

Adsorption and Desorption Characteristics of Semiconductor Volatile Organic Compounds on the Thermal Swing Honeycomb Zeolite Concentrator

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ABSTRACT

The use of a honeycomb zeolite concentrator and an oxidation process is one of the most popular methods demonstrated to control volatile organic compound (VOCs) emissions from waste gases in semiconductor manufacturing plants. This study attempts to characterize the performance of a concentrator in terms of the removal efficiencies of semiconductor VOCs (isopropyl alcohol [IPA], acetone, propylene glycol methyl ether [PGME], and propylene glycol monomethyl ether acetate [PGMEA]) under several parameters that govern the actual operations. Experimental results indicated that at inlet temperatures of under 40 °C and a relative humidity of under 80%, the removal efficiency of a zeolite concentrator can be maintained well over 90%. The optimal rotation speed of the concentrator is between 3 and 4.5 rph in this study. The optimal rotation speed increases with the VOCs inlet concentration. Furthermore, reducing the concentration ratio helps to increase the removal

efficiency, but it also increases the incineration cost. With reference to competitive adsorption, PGMEA and PGME are more easily adsorbed on a zeolite concentrator than are IPA and acetone because of their high boiling points and molecular weights.

INTRODUCTION

As the semiconductor manufacturing industry rapidly expands in Taiwan, the environmental regulations require the emissions control of volatile organic compounds (VOCs) to be over 90%. In addition, the ISO 14000 standard demands the proper treatment of VOCs exhaust. Accordingly, the market for equipments and systems to abate VOCs in the waste gases from the semiconductor industry has been increased.

The characteristics of exhaust gases from the semiconductor industry, including their volume and chemical contents, vary among various manufacturing processes. The gases can be treated by cooling, adsorption, or the combustion process, or by a combination of the processes. The honeycomb zeolite concentrator combined with an oxidation process has been commercialized and proven to be a viable solution that enables VOCs emitters to comply with the regulations in Taiwan, Europe, the United States, and other countries and regions.

For a combined concentrator/oxidation system, the concentrator removes the VOCs from the exhaust air to be vented from the stack. An oxidizer then treats the concentrated stream of the VOCs emitted from the concentrator. The VOCs introduced into a thermal oxidizer are destroyed at a high temperature. For exhaust air with a low concentration of VOCs at tens to hundreds of parts per million volume (ppmv), the zeolite concentrator with an oxidation process has performed very well. However,

IMPLICATIONS

The zeolite concentrator/incinerator system is one of the most popular VOCs abatement devices in the semiconductor and electro-optical industries owing to its high VOCs destruction efficiency. However, problems exist for industrial application of the zeolite concentrator system. These may be because optimal operation conditions were not obtained. This study demonstrates the effects of inlet flow conditions and operating parameters on the adsorption/desorption characteristics of a honeycomb zeolite concentrator. The results can provide information for field applications to the semiconductor and electro-optical industries to obtain their optimal operation conditions of the concentrator for both efficient VOCs controls and energy savings.

the design and control of all the parameters that govern the zeolite concentrator frequently raise problems in meeting the required removal efficiency of an exhaust gas treatment system. The design and control parameters include regeneration temperature, rotating speed, the area ratio of process/cooling/regeneration zone (i.e., the zone ratio), the flow rate ratio of the process flow to the regeneration flow (i.e., the concentration ratio), air face speed, humidity, VOCs species, and VOCs concentrations.

In a zeolite concentrator,¹ the adsorbent is coated onto a honeycomb substrate. Honeycombed support offers a very large surface area for a given volume and is, therefore, preferred over conventional pellets. The substrate is made of ceramic fiber paper. The virgin honeycomb substrate is formed with the desired shape and size. These elements are then impregnated with a dispersion of high-silica zeolite or activated carbon (C), inorganic binder, and silica solution, and dried to obtain the adsorbent of the honeycomb zeolite concentrator.

