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# Regeneration of the Deactivated SCR Catalysts

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**This study was for the development of the regeneration technology for the deactivated Selective Catalytic Reduction (SCR) catalysts used in the sintering plant to remove the NOx and dioxins contained in the flue gas. The optimum regeneration conditions were obtained by exploring the relationship between the regenerative process and the NOx and Dioxins removal efficiency. The regenerative process of the deactivated catalysts mainly includes four steps: water washing, acid washing, impregnation and drying. The recovery degree of the NOx removal efficiency for the regenerated catalysts was 105% when compared with the fresh catalysts at 300°C. Meanwhile, the removal efficiency of dioxins can be represented by the removal efficiency measured with 2-chlorphenol precursors. After regeneration, the removal efficiency of 2-chlorophenol was raised from 70% to 88% at 230°C. In comparison, the removal efficiency of dioxins of the regenerated catalysts was shown to be 91% at 250°C, which was close to that of the fresh catalysts. Using the regeneration technology developed in this study, 25 modules of regenerated catalysts were produced and installed at the sintering plant for performance testing. The NOx and dioxins removal efficiency of the regenerated catalyst was shown to reach the target values set by the Factory Acceptance Testing (FAT). Up to now, these regenerated catalysts have been continuously used for three years in the sintering plant and the measured activity is still in line with the set specifications.**

**Keywords: Selective Catalytic Reduction (SCR) catalyst, Regeneration, NOx and dioxin removal**

## 1. INTRODUCTION

Selective Catalytic Reduction (SCR) of Nitrogen Oxides (NOx) with ammonia ($NH_3$) is one of the most effective methods for eliminating the hazardous NOx emission from stationary sources within the narrow temperature window of 300 to 400°C (1). The $V_2O_5$-$WO_3$/$TiO_2$ catalysts are widely used for commercial SCR processes because of its high activity and $SO_2$ resistance(2). For the $V_2O_5$-$WO_3$/$TiO_2$ catalysts, anatase $TiO_2$ acts as a carrier, $V_2O_5$ is the active component, and $WO_3$ performs as the promoter to stabilize the catalyst and prevents the catalyst from sintering. At the same time, the SCR catalyst also has the ability to remove dioxins and convert dioxins to carbon dioxide, water and hydrochloride. Catalysts are the core of the SCR technology that determines the efficiency of the SCR system.

The SCR catalysts are placed in a high dust environment for a long period of time in the sintering plants of China Steel (CSC) and suffer from gradual deactivation during the operational period. The deactivation may attribute to the following factors(3–8): (1) Poisoning- the constituents, such as calcium oxide, potassium, sodium, arsenic, chlorine, fluorine, and lead, deactivate the catalysts by diffusing into active pore sites and occupying them irreversibly. Catalyst poisoning represents the main cause of catalyst deactivation; (2) Thermal sintering- high flue gas temperatures within the SCR reactor cause sintering, a permanent loss of catalyst activity due to a change in the pore structure of the catalyst; (3) Fouling or masking- ammonium sulphate salt, fly ash, and other particulate matter in the flue gas can cause blinding, plugging or fouling of the catalysts. The particulate matter deposits on the surface and in the active pore sites of the catalysts. This brings about a decrease in the number of active sites available for NOx reduction and an increase in flue gas pressure loss across the catalyst; (4) Erosion- impingement of particulate matter and high gas velocities erode the catalyst material. Catalysts with hardened leading edges or increased structural strength are less susceptible to erosion. Increasing catalyst strength through hardening, however, reduces the number of active sites.

To meet the NOx and dioxin emissions standard set by the Environmental Protection Agency (EPA), the sintering plants at CSC have adopted a pipe-end treatment method at the outlet of the sintering process. Owing to the high dust concentrations contained in the flue gas, CSC uses the plate-type SCR catalysts to remove both NOx and dioxins at the same time. These catalysts are often deactivated by alkali metals such as Na, K, Ca, Mg, and Fe, Mn, Cr, Ni, Cu, and other heavy metals and S components which appear in the sintering process environment. Considering the cost and the pollution, regeneration of deactivated catalyst is the priority.

