

THE COMBINED SO_x / NO_x / AIR TOXICS REDUCTION PROCESS USING ACTIVATED COKE FOR FLUE GAS CLEANUP

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INTRODUCTION

The dry desulfurization and denitrification process using activated coke(AC) as a dry type flue gas cleanup technology was originally researched and developed during the nineteen-sixties by Bergbau Forschung(BF)¹⁾, now called Deutsche Montan Technologies. Mitsui Mining company(MMC) concluded a licensing agreement with BF in 1982 to investigate, test and adapt the system to the facilities in Japan where the regulations are stricter towards SO_x/NO_x pollutants, as well as dust emissions from utility industries, oil refineries, and other industries. There are three commercial plants of this process installed to coal fired boiler, FCC units, and incinerator in Japan and two plants in Germany(the latter two plants were constructed by Uhd GmbH). Recently, the capability of AC process to adsorb and reduce toxic trace materials, such as Hg vapor and dioxines, is attractive for flue gas cleanup of waste incinerators or coal combustion boilers. General Electric Environmental Services, Inc.(GEES) signed a license agreement in 1992 with MMC. Under this agreement, GEESI will market, design, fabricate and install the AC process for flue gas cleaning applications in North America.

MMC also developed a technology to produce activated coke to be used in the DeSO_x/DeNO_x process, based on our own metallurgical coke manufacturing technology. The commercial plant with the capacity of 3,000tons per year to produce MMC's activated coke has been in operation. We have a plan to construct a larger plant of activated coke production in Japan preparing for the increase of demands for AC process in the near future.

In this paper, we would like to present some data of DeSO_x, DeNO_x and toxic removal with MMC's AC, which include basic data from laboratory tests, characteristic data of sampled AC from test plants, and performance data of commercial plants. Furthermore, we will put a focus on the relationship of the DeSO_x and DeNO_x activities of AC to the surface functionalities of chemically modified AC in both labo. tests and pilot tests.

MMC's ACTEVATED COKE AND GE-MITSUI-BF PROCESS

Activated coke(AC) is a formed carbonaceous material designed for dry DeSO_x/DeNO_x and Toxic removal process of flue gas cleanup. For this purpose, we selected a suitable raw coal from bituminous coals and investigated an appropriate process for production²⁾, which include a pretreatment of raw coal, blending of raw materials, briquetting, carbonization and activation, to give AC high DeSO_x/DeNO_x activities and high mechanical strength against abrasion and crush during circulation and handling in the flue gas cleanup process.

There are several differences in characteristics of MMC's AC compared to an activated carbon using criteria such as gas recovering or deodorizing processes. BET surface area of MMC's AC is 150-250m²/g, which is less than one-third that of activated carbon. BET surface area of the carbon materials represents their micro-porous structure, which becomes larger during the manufacturing process where the chemical activation condition is severe. As the activation becomes more severe, the yield of the product decreases and the mechanical strength of the product falls. A decrease in yield results in increased product cost and a decrease in mechanical strength causes greater material loss during the flue gas cleanup process. As MMC's AC is processed with a temperate activation procedure, it is one-fourth to one-third the price and has a higher mechanical strength compared to activated carbon. MMC's AC also has advantages in its abilities to remove SO_x and NO_x as compared with activated carbon.

Figure 1 illustrates a schematic of the GE-Mitsui-BF DeSO_x/DeNO_x/Toxic removal process, which is designed for SO_x/NO_x containing flue gas treatment system consisting of twin AC beds and an AC regenerator. In this system, AC moves continuously from top to bottom through the AC beds. The regenerated AC with some part of fresh make-up AC enters in DeNO_x zone(I) at first, where NO_x reduction occurs with the addition of NH₃. The discharged AC from I enters into DeSO_x zone(II), where the majority of the SO_x and air toxics adsorption and the minor NO_x reduction without NH₃ (we call now non-SCR DeNO_x) occur. The SO_x/air toxics-loaded AC discharged from II is sent to the regenerator by bucket conveyers. In the case of NO_x with low-SO_x or SO_x with low-NO_x containing flue gas treatments, single AC bed system can be designed. Table 1 summarizes a designed system, efficiencies and applications of GE-Mitsui-BF process.

