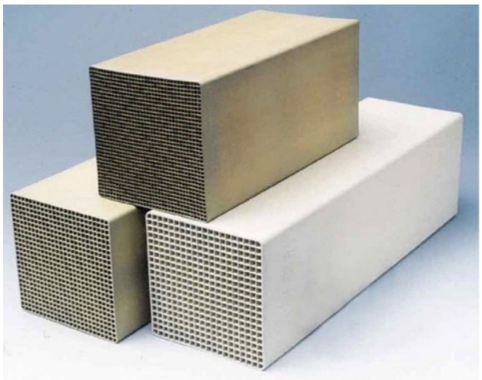
Recycling Technology of De-NOx Catalysts for the Effective Use of Thermal Power Plant's Recycled Resources



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It is essential to efficiently utilize recycled resources for the establishment of a sustainable society. For thermal power plants, the reduction of the amount of wasted valuable and useful resources is also required. Since De-NOx catalysts that detoxify nitrogen oxides (NOx) in combustion exhaust gas contain expensive metals such as titanium and tungsten, there is strong desire for technology to reuse them instead of discarding them after use in power plants. Therefore, Mitsubishi Power, Ltd. (Mitsubishi Power) has developed a technology for reusing De-NOx catalysts used for coal and heavy oil-fired exhaust gas. The technology for reusing spent catalysts not only reduces the amount of waste and the waste disposal costs of our customers, but also contributes to securing rare recycled resources and preserving the global environment.

1. Introduction

The development of dry De-NOx catalysts commenced in the 1960s, and in 1977, the world's first De-NOx device for thermal power generation was commercialized. Since then, De-NOx devices or De-NOx catalysts have been provided to more than 1700 commercial and industrial boilers or gas turbines[(1)].

A De-NOx catalyst is one of the key components of a De-NOx device that detoxifies NOx in the combustion exhaust gas. With the evolution of boilers and gas turbines, the development of NOx catalysts has continued so that solutions that meet the needs of our customers can be provided.

This report describes the catalyst improvement development that Mitsubishi Power has implemented in recent years as a technology for reusing De-NOx catalysts contributing to the reduction of waste from thermal power plants.

2. Technology for reusing De-NOx catalysts for coal-fired power plants

When ash (fly ash) generated by the combustion of coal flows through the gas passage hole of the honeycomb catalyst together with the exhaust gas, components such as calcium in the fly ash gradually adhere to the inner wall surface of the gas passage hole and the NOx removal reaction on the catalyst surface is inhibited. In addition, the fly ash itself partially accumulates inside the gas passage hole, which makes the exhaust gas flow difficult, and ultimately the gas passage hole becomes completely plugged and the NOx removal performance decreases. As a measure to maintain the NOx removal function, it is necessary to replace the spent catalyst periodically with a fresh one. However, De-NOx catalysts contain rare valuable resources such as titanium, tungsten and molybdenum, so the fresh one is expensive. For this reason, there is a strong need to reduce De-NOx catalyst renewal costs and waste (spent catalyst) treatment costs. Therefore, reusing spent

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catalysts that were previously discarded not only contributes to the reduction of waste from power plants, but also contributes greatly to the establishment of a sustainable society and the conservation of the global environment.

We have commercialized a regenerated catalyst that has NOx removal performance the same as that of a fresh one by removing the substances that cause the deterioration of the NOx removal reaction over time, and then applying an activation treatment of coating the surface with fresh catalyst components[(1)(2)]. Two types of regenerated catalyst manufacturing methods have been established: Ecotype I, which uses the spent catalyst removed from the De-NOx reactor as-is as a honeycomb substrate , and Ecotype II, which crushes the spent catalyst to make a raw material and then shapes it into a honeycomb shape for use as a substrate. Ecotype I uses the spent catalyst as a substrate as-is, so if the spent catalyst has significant cracks or damage, it cannot be reused and needs to be replaced with a fresh catalyst. On the other hand, Ecotype II crushes the spent catalyst to make a raw material and then shapes it into a honeycomb shape for producing a substrate, so a damaged catalyst can be effectively regenerated. The coating layer of the fresh catalyst component provided on the honeycomb catalyst by the activation treatment has been proven to have excellent durability due to the bimodal coating technology using our unique two-particle-size catalyst shown in **Figure 1** even in a coal-fired boiler exhaust gas environment where a large amount of fly ash is present. Both Ecotype I and Ecotype II have already been used in many plants.

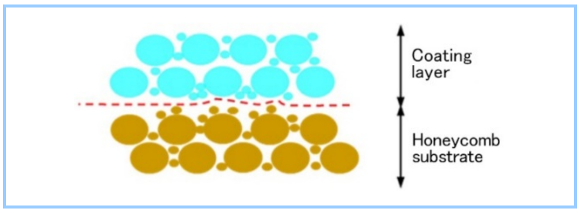

Figure 1 Schematic diagram of bimodal coating technology using two-particle-size catalyst
This figure indicates that a coating layer is provided on the honeycomb catalyst. The size of the circles in this figure indicates the coating particle size. A stable coating layer is formed by our unique bimodal coating technology.