According to the literature, some efforts have been made to develop a suitable material for the adsorbent coated on the concentrator. The results, obtained for hydrophobic zeolite as the solvent adsorbent, could be summarized as efficient adsorption over a wide range of concentrations and characteristics of VOCs.²⁻⁴ Further advantages of using zeolite include the lack of further requirements regarding control of the relative humidity (RH), fire protection, and the sacrificial adsorbent bed.

The removal efficiency of a zeolite concentrator is influenced by parameters such as process flow rate, rotation speed, thermal response, and the type of zeolite coated on the concentrator.⁵⁻⁷ Studies have been undertaken on estimating the nondimensional number between the efficiency and the optimal rotation speed of rotor with a specific set of operating and design parameters.^{8,9} Combining the zeolite concentrator with oxidation processes revealed that it is more economical, efficient, and yields fewer secondary emissions^{2,10,11} as compared with the single oxidation processes such as the regenerative thermal oxidizer (RTO), regenerative catalytic oxidizer (RCO), and catalytic thermal oxidizer (CTO) processes.

However, the aforementioned studies considered VOCs emission from traditional processes such as painting booth and tape-coating processes under limited conditions. This study shows quantitative results of laboratory tests on the removal efficiencies of a zeolite concentrator for major VOCs in semiconductor emissions (isopropylalcohol [IPA], acetone, propylene glycol methyl ether [PGME], and propylene glycol monomethyl ether acetate [PGMEA]). The effects of operating parameters and inlet conditions on the performance of the ZSM-5 zeolite concentrator are addressed. The investigated operation

parameters include regeneration temperature, rotation speed, concentration ratio, inlet flow temperature, humidity, and the concentrations of various species of VOCs. The results would provide information for field applications to the semiconductor and electro-optical industries to obtain their optimal operation conditions of the concentrator for both efficient VOCs controls and energy savings.

EXPERIMENTS

The zeolite concentrator used in this study was obtained from Seibu Giken Co. and was made from a ZSM-5-type zeolite material. The reason for choosing the ZSM-5 type instead of other types of zeolite is because of its high silicon (Si)/aluminum (Al) ratio that is effective for adsorbing organic molecules even in low-concentration, high-humidity, and high-temperature applications.^{12,13} Furthermore, the near-straight channel pore of ZSM-5 and its fine structure also lead the adsorption efficiency of VOCs to be better than that of the other zeolites.¹⁴ The element was formed into a honeycomb-shaped laminate, with several small channels from one end surface to the other, and the high-silica zeolite was coated on the surface of the small channels in the honeycomb. Detailed procedures for the preparation of the zeolite concentrator can be found in Kuma's U.S. Patent 5348922.¹

Table 1 specifies the characteristics of the honeycomb zeolite concentrator used in this study. The Si/Al ratio of the zeolite was determined by an energy-dispersive spectrometer analyzer (Hitachi S-4700I) to be 166. The surface area and pore volume were determined by a surface area analyzer (Micromeritics model ASAP2400) to be 241 m²/g and 0.321 cm³/g, respectively. The bulk density of the zeolite concentrator, 250 kg/m³, is determined as the total weight of adsorbent and substrate divided by the total volume of the honeycomb-shaped laminate sheet and the

Table 1. Specifications of the honeycomb zeolite concentrator.

Property	Value
Diameter (mm)	320
Height (mm)	400
Bulk density (kg/m ³)	250
Zone area ratio (process/regeneration/cooling)	10:1:1
Channel shape	parabolic honeycomb
Channel size (mm × mm × mm)	3 (pitch) × 1.6 (height) × 0.2 (thickness)
Cell per square inch (cpsi)	269
Brunauer-Emmett-Teller surface area (m ² /g)	241
Mass fraction of adsorbent in matrix (%)	36.66
Adsorbent type	ZSM-5
Si/Al ratio of adsorbent	166
Pore volume of adsorbent (cm ³ /g)	0.321

