Practical Reuse of Activated Carbon in the Exhaust Facility of Semiconductor Production Factory with Supercritical Carbon Dioxide Regeneration

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Abstract An possible reason why the activated carbon used in the exhaust facility of real semiconductor production factory could not be regenerated by $scCO_2$ regeneration was estimated to be attributable to its high boiling point adsorbates which showed a peak in TGA (Thermogravimetric analysis) curve at 400-900ºC. This study was conducted to experimentally verify the above insight by using TGA analysis and $scCO_2$ regeneration for the real samples with different loads from the factory. The experimental results showed that high boiling point ratio defined by TGA analysis was less than 4.0% in case of the heating treatment temperature of 200 ºC in the exhasut facility of real semiconductor production factory. This result suggested regeneration rate of the activated carbon was higher than 80%. Our $scCO_2$ regeneration process can achieve high efficiency as a practical application.

1 Introduction

Activated carbon has been widely used to prevent emissions of volatile organic compounds (VOCs) in industrial processes because of its high adsorption ability. Regeneration of used activated carbon is strongly demanded from viewpoint of reduction of industrial wastes for SDGs (sustainable development goals). Supercritical carbon dioxides ($scCO_2$) is a promising solvent for the regeneration of activated carbon because of its high diffusivity into the microstructure and ability to operate at a moderate temperature (critical point:304 K) resulting in less damage to the microstructure of activated carbon (Tamura *et al*., 2005).

We have studied the $scCO_2$ regeneration for activated carbon used in exhaust facilities of a real semiconductor production factories, which suggested that long-term used activated carbon could not be regenerated (Ito *et al*., 2019a). Thermogravimetric analysis (TGA) showed that $scCO_2$ could remove low boiling point adsorbates (100-400ºC) such as VOCs but could not remove high boiling point adsorbates (400-900ºC). The high boiling point ratio defined as the proportion of high boiling point adsorbates showed that regeneration rates of 90% and 80% were achieved at high boiling point ratios of 2.0% and 4.0%, respectively. **Table 1** summarizes the high boiling point ratio used in the exhaust facility with operational heating temperatures of 250-400ºC (Ito *et al*., 2019a). The high boiling point adsorbates were possibility caused by propylene glycol monomethyl ether (PGME) and propylene glycol monomethyl ether acetate (PGMEA) as main VOC components at practical semiconductor production processes. The experimental results showed that activated carbon loaded with PGME or PGMEA was influenced by heating treatment, and high boiling point adsorbates were observed in the case of heating temperature of higher than 250ºC, which suggested that heating temperature of 200ºC formation of prevented high boiling point adsorbates (Ito *et al*., 2019b).

We have operated the exhaust facility of the real semiconductor production factory in case of heating treatment temperatures of 200-300ºC and 200ºC effective preventing formation of high boiling point adsorbates for the efficiency $scCO_2$ regeneration process. In this work, the high boiling point ratio of the activated carbon used in the exhaust facility of the real semiconductor production factory in case of heating treatment temperatures of 200-300ºC and 200ºC were studied.

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Table 1. Activated carbon used in the exhaust facility with heating temperatures of 250-400ºC (Ito *et al*., 2019a)

	Heating Temperature [ºC]	Duration time [Month]	High boiling point ratio [%]
Lot. A	250-400	3	2.7
		4	2.4
		5	2.9
		6	2.8
		7	3.6
		8	3.1
		9	4.0
		10	5.2
Lot. B	250-400	1	2.7
		3	2.9
		4	3.3
		5	3.9
		7	4.2
Lot. C	250-400	2	3.3
		3	3.3
		4	4.7
		5	4.7
Lot. D	250-400	1	1.8
		2	3.1
		3	3.6
		4	4.8
		5	6.1
		6	6.9