The procedure of catalyst regeneration varies depending on the degree of deactivation. The regeneration method of deactivated catalysts has been reported in literature(11) and mainly includes four steps: (1) dry cleaning- to remove the fly ash attached to the catalyst surface by vacuum evacuation; (2) water washing- to wash out the soluble substances on the surface of the catalysts with water; (3) acid pickling- to leach heavy metal poisoning substances with acid agents; (4) impregnation- to replenish the active ingredients on the surface of the catalysts.

The main objective of this study was to report the relationship between the regeneration process and the NOx and dioxins removal efficiencies for the deactivated SCR catalysts obtained from the sintering plants of CSC.

## 2. EXPERIMENTAL

### *2.1 Regeneration procedure of the deactivated SCR catalysts*

The procedure for regenerating the deactivated SCR catalysts was referred to as the method reported in literature and was shown as follows:

(1) Water washing — to remove the fly ash and anion/cationic components on the surface of the deactivated catalysts by flushing with water;
(2) Acid pickling — to remove the heavy metals from the surface of the deactivated catalysts with acidic solvent;
(3) Impregnation — the catalysts were further treated by immersing in an aqueous solution containing different concentrations of active ingredients, such as Vanadium (V) and Tungsten (W) salts.

### *2.2 Measurement of activity for regeneration catalysts*

2.2.1 Test of the NOx removal efficiency

(1) Granular-type catalysts

The catalytic denitration (deNOx) activities over all regenerated catalysts were evaluated with granular form in a fixed quartz reactor (20 mm internal diameter by 300 mm length) operating at atmospheric pressure. The prepared catalysts (0.3 g with 200 mesh size) were loaded into the reactor between quartz wool and a type-K thermocouple was inserted into the middle of the oven that closed to the catalyst bed to monitor the reaction temperature. The reaction was tested at 300°C with a gas mixture stream consisting of 200 ppm NO, 200 ppm $NH_3$ and 3 vol% $O_2$ with $N_2$ as the balance gas. This reaction gas stream was fed into the reactor through mass flow controllers with a total flow rate of 820 ml/min which was corresponding to GHSV of 5000 $h^{-1}$. At each testing temperature, all the catalysts were kept on the gas stream for 1 hr before the measurements. The NOx conversion was calculated according to the following equation 1:

$$\eta_{NOx} = 100\% \times \frac{NOx_{in} - NOx_{out}}{NOx_{in}} \text{......................(1)}$$

Where $NOx_{in}$ and $NOx_{out}$ are the concentrations of NOx measured at the inlet and outlet of the reactor, respectively.

(2) Plate-type catalysts

The deNOx activity of the plate-type catalysts were measured in a heated micro reactor (Model CATA900, Best Instruments Co. Ltd.) using a catalyst sample size of 20mm×100mm. All connection tubes were made of glass in order to minimize the interactions between the catalysts and the surface of the materials. The reaction was tested at 300°C, which is a standard catalyst operating temperature in sintering plants. The gas mixture stream was composed of $CO_2$ (15 vol%), $O_2$ (3 vol%) and the relevant concentrations of NO and $NH_3$ with $N_2$ as the balance gas. The concentration of NO was amounted to 200 mg/m³ and the corresponding concentration of $NH_3$ was adjusted in order to achieve the $NH_3$/NO mol ratio of 1. The deNOx activity of the plate-type catalysts was then calculated according to the following equation 2:

$$K = - AV \ln (1-\Delta NO) \text{ ............................................(2)}$$

Where K is the activity constant, AV is the area velocity of the gas stream and ΔNO is the NO removal efficiency of the plate-type catalysts. The AV value is usually obtained by dividing the total flow rate by the total catalyst surface area (the geometric surface area, not the BET surface area) and expressed in unit of m/hr. All tests were conducted with an AV value of 51 m/h.

The criterion of the activity constants K for the catalyst sample size of 100mm×20mm is shown as: when the gas flow rate is 3400 ml/min and AV value is 51 m/h, the activity constants K of the fresh catalyst must be equal to or greater than 54.3, 62.5, and 68.1 at 300°C, 350°C, and 400°C, respectively, which were reported in literature and regarded as the criterion K values for the SCR plate-type catalysts(12).

2.2.2 Test of 2-chlorophenol oxidation

A 0.2 g granular regenerated catalyst was placed in a heated glass reactor. The precursor of dioxins — 2-chlorophenol was placed in a washing bottle with the outer layer wrapped with heating tape and the temperature was set at 40°C. The gaseous 2-chlorophenol was carried out with air into a glass buffer vessel and mixed with a $N_2$ stream before entering the reactor. The glass buffer vessel was wrapped with heating tape and the temperature was kept at 230°C to avoid condensation of 2-chlorophenol.