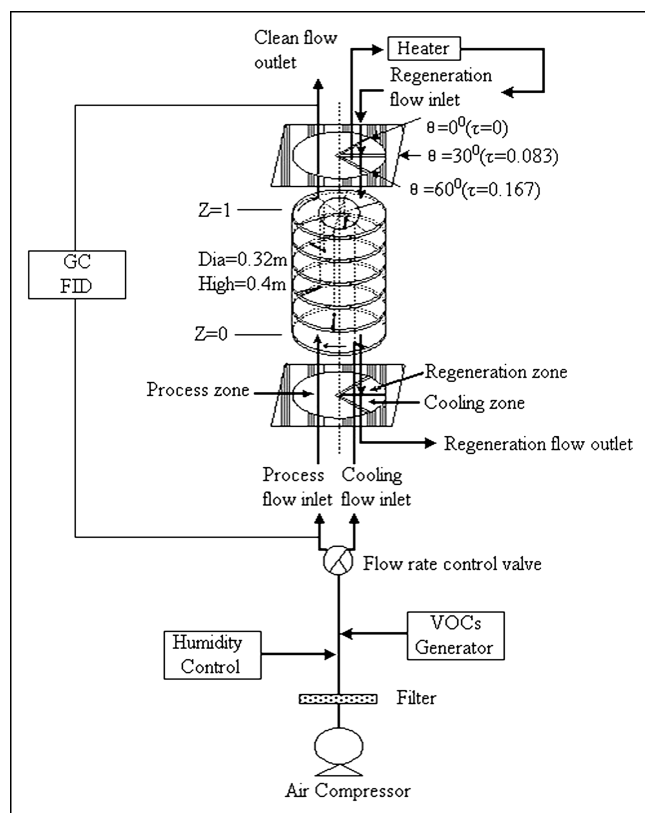


Figure 1. The zeolite concentrator testing facility.

honeycomb channel of the zeolite concentrator. The area ratio of each zone (process/cooling/regeneration) of the zeolite concentrator is 10:1:1.

Figure 1 presents a simplified flow diagram of the zeolite concentrator testing facility. The flow was generated from the air compressor. After passing through the filter, the humidity and the concentration of VOCs in the flow were adjusted using the humidity controller and the VOCs generator, respectively. The ratio of process flow rate to cooling (regeneration) flow rate determines the concentration ratio (f) of VOCs in the regeneration flow to that in the process flow. It was regulated using a flow rate control valve. The flow was separated into process flow and cooling flow, and these flows were passed through the process and cooling zones of the zeolite concentrator, respectively.

After the process and cooling flows were passed into the zeolite concentrator, they were quite clean and were detected by a gas chromatograph/flame ionization detector (GC/FID) before being exhausted. The clean cooling flow exiting from the zeolite concentrator was recycled and heated as regeneration flow. The high temperatures of the regeneration flow caused desorption of the VOCs and activated the process zone.

The concentration of the VOCs was measured by GC/FID to determine the efficiency of the zeolite concentrator. The samples were injected into the GC/FID

(Shimadzu GC14B) for analysis (the temperature of the FID was 200 °C). A Shimadzu C-R6A integrator was used to calculate the VOCs concentrations. The column used in the GC for analysis was J&W DB-WAX (30 m × 0.53 mm I.D., 1.0-μm film thickness). Six measurements were made to determine moisture and VOCs concentrations in the process zone, as shown in Figure 2, and the angle between adjacent measuring points was 60°. A known sample of 5 mL of the inlet and outlet flow, respectively, from the zeolite concentrator was autosampled every 60 sec.

The dimensional height was measured from the inlet to the outlet of the process zone. Dividing this height by the total height of rotor yields the dimensionless height (Z). The dimensional rotation angle was defined from the beginning of the regeneration zone to the point at which temperature and concentration were measured. The dimensionless value, τ , was obtained by dividing this angle by 360°, and the rate of rotation of the zeolite concentrator is adjusted at the stepping motor.

