A Study on Desulphurization of Flue Gases by the Active Carbon Process Using Steam Desorption (Part 4)

—Deterioration and Regeneration of Active Carbon*—

by Yasumi Kamino**, Kenji Yasuda** Shiro Inoue** and Shigenori Onitsuka**

Summary: As a way to clarify the causes for deterioration of sulphur dioxide adsorption capacity of active carbon, the environmental conditions which bring deterioration to active carbon were investigated. The results indicated that exposure to oxygen at a temperature level of around 300°C gives large influence on sulphur dioxide adsorption capacity of active carbon.

Consequently, the relationship among the degree of activity for sulphur dioxide, concentration of oxygen in the atmosphere, temperature of the gas, and exposure time to oxygen was investigated. The results clarified that all these factors are related to deterioration of the degree of activity.

Then, regeneration method of the deteriorated active carbon was studied, that is, the deteriorated active carbon was heated at 300~800°C in the various surrounding gases.

After this treatment, change in sulphur dioxide adsorption capacity of active carbon was investigated. It was clarified that the deteriorated active carbon is regenerated nearly to the initial capacity of original active carbon when heated at 550°C and 730°C respectively in the hydrogen stream and the other gases.

1 Introduction

Authors have made a long run test on the test plant for desulphurization of flue gases by the active carbon with flue gas desulphurization capacity of 1,200 Nm³/hr. As was reported in the previous paper¹⁾, it was clarified that deterioration of sulphur dioxide adsorption capacity of active carbon takes place. There are few reports about this phenomenon. Therefore, along with the study on properties of deteriorated active carbon, the environmental conditions which invite deterioration of active carbon were investigated to clarify the causes for deterioration. And for regeneration of sulphur dioxide adsorption capacity of deteriorated active carbon, heat treatment experiments have been conducted. The results are reported in this paper.

2 Simulation Tests of Deterioration

It was planned to investigate the causes for deterioration by the following procedures.

(1) The environmental conditions which were given to the active carbon in the test plant

operation were picked up and arranged.

(2) Then several kinds of simplified experimental conditions were established for the scale of beaker test. Through long run test, the change in sulphur dioxide adsorption capacity was investigated. From this results, the environmental conditions which may indicate the causes for deterioration were selected.

(3) Experiments in order to make detailed observation on the estimated conditions being the factors for deterioration were conducted. Then, it was confirmed that the deterioration phenomenon which occurred in the test plant operation is reproduced.

2.1 Experimental Methods and Apparatus

Table 1 shows the conditions of experiments conducted. **Fig. 1** illustrates the apparatus used for the experiments. The following is an explanation on Experiment No. 1 among those in **Table 1**.

As the first step, the mixed gas consisted of carbon dioxide, oxygen and nitrogen was introduced to the system at a flow rate of 1.5 l/min from the gas cylinder. The gas was saturated with steam in the humidity bath *W* located in the thermostat 1 with 50°C, and was introduced into the tube *R* packed with active carbon. In front of the solenoid valve *V*₂, the gas was mixed

* Received June 15, 1972.

** Technical Research Laboratory, Hitachi Shipbuilding & Engineering Co., Ltd. (60, Kitano-cho, Sakurajima, Konohana-ku, Osaka, Japan)

Fig. 1 Experimental Apparatus I

Table 1 Experimental Conditions

No.	Experimental Conditions
1	SO ₂ + CO ₂ + H ₂ O + O ₂ + N ₂ → H ₂ O (+air) (120°C, 5 hr) 40 cycles (300°C, 1 hr)
2	CO ₂ + H ₂ O + O ₂ + N ₂ → H ₂ O (+air) (120°C, 5 hr) 40 cycles (300°C, 1 hr)
3	N ₂ → H ₂ O (+air) (120°C, 5 hr) 40 cycles (300°C, 1 hr)
4	H ₂ O (+air) (300°C, 40 hr)
5	N ₂ (300°C, 40 hr)
6	N ₂ + 5% O ₂ (300°C, 40 hr)

with sulphur dioxide sent from the gas holder by the plunger type constant feed pump. Thus the gas was prepared into the state of simulated nitrogen-based flue gas consisting of sulphur dioxide 1,500 ppm, carbon dioxide 12%, oxygen 4% and water 12%. Sulphur dioxide in the gas was adsorbed in the tube packed with active carbon installed in the thermostat of 120°C. After this process, the gas was introduced to the infra-red ray type sulphur dioxide analyzer for measurement of the remaining sulphur dioxide

concentration. The same fresh active carbon as used for the test plant was used for this test. 20.0 g of the active carbon was packed in the tube R. The adsorption time was set for 5 hours by the timer. After the set time, all the valves were closed, and the temperature of thermostat was increased. After about two hours, the temperature was reached to 300°C. At the same time, steam was sent to the above-mentioned tube R packed with active carbon through the steam trap S_T from the laboratory size steam generator. In this time, sulphur dioxide adsorbed on active carbon was desorbed. The mixed gas consisting of sulphur dioxide and steam was cooled by the cooler, and separated into condensate and non-condensed gas. After one hour, the temperature was decreased. The solenoid valve V_4 was opened, tap water flowed into the cooler to cool to 120°C after about 30 min. When the temperature was reached to 120°C, the solenoid valve and the pump started to operate and became the same state as the original state, namely

the second adsorption process.