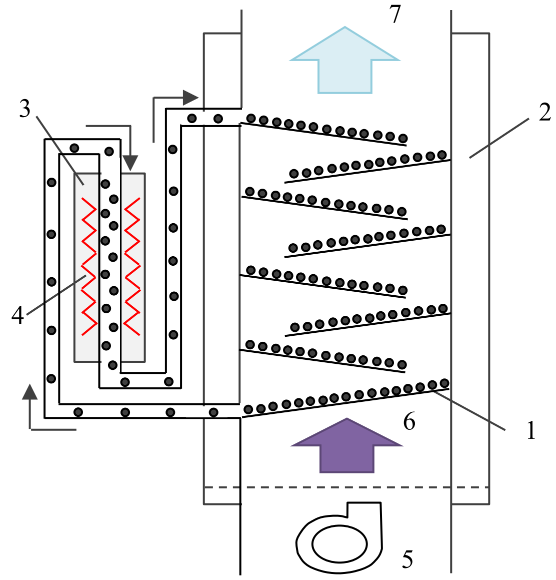
2 Experiment

2.1. Materials

Table 2. Activated carbon used in the exhaust facility with heating temperatures of 200-300 ºC (Lot. E), 200 ºC (Lot. F)

	Heating Temperature [ºC]	Duration time [Month]	High boiling point ratio [%]
Lot. E	200-300	3	2.0
		5	2.8
		7	3.5
		9	4.1
Lot. F	200	5	2.4
		7	2.3
		9	2.8
		11	3.3
		13	3.5
		16	3.9

Activated carbon samples in this study are summarized in **Table 2**. Specific surface area of the activated carbon is 1388 m^2/g on new state was determined by the *t* method (de Boer *et al*., 1965) using a nitrogen adsorption measurement apparatus (Belsorp mini, MicrotracBEL CO., Japan). These samples are continuously used in the exhaust facility of the real semiconductor production factory. **Figure 1** shows schematic diagram of the exhaust facility consisted of adsorption tower (activated carbon on new state: ca. 1000 kg) and desorption tower. Adsorption tower removed hazardous substance such as VOCs, including, PGME and PGMEA, then activated carbon in the desorption tower was continuously regenerated by heating treatment. Heating treatment temperature of the desorption tower was controlled at temperatures of 200-300ºC (Lot. E) and 200ºC (Lot. F).



1. Activated carbon, 2. Adsorption tower, 3. Desorption tower, 4. Electric heater, 5. Exhaust fan, 6. Polluted exhaust gas, 7. Purified exhaust gas

Figure 1. The schematic diagram of the exhaust facility of semiconductor production factory

2.2 Analysis

The amounts of high boiling adsorbate in the activated carbon were determined by TGA-DTA (EVO, Rigaku CO., Japan). TGA conditions are mass of sample (activated carbon): 20 mg, heating temperature: 25-1000ºC, temperature rate: 10ºC/ min, Atmosphere: N_2 (99.9%) and N_2 flow: 500 ml/min. **Figure 2** shows TGA result of the used activated carbon in the exhaust facility (Lot .F, used duration time : 16 month). DTG (Derivative TG) curve shows bimodal shapes corresponded to low boiling point adsorbates (100-400ºC) and high boiling point adsorbates (400-900ºC). The high boiling point ratio was defined by equation (1) (Ito *et al*., 2019a).

$$\text{High boiling point ratio [\%]} = \frac{W_{400}-W_{900}}{W_{100}} \times 100 \quad (1)$$

where W_{100}, W_{400} and W_{900} are TG value (mass of activated carbon) at 100ºC, 400ºC and 900ºC, respectively.

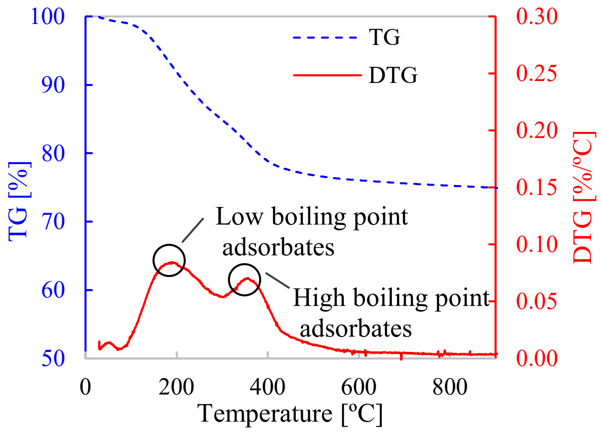


Figure 2. TGA of used the activated carbon in the exhaust facility of semiconductor production factory (used duration time : 16 month)

3 Result and Discussion

Figure 3 shows relationship between high boiling point ratio and used duration time at heating temperatures of 250-400ºC in the exhaust facility of the real semiconductor production factory. The high boiling point ratio was linearly and dramatically increased with passage of time. 4 types of used activated carbon (Lot. A-D) were each of different semiconductor manufacturing processes of loads (Ito *et al*., 2019a).