RESULTS AND DISCUSSION

Effects of Inlet Gas Temperature and Moisture

Because IPA is the major VOCs emitted from the semiconductor industry, the present study addresses more on this compound. Figure 3 shows the effect of temperature on the removal efficiency of IPA. The inlet flow has an IPA inlet concentration of 250 ppmv, a regeneration temperature of 180 °C, humidity ratio in inlet flow of 11 g/kg, a regeneration flow velocity of 1.77 m/sec, a concentration ratio (f) of 13 (i.e., the concentrations of VOCs in the regeneration flow are 13 times higher than those in the process flow), and an optimal rotation speed of 3.3 revolutions per hr (rph). The results suggest a strong inverse correlation between removal efficiency and the inlet temperature because the temperature is above 25 °C. This is because, as the inlet temperature is increased, the

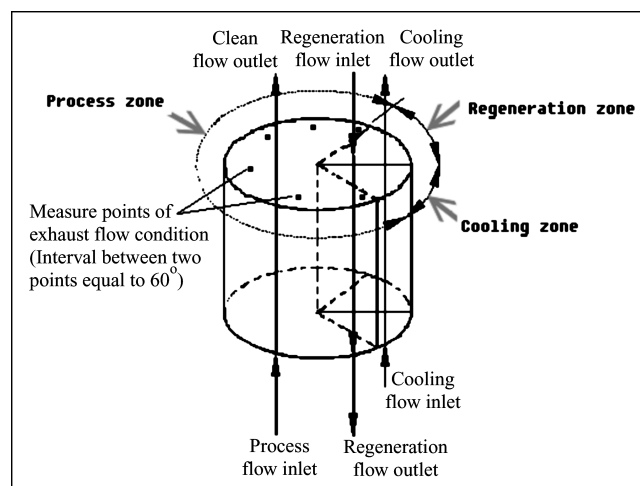


Figure 2. Locations at which concentration profile is measured.

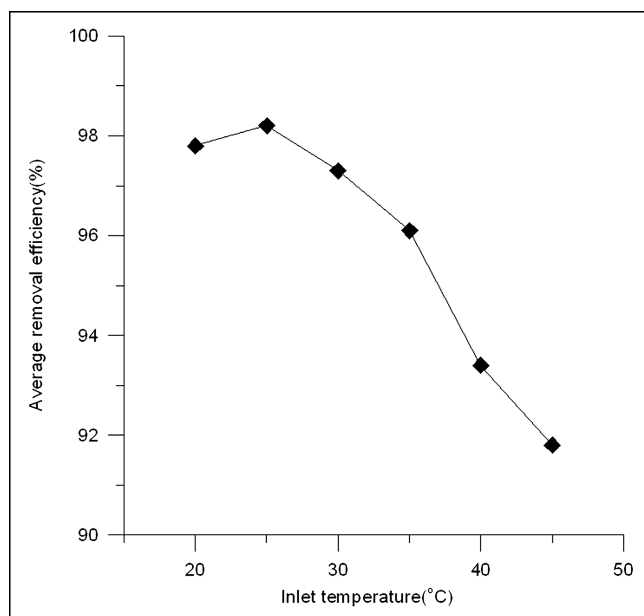


Figure 3. Effect of temperature on the removal efficiency of IPA.

temperature gradient between the process and the regeneration zones falls. Consequently, insufficient heat energy is provided to regenerate the VOCs from the zeolite concentrator, especially in the regeneration zone close to $Z = 0$, downstream of the regeneration process. Therefore, the overall efficiency of the zeolite concentrator system falls as the temperature increases.

However, this phenomenon is observed only for an inlet temperature of greater than 25 °C. The reduction in efficiency below 25 °C can be attributed to an increase in RH. For the same humidity ratio (11 g/kg in this case), the RH of flow is 75% at 20 °C and 56% at 25 °C. A higher RH is associated with more adsorbed moisture, causing adsorption sites to be blocked up by water vapor condensation.