After the reaction, the gaseous 2-chlorophenol at the outlet of the reactor was trapped with an ice bath. The collected 2-chlorophenol sample was diluted with ethanol and further analyzed by Gas Chromatography (GC) with Flame Ionization Detector (FID) as the detector.

2.2.3 Test of dioxins removal efficiency

In general, dioxins mainly consist of two series, one for the dioxins series (an aromatic diether, which two benzene rings are joined by two oxygen bridges), its full name is polychlorinated dibenzo-p-dioxins and referred to as PCDDs; the other for the furan series (an aromatic ether, which two benzene rings are joined by one oxygen bridge), its full name is polychlorinated dibenzo-p-furans and referred to as PCDFs.

The dioxins source was generated by extracting the fly ash obtained from the Electrostatic precipitator (ESP) of the sintering plant with n-hexane. n-Hexane solution was injected into the reaction system by a high precision micro pump and decomposed at 500~550°C before dioxins were carried by air into the glass flow reactor. The generated dioxins concentration was around 5 ng-TEQ/$Nm^3$. Dioxins removal reactions were tested in a glass flow reactor in which the catalyst bed height was 34 mm and the diameter was 12 mm. 0.4 g catalyst sample was mixed with quartz sand in the reactor and the particle sizes of the catalysts were around 1mm in diameter. The reaction temperature was maintained at 250°C, and the inlet total flow rate of the carrier gas (15% $O_2$ with $N_2$) was 320 ml/min. The GHSV of the reaction flow was controlled at around 5000 $h^{-1}$.

The sampling, cleaning and quantification of PCDD/Fs collected at the outlet of the reactor were conducted in accordance with the USEPA Method 23A. The analysis of the 17 dioxin-like and furan-like congeners was performed with a High Resolution Gas Chromatography (HRGC, HP6890 plus) and a High Resolution Mass Spectrometer (HRMS, JEOL JMS-700) equipped with a fused silica capillary column DB-5 MS.

## 3. RESULTS AND DISCUSSION

In order to remove the fly ash, cationic and anion components from the surface of the deactivated catalysts, water washing, acid pickling and impregnation steps were adopted to regenerate the deactivated catalysts. The relationship between the regeneration process and the removal efficiencies of NOx and dioxins were discussed in this study.

As shown in Table 1, the deactivated SCR catalysts after washing with water, the deNOx efficiency was raised from 65% to 72% at 300°C, indicating that the removal of water-soluble substances on the surface can effectively enhance the deNOx activity of the catalysts.

The deactivated catalysts were then further pickled with an acidic solvent and the deNOx efficiency declined to 67% as shown in Table 1. In addition to removing the heavy metal components such as Fe on the surface of the catalysts, the V and W metal active components were also removed simultaneously in the acid pickling process, thereby lowering the catalytic activity of the regenerated catalysts.

In order to improve the catalyst performance, an impregnation method was used to replenish V and W components which had been lost in the acid pickling process. As indicated by the results in Table 1, the deNOx efficiency of the catalysts was increased from 67% to 88% at 300°C after impregnation.

In addition, as shown in Table 2, the activity con-

**Table 1** NOx removal efficiency test for the granular-type SCR catalysts

| Catalyst | Regeneration process steps | | | DeNOx efficiency (%) |
|---|---|---|---|---|
| | Water washing | Acid pickling | Impregnation | 300°C |
| Fresh Catalyst | | | | 87 |
| Deactivated catalyst | | | | 65 |
| Regeneration catalyst | ※ | | | 72 |
| | ※ | ※ | | 67 |
| | ※ | ※ | ※ | 88 |

stants K of the plate-type deactivated SCR catalysts were shown to be 26.5, 34.3, and 40.2 after water washing, but were further declined to 22.4, 28.7, and 31.5 after the acid pickling process at 300°C, 350°C, and 400°C, respectively, which was similar with the results obtained for the granular-type catalysts. The catalysts were further immersed in the solution containing the V and W active ingredients, which resulted in the increase of the activity constants K to 59.5, 70, and 72.8, respectively. The recovery degrees of the NOx removal efficiency after the regeneration process were 105%, 112%, and 107% when compared with those of the fresh catalysts at 300°C, 350°C, and 400°C, respectively.