Furthermore, in recent years, we have developed a chemical cleaning technology that restores the NOx removal performance of spent catalysts by cleaning them with a unique chemical in order to deal with various substances that cause deterioration over time. This technology can remove not only fly ash and the calcium component contained in fly ash, but also catalyst poisoning components causing the deterioration of the catalyst that cannot be removed by cleaning with water. Catalysts regenerated using this technology have a small amount of highly-insoluble catalyst poisoning component residue, and the NOx removal performance is slightly lower than that of a fresh catalyst, but we used our unique chemical to realize an optimal cleaning process that does not require activation (**Figure 2**). As a result, significant recovery of the NOx-removal performance without increasing the SO_2 oxidation rate compared with the spent catalyst before cleaning was made possible (**Figure 3**). Catalyst regeneration using chemical cleaning technology is applied to each of the catalyst modules, so the process is simple (**Figure 4**). This technology can satisfy the demands of our customers for short delivery times, while also being economical. With this technology, we succeeded in greatly expanding the after-sales service options for catalyst replacement and have already successfully completed the catalyst regeneration work for coal-fired power plants in Japan. We have also demonstrated that the catalysts regenerated using this technology have excellent durability.

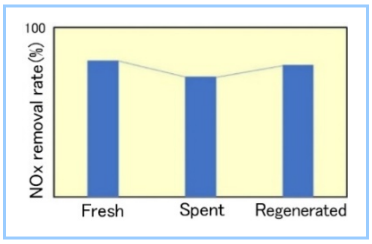

Figure 2 Comparison of De-NOx performance

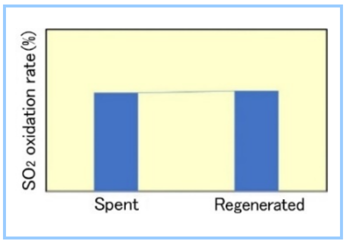

Figure 3 Comparison of SO_2 oxidation rate

Figure 4 Photograph of catalyst cleaning

3. Technology for reusing De-NOx catalysts for heavy oil-fired plants

In the case of a heavy oil-fired power plant, when dust generated by combustion flows through the gas passage hole of the honeycomb catalyst together with the exhaust gas, components such as vanadium contained in the fuel gradually adhere to the inner wall surface of the gas passage hole and the NOx removal reaction on the catalyst surface is inhibited. Vanadium is known to be a component that increases the SO_2 oxidation rate of De-NOx catalysts and when deposited on the catalyst, not only decreases the NOx removal performance over time, but also increases the SO_2 oxidation rate. Since this vanadium compound contains an insoluble compound and is firmly deposited on the catalyst, it was difficult to remove the insoluble compounds to restore NOx removal performance while reducing the SO_2 oxidation rate.

Therefore, in order to remove the firmly deposited insoluble vanadium compound, we developed a cleaning and regeneration technology using our unique chemical. This technology can selectively remove the insoluble vanadium compound, which is a component that inhibits catalyst performance, while suppressing the elution of active vanadium components contained in the catalyst in order to control the NOx removal performance. We realized an optimal cleaning process that does not require activation by using our own chemicals and developing an efficient cleaning method. As a result, the NOx removal performance was restored to almost the same level as the fresh catalyst and the SO_2 oxidation rate could be significantly reduced compared to that before cleaning (**Figure 5** and **Figure 6**). Similar to the regeneration of catalysts for coal-fired plants, this catalyst regeneration using chemical cleaning technology is applied to each of the catalyst modules, so the process is simple. This technology can satisfy the demands of our customers for short delivery times, while also being economical (**Figure 7**). We have successfully completed the catalyst regeneration work for heavy oil-fired power plants in Japan using this technology and have also demonstrated that the regenerated catalysts have excellent durability.

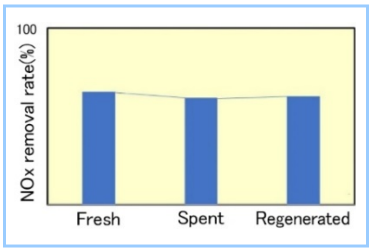

Figure 5 Comparison of De-NOx performance

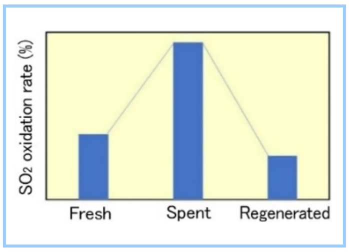

Figure 6 Comparison of SO_2 oxidation rate

Figure 7 Photograph of catalyst cleaning

4. Conclusion

In recent years, there has been demand for catalyst reuse technology that can contribute not only to reducing waste from thermal power plants, but also to environmental conservation. Therefore, Mitsubishi Power has developed (1) technology for reusing spent De-NOx catalysts for coal-fired plants and (2) technology for reusing spent De-NOx removal for heavy oil-fired power plants. Currently, both reuse technologies have been put into practical use. In the future, it is expected that the effective utilization of recycled resources will be promoted toward the establishment of a sustainable society, and that waste including valuable resources from power plants will be reduced. We will continue to respond to customer requests and accelerate related development in order to offer NOx removal device that can contribute to environmental conservation and resource security, while also being economical.

References

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