DESULFURIZATION (DESOX) WITH ACTIVATED COKE

Figure 2 shows the SO₂ adsorption capacity of activated coke and a commercial activated carbon with fresh one and used one. With fresh one, the SO₂ adsorption capacity becomes higher as surface area of adsorbent increases. On the other hand, with used one, which has experienced four times of desulfurization-regeneration cycle of labo. test, SO₂ adsorption capacity of the used activated carbon drastically decreased to about one-third of the fresh one, while the used activated cokes, having lower surface area and still less micro-porous than activated carbon, are less influenced. There has been several observations^{3, 4)} of the similar phenomenon with activated carbons of those surface area ranging 300-900m²/g, where a marked decrease in adsorbed SO₂ amount along with cycle has been explained due to the increase in the amount of acidic groups on the surface of activated carbons. It is supposed that there is an appropriate activation level where the SO₂ adsorption capacity is less influenced with the cycle of SO₂ adsorption-desorption. MMC's activated coke seems to be on a such level. It has been confirmed that MMC's activated coke keeps a stable deSOx performance during the process⁵⁾. Table 2 shows the characteristics and the deSOx activities measured in labo. test with MMC's activated coke, fresh one and used ones, which were sampled from two test plants under operation. Used ones are characterized with an enlarged surface area, an increased O/C and N/C values, and an enhanced deSOx activity than fresh one. These changes in characteristics are derived from operation conditions, such as the molar ratio of adsorbed NH₃-SOx species on AC and the types of reactions(oxidation-reduction) between NH₃-SOx species and AC surface in regenerator. It is noticeable that the surface area and O/C value are higher in used I (the adsorbed NH₃/SOx molar ratio is approx. 0.2) and N/C value is higher in used II (the ratio is approx. 1.5). The increased deSOx activities(η SOx %) of used AC to fresh one relate to both the surface area enlargement and the modified surface functionality. It is supposed that k(rate constant) especially correlates to N/C and q₀ (adsorption capacity) relatively correlates to surface area. η SOx is the highest in used II, supporting that N/C is the most influencing factor to deSOx rate. It has been reported that nitrogen-containing activated carbon⁶⁾ and activated carbon fiber⁷⁾ from PAN and brown coal char via sulfuric acid activation followed by ammonia treatment⁸⁾ show the remarkable high deSOx activities.

DENITRIFICATION (DENOX) WITH ACTIVATED COKE

Figure 3 shows the profiles of two types DeNOx(SCR and non-SCR) reactions in labo. tests with the used II AC(Table 2), which exhibited a high non-SCR DeNOx activity. Non-SCR DeNOx proceeds without NH₃ in gas phase and an active N-species on AC surface seems to react with NOx, because non-SCR activity is deactivated along with reaction time. NH₃ treatment at 400-500 °C is effective to reactivate AC for the non-SCR reaction. There has been several observations of the effects of NH₃ treatment to the preoxidized activated carbon⁹⁾ and brown coal char¹⁰⁾ on the enhancement of their SCR DeNOx activities. Now, we would like to put attention upon the non-SCR DeNOx activity of AC and have interest in the effect of NH₃ treatment on the non-SCR DeNOx activity of AC, because the non-SCR DeNOx is useful as a no NH₃ leakage process for flue gas cleanup with AC. We can expect to remove approx. 10-20% of inlet NOx concentration with non-SCR DeNOx in the DeSOx zone, where no NH₃ is added in gas phase, under coexisting of high SOx concentration in the DeSOx/DeNOx proces(Figure 1). The efficiency of non-SCR DeNOx becomes higher in proportion with lowering of inlet NOx concentration. Figure 4 shows approx. 60-70% high efficiencies of non-SCR DeNOx with 24ppm of inlet NOx concentration. Figure 4 also shows the increasing non-SCR DeNOx efficiency along with a cycle testing, where simultaneous deSOx/deNOx run, regeneration after the run and NH₃ treatment at 500 °C to the regenerated AC were cycled 10 times, showing the effect of NH₃ treatment. DeSOx efficiency is also increasing with this cycle test, supporting the effect of NH₃ treatment on the DeSOx activity of AC(former discussion). Figure 5 shows the increasing non-SCR DeNOx efficiency with increase of NH₃ treatment amount. Although we scarcely have informations to identify an active N-species on AC surface, it is probably thinkable that an active N-species being produced by NH₃ treatment contributes to the non-SCR DeNOx reaction.

TOXIC REDUCTION WITH ACTIVATED COKE

The AC process can also remove trace toxic compounds such as mercury and dioxines that are present in waste incinerator flue gas. Several pilot and demonstration tests^{10, 11)} have been done to confirm the ability of the AC process to remove NOx and trace toxic compounds with AC from waste incinerator flue gas at low temperature, where the mercury removal efficiencies of approx. 80-90% at 150-180 °C and the dioxines removal efficiencies of approx. 90-98% at the same temperature range were observed.