The above-mentioned process was taken as one cycle. 40 cycles of adsorption and desorption were conducted. The sulphur dioxide adsorption capacity of the sample after treatment was measured by the adsorption amount measuring equipment as explained in the previous paper²⁾.

No. 2 and further experiments were carried out in accordance with the method similar to the method for Experiment No. 1 as described above.

As the conditions of experiments showed in **Table 1**, desorption by the state of pure steam was not possible contrary to our intent, because air came in to the steam when draining through the steam trap in steam desorption process. For the test under the atmospheric conditions consisting of nitrogen and oxygen (to be explained in the following chapter), the same equipment was employed with the different program suitable for the conditions. For some samples after treatment, benzoic acid and diphenylguanidine were adsorbed to measure the adsorption amounts of acidic and basic groups. This measurement method was reported in the previous paper.

2.2 Experimental Results and Consideration

2.2.1 Simulation Tests of Deterioration

Fig. 2 illustrates the plotted results of the change in sulphur dioxide adsorption capacity to the number of cycle of adsorption/desorption as calculated from the data of test plant and the breakthrough curve of sulphur dioxide concentration at the outlet of active carbon layer in the test No. 1. This was done in order to check whether the test that was thus conducted reproduced the deterioration took place in the test plant. It can be judged that the test showed nearly same trend of virtual deterioration as that in the test plant.

Table 2 shows the results of adsorption capacity tests on new active carbon, deteriorated active carbon through the test plant experiment, and

Fig. 2 The Result of Deterioration Test No. 1

Table 2 Experimental Results

Sample	Adsorbed SO ₂ [$\frac{\text{mg-SO}_2}{\text{g-C}}$]	Degree of Activity to SO ₂ α [-]
Original Active Carbon	55.5	1.00
Deteriorated Active Carbon	19.6	0.353
No. 1	22.8	0.411
No. 2	23.2	0.418
No. 3	29.2	0.526
No. 4	37.0	0.667
No. 5	58.4	1.052
No. 6	35.0	0.630

samples through treatments Nos. 1 through 6. The degree of activity α in **Table 2** is the adsorption amount ratio between the new active carbon and each treated sample adsorbed for 5 hours.

From the results of **Table 2**, the following statement can be made.

(a) Active carbon does not show deterioration when heated to 300°C in the environment of nitrogen.

(b) The results of Experiment No. 2 and further experiments, it is clear that deterioration takes place even without sulphur dioxide adsorption and desorption.

(c) The conditions of experiments which showed deterioration indicated a common factor that active carbon was heated to 300°C with the presence of oxygen.

From these experimental results, it was estimated that oxygen gives a large influence on deterioration of active carbon. Consequently, the following study was made.

2.2.2 Influence of Oxygen on Deterioration of Active Carbon

In accordance with the method of previous experiment, active carbon samples were treated by oxygen-nitrogen mixed gas. Then the change in sulphur dioxide adsorption capacity of active carbon after the treatment was investigated. **Fig. 3** and **4** illustrate the results of this experiment.

As is clear from these figures, deterioration of active carbon in the presence of oxygen develops further when the oxygen concentration is higher. It is also clear that existence of even very small amount of oxygen rapidly accelerates deterioration. In this case, temperature gives a special influence. At 150°C, the rate of deterioration is small. However, at 350°C, deterioration develops rapidly.

Fig. 5 and **6** show the relationship between the acidic and basic groups adsorption amounts

Fig. 3 The Effect of O₂ Concentration Fig. 4 The Effect of Contact Time in O₂ Containing Gas

of samples after treatment and the degree of activity. From this result, it can be estimated that in the environment with oxygen at the high temperature within the scope of experiment, increase in acidic group and decrease in basic group take place in the surface oxides of active carbon. This results in deterioration of sulphur dioxide adsorption capacity.

From the results of experiments as described above, the deterioration process of active carbon in the test plant can be assumed as follows.

It is considered that the state of inside of desorber is the most serious condition for deterioration. When the active carbon flows into the desorber from the hopper of desorber, air contained among the particles of active carbon and air contained in the pores of active carbon are brought in. Because of high temperature of desorber being 300°C, the existence ratio of surface oxides of active carbon changes in the environment with oxygen. It is judged that this fact invited deterioration in sulphur dioxide adsorption capacity.

The results of this experiment also indicate

Fig. 5 Relation between Adsorption Amount of D.P.G. and Degree of Activity to SO₂ Fig. 6 Relation between Adsorption Amount of B.A. and Degree of Activity to SO₂

possibility of very slow deterioration due to oxidation even at a temperature level of around 150°C. For this reason a special attention must be paid to the adsorption process.

3 Regeneration of Deteriorated Active Carbon

In the preceding chapter, it was assumed that the deterioration is invited by the change by oxygen of surface oxides of active carbon which function effectively for sulphur dioxide adsorption.