Figure 4 shows relationship between high boiling point ratio and used duration time in cases of heating temperatures of 200-300ºC (Lot. E) and 200ºC (Lot. F) in the exhaust facility of the real semiconductor production factory. Our previous works showed that high boiling point adsorbates were possibility caused by PGME and PGMEA with heating temperature of higher than 250ºC in a laboratory-scale (Ito *et al*., 2019b). The activated carbon with heating treatment of temperature of 200ºC for 63 h was not observed high boiling point adsorbates, suggesting that the treatment temperature of 200ºC was effective for preventing formation of the high boiling point adsorbates. The activated carbon of Lot. E was heated mainly temperature of 200ºC additionally partial heating temperatures of 250ºC and 300ºC by means of practical operation. It was supposed that high boiling point ratios of Lot. E were relatively lower than Lot. A-E because of decreasing heating temperature of desorption tower. The activated carbon of Lot. F was heated temperature of 200ºC. The high boiling point ratio of Lot. F (used duration time: 5-16 month) was less than 4.0%, which suggested higher regeneration rate of than 80%.

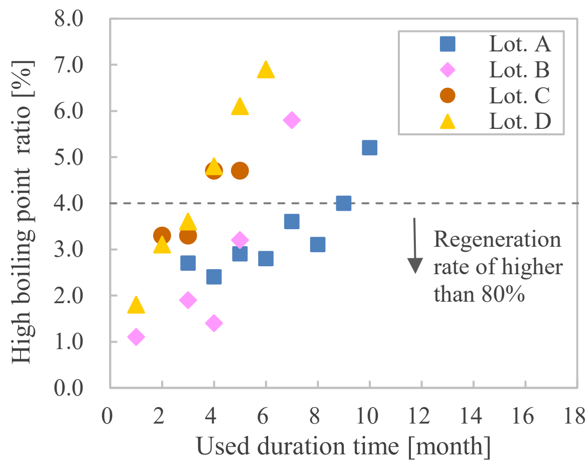


Figure 3. Relationship between high boiling point ratio and used duration time (heating temperatures of 250-400ºC)

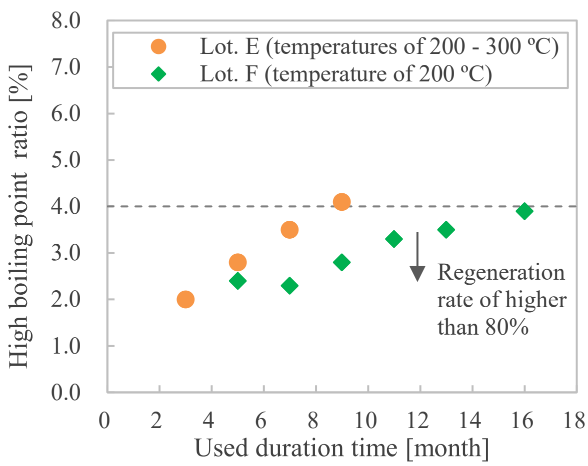


Figure 4. Relationship between high boiling point ratio and used duration time (Lot. E (heating temperatures of 200-300ºC), Lot. F(heating temperature of 200ºC))

4 Conclusion

The $scCO_2$ regeneration of activated carbon used in exhaust facility of the real semiconductor production factory was studied. The heating temperature of 200ºC in the exhaust facility of desorption tower was effective for preventing formation of high boiling point adsorbates similarly laboratory-scale results. The $scCO_2$ regeneration activated carbon was high boiling point ratio of less than 4.0%, suggesting higher regeneration rate than 80%. Our $scCO_2$ regeneration process could achieve high efficiency as a practical application.

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