CONCLUSION

- The dry DeSO_x/DeNO_x/Toxic removal process with activated coke is applicable for various flue gas cleanup with high efficiencies (Table 1).
- Activated coke has an appropriate activation level where the SO₂ adsorption capacity is less influenced with the cycle of SO₂ adsorption-desorption. It has been confirmed that MMC's activated coke keeps a stable deSO_x performance during flue gas cleanup process. It is supposing that N/C value of AC is influencing factor to the deSO_x activity.
- Activated coke has non-SCR DeNO_x activity, which proceeds without NH₃ in the gas phase. The non-SCR DeNO_x is useful as a no NH₃ leakage process for flue gas cleanup. It is supposing that an active N-species being produced by NH₃ treatment at 400-500 °C contributes to non-SCR DeNO_x reaction.
- Activated coke can also remove trace toxic compounds such as mercury and dioxines with high efficiencies from flue gases of waste incinerators and coal combustion boilers at low temperature.

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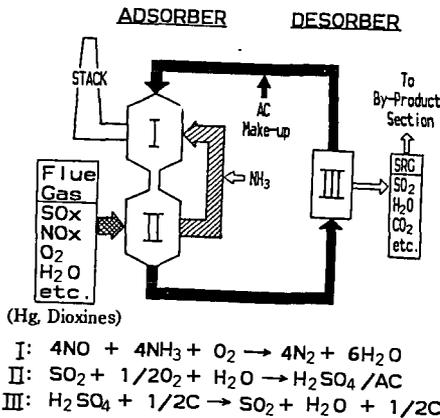


Figure 1 : The combined SO_x/NO_x/Air toxics reduction process using AC
 (GE-Mitsui-BF Process / Schematic flow diagram with twin AC beds)

Table 1 : A designed system and efficiencies of GE-Mitsui-BF process applications

| Flue Gas | Designed system | Efficiencies | Applications |
|------------------|-----------------|--|---|
| SOx and NOx | Twin AC beds | <ul style="list-style-type: none"> η SOx \geq 98% η NOx \geq 80% | <ul style="list-style-type: none"> Utility boilers RFCC Units Other industries |
| NOx with-low SOx | Single AC bed | <ul style="list-style-type: none"> η NOx \geq 80% η SOx \geq 98% | <ul style="list-style-type: none"> FBC boiler Waste incinerator (After pre-scrubber) |
| SOx with low-NOx | Single AC bed | <ul style="list-style-type: none"> η SOx \geq 98% non-SCR DeNOx expected | <ul style="list-style-type: none"> Combination with other DeNOx system |

All systems can remove trace toxic materials such as Hg vapour and dioxines with high efficiencies.

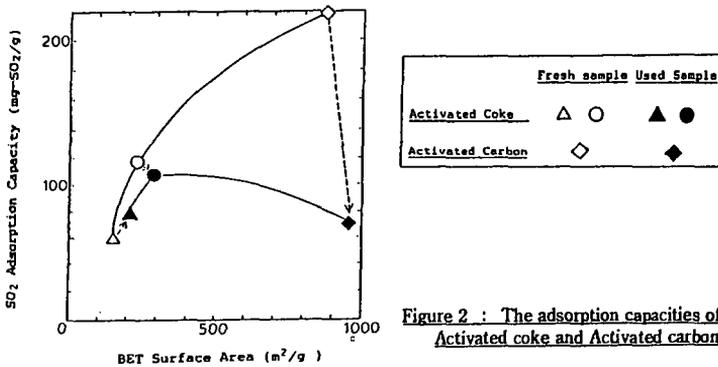


Figure 2 : The adsorption capacities of Activated coke and Activated carbon

- Used samples are those after the 4th cycle of deSOx (SO : 2000ppm, O : 5%, H : O 10%) at 130 °C and regeneration under N₂ at 400 °C .
- SO₂ adsorption capacity was measured by contacting 10cc of AC sample with SO₂ containing gas flow (SO : 2%, O : 5%, H : O 10%) at 100 °C for 3hours.