Figure 4 presents the effect of the humidity ratio in the inlet flow on the efficiencies of removal IPA and acetone. The inlet flow has an IPA inlet concentration of 200 ppmv, an acetone inlet concentration of 100 ppmv, a regeneration temperature of 180 °C, a regeneration flow velocity of 1.77 m/sec, a concentration ratio of 13, a rotation speed of 3.3 rph, and an operating temperature of 25 °C. Clearly, while the humidity ratio was between 8 and 16 g/kg (corresponding to 40 and 80% of RH), the overall efficiencies of IPA and acetone were found to exceed 95%. When the humidity ratio exceeded 18 g/kg (RH = 90%), the overall efficiency of VOCs was only 80%, and the differences between the IPA and acetone removal efficiencies did not exceed 10%. The removal efficiency of IPA exceeded that of acetone. This is because the boiling point of IPA is higher than that of acetone, so it is adsorbed on a zeolite concentrator more easily than acetone. Although the zeolite is hydrophobic to some extent,

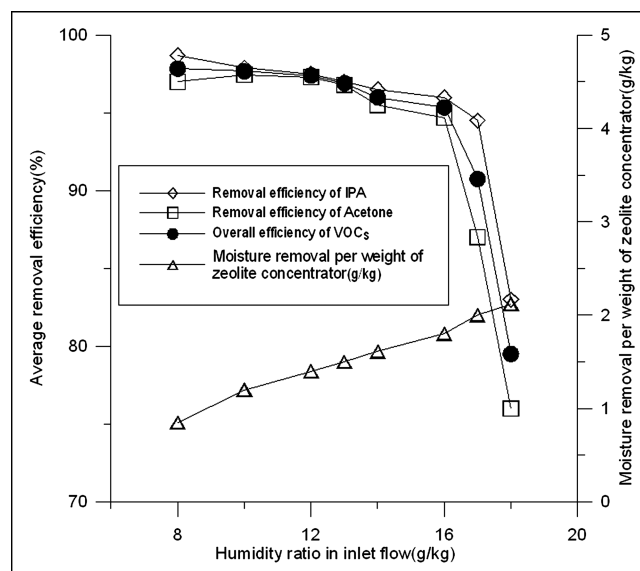


Figure 4. Effects of humidity ratio (g water/kg air) on the removal efficiencies of IPA and acetone.

the decreased efficiency of VOCs removal in the presence of a large excess of moisture content should be caused by the moisture condensation effect and thus occupy the adsorption sites. Furthermore, it may form clusters around those sites thereby creating a diffusion block for VOCs molecules.

Effects of Operating Parameters on the Removal Efficiency

Figure 5 presents the effect of the rotation speed of the concentrator (n) on the removal of IPA. It shows that an

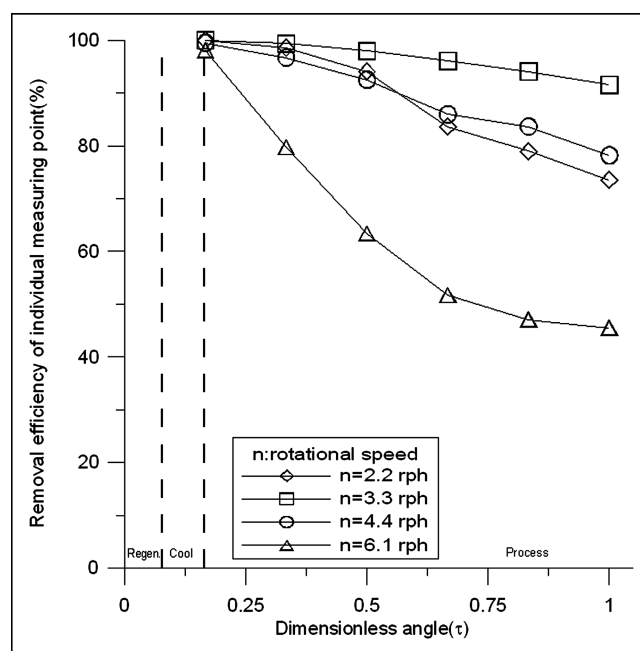


Figure 5. Effect of the concentrator rotation speed on the removal efficiency of IPA.