As to the surface oxides of active carbon and their formation temperature, it has been reported^{3),4)} that the acidic surface oxides are formed at 300~800°C (especially 400~500°C), and basic surface oxides start to exist at 800~1,000°C. This formation is reported to be influenced by the partial pressure of oxygen. It was expected that the deteriorated active carbon might be activated by heat treatment. Authors employed the deteriorated active carbon obtained from the test plant as samples.

The samples were heat-treated in the atmosphere with various kinds of gases. And the

degrees of regeneration in sulphur dioxide adsorption capacity were measured.

3.1 Experimental Method

Fig. 7 illustrates the apparatus for experiment. The tube for sample having an inner diameter of 23 mm and an overall length of 450 mm was made of stainless steel. The tube was inserted into the cylindrical electric furnace for heating, 20.0 g of deteriorated active carbon from the test plant was packed in the test tube as sample. Steam from the laboratory size steam generator and nitrogen, hydrogen, carbon monoxide, carbon dioxide from gas cylinders were used for the gases for treatment. These gases were flowed by switching with the three-way cock in accordance with the experimental conditions. As the procedures of experiment, the sample carbon was packed in the test tube, sealed with nitrogen, and heated to the specified temperature. After arriving at the set temperature, the gas for treatment was flowed for the specified hours at a flow rate of 1 l/min. Then it was sealed again with nitrogen and cooled. The sulphur dioxide adsorption capacity of treated active carbon was

Fig. 7 Experimental Apparatus 2

Fig. 8 The Effect of Temperature to Degree of Activity to SO_2

measured by the adsorption capacity testing equipment explained in the previous paper²⁾.

3.2 Experimental Results

Fig. 8 and **9** illustrate the results of experiment. From these results, it has been clarified that the sulphur dioxide adsorption capacity can be regenerated by heat-treatment. Degree of regeneration in adsorption capacity becomes higher when the treatment temperature is higher regardless of the kind of treatment gas used. The deteriorated active carbon is regenerated to show the initial adsorption capacity when heated to 550°C and 730°C respectively with hydrogen and other kinds of gas. Treatment for regeneration was not done at a higher temperature than 800°C. It is considered that deterioration in activity may occur when heated to a temperature higher than 1,000°C due to start in crystallization of graphite³⁾. This means that further increase in treatment temperature will not result in proportional increase in the sulphur dioxide adsorption capacity.

The influence of treatment hours, namely, the minimum treatment hour for regeneration was not investigated in this experiment. As is clear from **Fig. 9**, the influence on the adsorption capacity is small if the time is over 30 min. A study result on the change in weight of active carbon before and after treatment indicated a proportional relationship between the degree of activity and the decrease in weight. Particularly when steam was used, the decrease was larger.

The adsorption amounts of benzoic acid and diphenylguanidine by the samples after treatment were measured.

As is illustrated in **Fig. 10**, it was confirmed,

Fig. 9 Relation between Treatment Time and Degree of Activity to SO_2

Fig. 10 D.P.G. and B.A. Adsorption Amount of Regenerated Carbon

to the contrary to the case of deterioration, the active carbon with regenerated sulphur dioxide adsorption capacity after regeneration treatment shows decrease in acidic group and increase in basic group. Effect of hydrogen as a strong reducing gas was predicted. From the facts that the existence ratio of surface oxides is changed even by simple heating in an inert gas and the amount of consumption becomes large proportionally with the improvement in sulphur dioxide adsorption capacity, it is considered that oxygen contained in the pores of active carbon reacts with carbon which results in the structural change in functional group in the surface of active carbon.

4 Conclusion

In order to clarify the causes for deterioration in sulphur dioxide adsorption capacity of active carbon generated in the test plant experiment,

history was given to the fresh active carbon under the conditions of different gas composition and temperature. Thus occurrence of deterioration was investigated. The following points have been clarified through this investigation.

As to the deterioration phenomenon of sulphur dioxide adsorption capacity of active carbon as generated in the test plant, it is considered that the surface compounds existing on the surface of active carbon are oxidized by the oxygen existing in the conditions of adsorption and desorption, which invites decrease in basic group and increase in acidic group, and results in deterioration of the sulphur dioxide adsorption capacity of active carbon.

The deteriorated carbon can be regenerated to regain the initial adsorption capacity by heating at a high temperature in the environment with an inert gas or reducing gas. In this case, the regenerated active carbon showed the trend of decrease in acidic group and increase in basic group as expected.

These facts prove that acidity and basicity of the surface oxides in active carbon are closely related to the sulphur dioxide adsorption capacity of active carbon.

Literatures

- 1) Kamino, Y., Onitsuka, S., Yasuda, K., *Bull. Japan. Petrol. Inst.*, **14**, (2), 135 (1972).
- 2) Kamino, Y., Onitsuka, S., Yasuda, K., *ibid.*, **14**, (2), 141 (1972).
- 3) Hassler, J. W., "Activated Carbon," (1967) Leonard Hill-London.
- 4) Bratzler, K., "Adsorption von Gasen und Dampfen," (1944) Verlag von Theodor Steinkoff-Dresden, Leipzig.