Table 2 : The characteristics and DeSOx activities of sampled AC from test plants

| AC sample | Surface area(m ² /g) | | Elemental analysis | | DeSOx Activity [labo. test] | | |
|-----------|---------------------------------|--------------------|--------------------|-------|-----------------------------|----------------------|------------------------------------|
| | S(CO ₂) | S(N ₂) | O/C | N/C | η SOx(%) | k(10 ⁻⁴) | q _o (10 ⁻²) |
| Fresh | 150 | 150 | 0.019 | 0.012 | 64.7 | 3.87 | 0.87 |
| Used I | 300 | 500 | 0.073 | 0.034 | 91.3 | 4.62 | 2.15 |
| Used II | 230 | 270 | 0.046 | 0.040 | 98.3 | 5.82 | 1.78 |

- Used I and II were sampled at the operation time of approx. 4000hours from the outlet of regenerator of test plant I and II, respectively.
 - Test plant I was a DeSOx/DeNOx plant with twin AC beds as illustrated in Figure 1. NH₃ was added after DeSOx zone(II). The adsorbed NH₃/SOx molar ratio was approx. 0.2 [SOx rich] with AC of the inlet of regenerator.
 - Test plant II was a DeNOx plant with single AC bed, which is almost equivalent to the DeNOx zone(I) in Figure 1. The adsorbed NH₃/SOx molar ratio was approx. 1.5 [NH₃ rich] with AC of the inlet of regenerator.
 - DeSOx activity was measured by contacting 4.3 liters of AC sample with 28.7 liters of SO₂ containing gas flow (SO₂ 2000ppm, O : 5%, H : O 10%) at 130 °C .
- η SOx is the DeSOx efficiency(average of integration during 25 hours reaction)
k is the deSOx reaction rate constant.
q_o is the amount of adsorbed SO₂ at equilibrium condition.

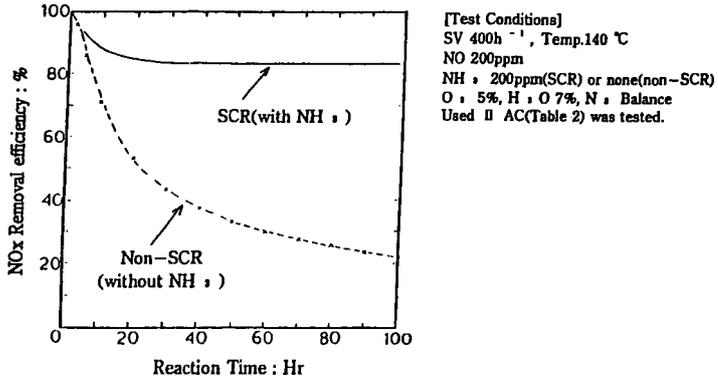


Figure 3 : The DeNO_x profile of SCR and Non-SCR reactions on Activated coke

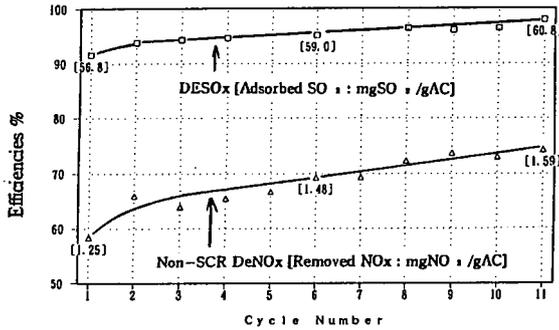


Figure 4 : The effect of NH₃ treatment on Non-SCR DeNO_x and DeSO_x activities of AC

- DeSO_x/DeNO_x Run Conditions : SV 400h^{-1} , Temp. 140°C , Time 70Hr
 NO 24ppm, SO₂ 500ppm, NH₃ 250ppm, O₂ 5%, H₂O 7%, N₂ Balance
- NH₃ will react with SO₂ almost selectively. SCR DeNO_x can't proceed.
- Efficiencies denotes an average of integration during 70 hours reaction.
- NH₃ leakage was not detected during the DeSO_x/DeNO_x test run.
- NH₃ treatment (1.48ccNH₃ /ccAC) was done at 500°C to the regenerated AC
- Testing AC is a used AC sampled from another test plant differing from I, II (Table 2).

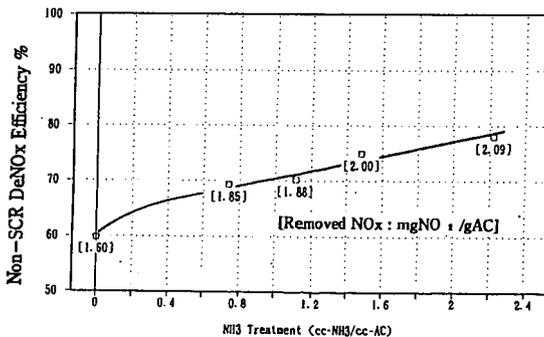


Figure 5 : Increasing Non-SCR DeNO_x activity with increase of NH₃ treatment amount

- Test conditions is the same as Figure 4.
- Used II AC(Table 2) was tested.