optimal speed of ~ 3.3 rph as determined in this study yields a maximum IPA removal efficiency. At speeds above optimal, VOCs adsorbed on the rotor are not regenerated effectively because of the limited regeneration residence time. At speeds below optimal, the adsorbent breaks through and cannot adsorb more VOCs. In both cases, the removal efficiency is adversely impacted. Consequently, the rotation of the rotor must be maintained at an optimal speed to balance the adsorption and desorption.

Operating conditions may slightly alter this balance, as illustrated in Figures 6a and b. At a regeneration temperature of 180°C and a concentration ratio of 13, the

optimal rotation speed is 4.5 rph at an inlet total VOCs concentration of 250 ppmv, and ~ 4 rph at an inlet VOCs concentration of 100 ppmv. The overall efficiencies exceeded 90% at any rotation speed when the total VOCs concentration was 100 ppmv (IPA 30%; acetone 35%; PGME 20%; PGMEA 15%), but exceeded 90% at rotational speeds between 2.8 and 4.5 rph when the total VOCs concentration was 250 ppmv (IPA 30%; acetone 35%; PGME 20%; PGMEA 15%).

Figures 6a and b also present the relationships between rotation speed and the removal efficiencies of each VOCs species. The removal efficiencies of the VOCs compounds follow the order PGMEA > PGME > IPA > acetone. The boiling points of PGMEA and PGME are 146°C and 120°C , respectively, and those of IPA and acetone are 82°C and 56.5°C , respectively. The removal efficiencies of the VOCs compounds follow the order of boiling points and molecular weights. The competitive adsorption of VOCs in the zeolite concentrator has been discussed in the experimental results of Clausse et al.¹⁵ Similar to a distillation process, the adsorbate with a high boiling point displaced the adsorbate with a low boiling point from the zeolite. This behavior is also similar to the result of the activated C test.¹⁶ And because all four compounds are low-polar compounds, dipole moment is not an important factor that governs the adsorption of the four VOCs.

Although PGMEA and PGME are preferably adsorbed onto the zeolite concentrator, unless sufficient heat energy is supplied, VOCs with high boiling points may not be desorbed effectively downstream ($Z = 0$) of the regeneration zone. Theoretically, a typical regeneration temperature of 180°C is effective for desorbing PGME and PGMEA. However, the rear of the regeneration zone cannot obtain sufficient heat energy because of the heat transfer of the rotor material and the regeneration flow velocity.

If VOCs with high boiling points cannot be well desorbed, as the days pass, they saturate to form mists of high viscosity and occupy the adsorption sites at $Z = 0.1\text{--}0.3$. Thus, the working mass transfer zone is lost and the efficiency of the zeolite concentrator deteriorates. This work suggests that the regeneration temperature has a maximum of 210°C . According to the operational safety conditions and the cooling efficiency, the concentration ratio should be reduced. Therefore, the regeneration heat capacity to the concentrator is increased and the rotor is being purged regularly. The aforementioned processes promote the desorption of the high-boiling-point VOCs and their removal from the zeolite concentrator.

Figure 7 shows an inverse relationship between the removal efficiency and the flow concentration ratio (f). An increase in the concentration ratio corresponds to