Besides the formation of NOx, dioxins are also formed in the sintering process. Therefore, the plate-type regenerated catalysts should have the ability to remove dioxins besides removing NOx. Dioxins can be oxidized and cleaved to $CO_2$, $H_2O$, and HCl by SCR catalysts. Since chlorophenols were found to convert into dioxin-PCDD at 250~300°C under the fly ash catalysis(13), this further points to that chlorophenols can be regarded as a precursor of dioxins. Therefore, 2-chlorophenol instead of dioxins was adopted as the reactant in the test of dioxins removal efficiency in this study.

As indicated by the results in Table 3, 2-chlorophenol removal efficiency of the deactivated SCR catalysts was shown to be 70% at 300°C and was raised to 72% after water washing, but dropped to 68% after further pickling with the acid solvent. This was caused by the loss of the V component in the acid pickling process, which would result in the reduction of the oxidation ability of the catalysts. Thus, the efficiency of the removal of 2-chlorophenol on the catalysts was increased to 85% after supplementing V and W components. The effect of the concentrations of V and W active ingredients prepared in the impregnation step on the removal efficiencies of NOx and 2-chlorophenol were also further discussed in the study.

As shown in Table 4, when the respective concentrations of V and W contained in the impregnation solution were 1~2 wt% and 7~8 wt%, the activity constants K were shown to be 51.5, 61.3, and 66.7 for the regenerated catalysts at 300°C, 350°C, and 400°C, respectively. In contrast, when the respective concentrations of V and W were further increased to 3~4 wt% and 8~9 wt%, the activity constants K of the regenerated catalysts were increased slightly to 53.8, 62.4, and 67.9, respectively and then obviously raised to 59.5, 70, and 72.8 after the respective concentrations of V and W were further increased to 5~6 wt% and 12~14 wt%,

**Table 2** NOx removal efficiency test for the plate-type SCR catalysts

| Catalyst | Regeneration processing steps | | | Activity constants K | | |
|---|---|---|---|---|---|---|
| | Water washing | Acid pickling | Impregnation | 300°C | 350°C | 400°C |
| Fresh Catalyst | | | | 54.3 | 62.5 | 68.1 |
| Deactivated catalyst | | | | 18.2 | 28.0 | 31.2 |
| Regeneration catalyst | ※ | | | 26.5 | 34.4 | 40.2 |
| | ※ | ※ | | 22.4 | 28.7 | 31.5 |
| | ※ | ※ | ※ | 59.5 | 70 | 72.8 |
| Activity recovery | ※ | ※ | ※ | 109% | 112% | 107% |

**Table 3** 2-chlorophenol removal efficiency test for the granular-type SCR catalysts

| Catalyst | Regeneration processing steps | | | 2-chlorophenol removal efficiency (%) |
|---|---|---|---|---|
| | Water washing | Acid Washing | Impregnation | 300°C |
| Fresh Catalyst | | | | 84 |
| Deactivated catalyst | | | | 70 |
| Regeneration catalyst | ※ | | | 72 |
| | ※ | ※ | | 68 |
| | ※ | ※ | ※ | 85 |

which were higher than those of the fresh SCR catalysts. On the contrary, when the concentrations of V and W were increased to 7~8 wt% and 15~17 wt%, the activity constants K of the regenerated catalyst were found to decrease to 56.1, 64.5, and 65.7, respectively. This indicates that the regenerated catalysts should have the optimum concentrations of V and W on the surface of the catalysts; otherwise the excess V active ingredient would convert $NH_3$ into NOx, thus lowering the NOx removal efficiency.

Meanwhile, when the respective concentrations of V and W were 3~4 wt% and 8~9 wt%, 2-chlorophenol removal efficiency of the regenerated catalysts was found to be 85% at 230°C, which was close to that of the fresh catalysts, as shown in Table 5.

In order to further confirm the catalytic abilities of the regenerated catalysts, a 56 hours long-term test was conducted on the regenerated catalysts. As indicated by the results in Table 6, the removal efficiencies of NOx and 2-chlorophenol were maintained at 84~85% and 82%, respectively. It can be seen that the regenerated catalysts have quite stable catalytic activities for the removal of NOx and 2-chlorophenol.

