific surface area

It can be seen from figure 4 and figure 5 that the specific surface area of the A1 and B1 samples is slightly lower than that of the catalyst installed in 2016 (5.29%, 4.23%, respectively), and the specific surface area of A2, A3, B2, and B3 samples decreased to a large extent relative to the catalysts at the beginning of 2014 (39.47%, 37.87%, 29.63%, and 34.10%, respectively). The decrease in specific surface area is mainly due to the clogging of the microscopic pores by the soot, and the microscopic pores become smaller after the abrasion, so that the specific surface area of the catalyst becomes small. The decrease of the specific surface area of the catalyst micropores is not conducive to the diffusion of the reaction gas and its sufficient contact with the active site, resulting in mass transfer resistance during the catalytic reaction, affecting the adsorption and activation ability of the catalyst to the reaction gas, resulting in a decrease in the denitrification activity of the SCR [9,10].

4 Catalyst Management Program
The catalyst amount of the single unit was 1137.4m$^3$. The initial two-layer catalyst was put into operation in August 2014, and the additional layer catalyst was put into operation in May 2016. The chemical life of the catalyst was 24000h. The catalyst test was sampled in July 2019 and was designed for replacement in June 2020. The catalyst replacement scheme is shown in table 5.

Option 1: Replace the initial layer catalyst (ie, the volume of the additional layer 440 squares) according to the ultra-low emission requirements, and calculate the overall chemical life on this basis.

Option 2: Replace the two-layer initial layer catalyst (ie, the volume of 880 square layers of the two layers) according to the ultra-low emission requirements, and calculate the overall chemical life on this basis.

Option 3: Calculate the volume of catalyst replacement according to the overall chemical life of the catalyst of 24000h.
Table 5. Catalyst replacement program

| Project                      | Unit | Option 1 | Option 2 | Option 3          |
|-----------------------------|------|----------|----------|-------------------|
| Catalyst unit height       | mm   | 606      | 606      | 514               |
| Single unit catalyst volume| m³   | 440      | 880      | 742.6 (replace two layers) |
| Catalyst chemical life      | hr   | 9600     | 28000    | 24000             |

5 Conclusion
1) With the new catalyst and in-service catalyst of 600MW unit, the denitration performance test under different operating time found that the catalyst activity decreased yearly by year, and the results of the year of 2018 test showed that the catalyst could not meet the requirements of denitration equipment. The content of V-Ti-Mo active component in the main chemical composition decreases, the content of alkali metal and alkaline earth metal increases, and the specific surface area of the catalyst decreases, which is the cause of the decrease in catalyst activity.

2) The denitration performance of the catalyst should be tested at least once a year, and the operation status of the catalyst should be monitored in real time, and the related account management should be established to accumulate basic data for catalyst addition or replacement. The equipment maintenance and repair work of the denitration system shall be included in the maintenance plan of the power plant and a strict maintenance and management system shall be formulated. During shutdown, the catalyst should be inspected for sintering, corrosion, wear, blockage, etc., and the deposited dust should be cleaned.

3) For the catalyst that can not meet the denitration equipment, timely replacement and installation, for the actual operating conditions and the original design conditions vary greatly, when adding or replacing the catalyst, the catalyst needs to be re-selected and designed.

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