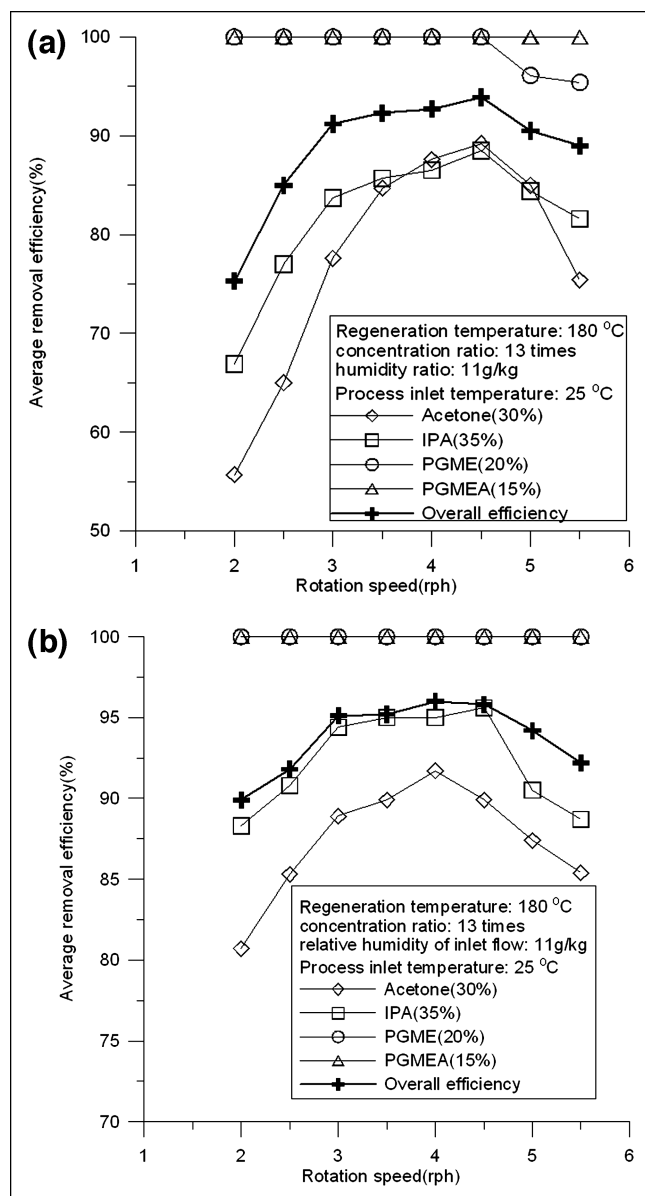


Figure 6. (a) Relationship between rotation speed and VOCs removal efficiencies at an inlet concentration of 250 ppmv. (b) Relationship between rotation speed and VOCs removal efficiencies at an inlet concentration of 100 ppmv.

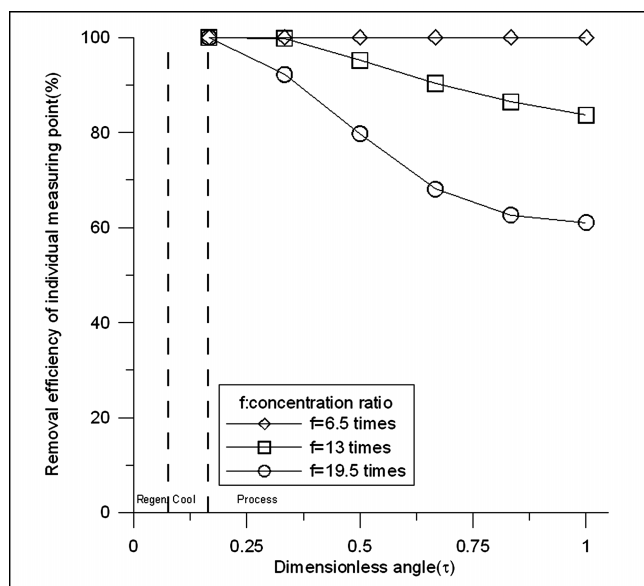


Figure 7. Effect of the concentration ratio (f) on the removal efficiency of IPA.

either a fall in regeneration flow or an increase in process flow. Clearly, the greatest overall efficiency of almost 100% is achieved at a concentration ratio of 6.5. This implied that a large regeneration flow rate possesses more heat energy than a small regeneration flow rate at the same regeneration temperature and thus could desorb more VOCs from the zeolite concentrator and produce more adsorbant sites in the process zone. However, on the actual operation of zeolite concentrator plus incineration, reducing the concentration ratio indicates that more flow rate will be introduced into the incinerator, thus leading to increases in the operating cost. Therefore, based on desirable removal efficiency and economical running cost, this illustrated that the optimum concentration ratio of a zeolite concentrator is ~ 13 for controlling IPA from a semiconductor plant. This is analogous to the concentration ratio of 12–14 for butylacetate⁷ and 14 for cyclohexanone⁸ emissions control.