Besides, the catalytic activity was also measured with dioxins as the reactant, but only at a temperature of 250°C and GHSV of 5000 $h^{-1}$. The removal efficiencies of PCDDs and PCDFs were shown to be 90.9% and 90.86%, respectively. Thus, the total removal ability of dioxins for the regenerated SCR catalysts was 91%, which were close to the results measured by the fresh SCR catalysts.

From this study, it has shown that he deactivated catalysts can be regenerated through a process of water washing, acid pickling and impregnation with the optimum concentrations of 5~6 wt% V and 12~14 wt% W, and the removal efficiencies of NOx and dioxins

**Table 4** Effect of the concentrations of V and W on the NOx removal efficiency of the regenerated catalysts

| Catalyst | The concentration of the impregnation solution | | Activity constants K | | |
|---|---|---|---|---|---|
| | V (wt %) | W (wt %) | 300°C | 350°C | 400°C |
| Fresh Catalyst | | | 54.3 | 62.5 | 68.1 |
| Regeneration catalyst | 1~2 | 7~8 | 51.5 | 61.3 | 66.7 |
| | 3~4 | 8~9 | 53.8 | 62.4 | 67.9 |
| | 5~6 | 12~14 | 59.5 | 70 | 72.8 |
| | 7~8 | 15~17 | 56.1 | 64.5 | 65.7 |

**Table 5** Comparison of 2-chlorophenol removal efficiency of the SCR catalysts

| Catalyst | The concentration of the impregnation solution | | 2-chlorophenol removal efficiency (%) |
|---|---|---|---|
| | V (wt%) | W (wt%) | 300°C |
| Deactivated Catalyst | | | 70 |
| Regeneration catalyst | 5~6 | 12~14 | 85 |
| Fresh Catalyst | | | 84 |

**Table 6** Long-term activity test of the regenerative catalyst

| Reaction time (hr) | DeNOx efficiency (%) | 2-chlorophenol removal efficiency (%) |
|---|---|---|
| 8 | 85 | 83 |
| 16 | 85 | 83 |
| 24 | 84 | 82 |
| 32 | 85 | 83 |
| 40 | 84 | 83 |
| 48 | 85 | 84 |
| 56 | 84 | 83 |

can be restored to the criterion values set by the fresh catalysts.

Using the regeneration technology developed in this study, Himag Magnetic Corporation (HMC), which is a sub-company of CSC, had completed 25 modules of regenerated catalysts under the technical assistance of CSC. Meanwhile, the regenerated catalysts were installed at the sintering plant for the performance test. The NOx and dioxins removal efficiencies of the regenerated catalysts were shown to reach the criterion values set by the Factory Acceptance Testing (FAT). Up to now, these regenerated catalysts have been continuously run for three years in the sintering plant and the measured activity is still in line with the set specifications.

Besides the regenerated catalysts for sintering plants, HMC regenerated 12 modules coal-fired SCR deactivated catalysts for the power plants of CSC. The recovery degree of the NOx removal efficiency for the regenerated catalysts was 105% when compared with the fresh catalysts at 300°C. The regenerated catalysts have been installed in the power plant and have been operating for 4 months.

## 4. CONCLUSIONS

This study was to regenerate deactivated SCR catalysts which were used in the sintering plants of CSC. The relationship between the regeneration process and the removal efficiencies of NOx and dioxins were discussed and the results were concluded as follows:

1. The optimum concentrations of V and W active ingredients in the impregnation solution were shown to be 5~6 wt% and 12~14 wt% after the deactivated catalysts had been treated with water washing and acid pickling steps. The recovery degree of the NOx removal efficiency for the regenerated catalysts was 105% when compared with the fresh catalysts at 300°C. Meanwhile, the removal efficiency of 2-chlorophenol was raised from 70% to 88% at 230°C.
2. The concentration of V in impregnation solution cannot be too high or $NH_3$ will be oxidized into NOx, resulting in the reduction of NOx removal efficiency of the regenerated catalysts.
3. The removal efficiency of dioxins over the regenerated SCR catalysts was found to be 91% at a temperature of 250°C and GHSV of 5000h-1, which is similar with that of the fresh SCR catalysts.
4. The regeneration technology has been successfully applied to produce 25 modules of regenerated catalysts, and installed at the sintering plant for performance test. These regenerated catalysts have been continuously operating for three years and the measured activities are consistent with the set criterion.

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