Figure 8 plots the effect of regeneration temperature on IPA removal efficiency. Clearly, increasing the regeneration temperature promotes desorption of VOCs. However, operating at an excessively high regeneration temperature raises difficulties in cooling in the cooling zone; perhaps it also reduces the overall efficiency of VOCs. Figure 8 shows that when the regeneration temperatures were increased from 210 to 240 °C or beyond, the increased temperature of the residual heat hindered the adsorption of VOCs in the process zone and reduced the overall efficiency.

According to the results of Gonzalez-Velasco et al.,¹³ the catalytic effect can only exist at relatively high temperatures. For the regeneration and process temperatures of below 240 °C, it is expected that the catalytic

effect accounts for less than 20% of the VOCs destruction in the regeneration (desorption) zone and almost no catalytic effect in the process (adsorption) zone. Thus, the whole concentrator process should be dominated by the physical adsorption/desorption process instead of the catalytic process where Bronsted acid sites may be presented.

CONCLUSIONS

This work showed the effects of various inlet flow conditions and operating parameters on the characteristics of adsorption and desorption of semiconductor VOCs in terms of their removal efficiencies by a thermal swing honeycomb zeolite concentrator. The VOCs removal efficiency by the zeolite concentrator was found to be highest if the concentrator operated at an optimal rotation speed of between 3 and 4.5 rph; it varied slightly with the operating conditions. Increasing the concentration ratio reduces the overall efficiency of VOCs removals, but it also reduces running cost of the incinerator. Accordingly, the zeolite concentrator can be operated at a suitable concentration ratio according to the need for an individual application to meet stringent regulations or save operating costs. The adsorption rates of the four VOCs species on the zeolite concentrator followed the order PGMEA > PGME > IPA > acetone. This sequence was mainly caused by their relative boiling points. Notably, unless sufficient heat energy is supplied, the VOCs with high boiling points, including PGME and PGMEA, may not be desorbed effectively downstream in the regeneration zone. If VOCs with high boiling points cannot be well desorbed, as days pass, they become saturated and form high-viscosity mists and occupy the adsorption

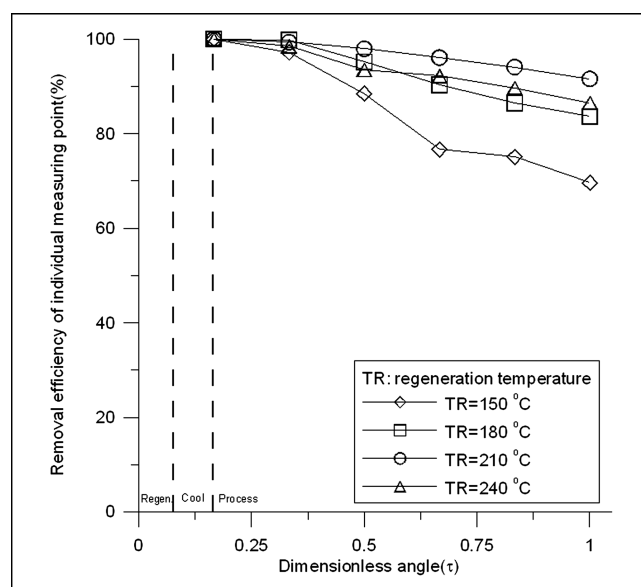


Figure 8. Effect of the regeneration temperature on the removal efficiency of IPA.

sites. This study also showed that the inlet RH and temperature of the adsorption process affect the removal efficiency of VOCs, of which the RH has a particularly strong effect.

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