

Cyclic Adsorption of Hydrogen Cyanide Cyanogen Chloride and Phosgene on BPL Carbon

Alvin H. Weiss and Chandra M. Venkat
Chemical Engineering Department
Worcester Polytechnic Institute
Worcester, Massachusetts 01609

Abstract. Fresh dry BPL carbon capacity for HCN, CNCl and COCl₂ was 23, 62 and 153 mg/gm respectively at 5°C and 17 cm/sec superficial air velocity. Desorption was at 100°C and 8.5 cm/sec. Capacity dropped to 18, 49 and 44 mg/gm respectively after twenty cycles. The effects of humidity, temperature and desorption parameters are compared to those obtained for heavier adsorbents, which deactivate even more rapidly.

Introduction

Toxic chemicals can be removed from air by adsorbents such as activated carbon. The carbon has to be replaced periodically since it has a limited capacity. The carbon can be regenerated thermally at higher temperatures and can be reused. Thus a two adsorber system where one bed is adsorbing while the other is being regenerated will have a long operating time and carbon replacements will be needed only occasionally. However, previous studies^{1,2} have shown that the carbon bed when regenerated loses some of its capacity due to 'deactivation'. The present study determined experimentally the deactivation of BPL carbon by Hydrogen Cyanide, Cyanogen Chloride and Phosgene. A two adsorber cyclic design is compared with a single adsorber in terms of operating time for each of the three chemicals. Results obtained with Di-methyl methyl phosphonate (DMMP) and Styrene are presented for comparison.

Experimental Apparatus

Three air streams were mixed in required proportions to generate the adsorption inlet flow. The first was a dry air stream, the second a humidified air stream with known humidity, and the third an air stream with a known concentration of the pollutant. Air mixtures with 1-2 volume percent of HCN, CNCl or COCl₂ were purchased from Matheson Gas Co.

Activated carbon was packed in a column in an oven. In addition to the heating coil, the oven was provided with a refrigeration system. The column could be maintained at a steady temperature ranging from 5°C to 200°C. Three way solenoid valves were provided at the adsorption inlet and outlet. When adsorption breakthrough concentration was detected the valves were positioned such that clean air flowed in the reverse direction and simultaneously the oven switched to the desorption

mode and maintained the column at a higher temperature (100-150°C). When the desorption breakthrough concentration was detected the flow was again switched so that the adsorption inlet stream flowed through the column. Adsorption and desorption breakthroughs were detected by two Varian flame ionization detectors (FIDs). One eighth inch SS tubing was used for connections and Matheson rotameters for flow measurements.

Experimental Results

All experiments were done with an inlet pollutant concentration of 3000-3300 mg/m³. Desorption temperature was 100°C and adsorption temperature was 5°C. Desorption breakthrough concentrations were 600 mg/m³ for HCN and CNCl. For Phosgene it was 1400 mg/m³. Superficial air velocities were 17 and 8.5 cm/sec for adsorption and desorption respectively. Desorption breakthrough concentration, desorption flow rate, adsorption temperature and desorption temperature were changed for a few cycles in the course of the aging tests to study their effect on the process.

Desorption temperature and desorption breakthrough concentration were chosen keeping the feasibility of the process in mind. At a desorption temperature of 100°C cyclic operation was feasible for all the three chemicals. A very low desorption breakthrough concentration ensured a high degree of regeneration, however the regeneration time becomes very large. The adsorption capacity for the next cycle will not be proportionally higher. Desorption breakthrough concentrations (600-1400 mg/m³) were chosen so that for the operating conditions desorption breakthrough times were less than adsorption breakthrough times. Experiments were generally done in dry air. Humid air was used for a few cycles to study the effect of inlet humidity.

A thirty-six cycle experiment was done with HCN. The capacity of fresh BPL carbon was 22.9

Table 1 Comparison of Conventional and Cyclic Adsorber Designs

Adsorbate Number of adsorbers Adsorbent	HCN		CNC1			COCl ₂		
	1	2	1	2		1	2	
	ASC Wt	BPL C	ASC Wt	BPL C		ASC Wt	BPL C	
Fresh Bed Capacity mg/g	117.5	22.9	454.0	62.6		359.0	153.0	
1st cycle BT Time min.	1742	2x64	2980	2x76.5		1468	2x117.5	
Cycle number at termination	1	263	1	157		1	10	
Total Operating Time, Hrs	29.1	363.1	49.7	270.9		24.5	28.0	

mg/gm. After five cycles the capacity reduced to 18.1 mg/gm. After that there was very little deactivation. Adsorption capacity for the thirty-sixth cycle was 17.2 mg/gm. The deactivation of BPL carbon by Cyanogen Chloride was studied in two separate experiments. The first one was done for thirty-six cycles. The fresh BPL carbon capacity (at 5°C) was 61.7 mg/gm. After five cycles the capacity was 51.2 mg/gm. After thirty-six cycles it was 47.5 mg/gm. The second experiment was done for fourteen cycles. The results were consistent with the previous run. Also the effect of inlet humidity was studied. Cycles 8,9,10 and 11 were done with 70% inlet RH. The results showed a capacity decrease from 51.5 to 44.2 mg/gm presumably due to competitive adsorption of water. When the bed was presaturated with 70% humid air for eight hours the capacity dropped from 50 to 38.3 mg/gm (cycle 13 and 14).

An eighteen cycle run was done with Phosgene by Mr. Paul Nowak. The greatest decrease in capacity took place between the first and second cycles (153.2 to 136.3 mg/gm). The capacity continued to decrease and at the end of 18 cycles it was 44.6 mg/gm, only 35% of the fresh carbon capacity. Cycles 9,10 and 11 were done with 70% inlet RH. The results showed a capacity decrease from 84.4 to 63.9 mg/gm.

Cyclic Adsorber Designs

Experiments in our laboratory⁴ including the present study have shown that ASC Whetlerite has a very high capacity for most pollutants. However ASC Whetlerite is not suitable for regeneration. Therefore, a two adsorber cyclic design with BPL carbon must be compared with a conventional design using ASC Whetlerite. A two adsorber design with each adsorber having 1/4 by weight of adsorbent compared to the conventional single adsorber was chosen for comparison. An air flow basis of 1 cfm/lb carbon was chosen for the conventional design. In order to produce the same quantity of pure air, the cyclic design will need 4 cfm/lb carbon of air flow. In addition at least 25% of the air flow will be needed for regeneration. This gives an air flow of $4/0.75 = 5.33$ cfm/lb carbon. The cyclic operation was terminated arbitrarily when BPL carbon's capacity reduced to 1/2 of fresh capacity. With adsorption inlet concentration of 40 mmole/m³, adsorption temperature of 5°C and desorption temperature of 100°C, above results (Table 1) were obtained. A comparison of the total operating times shows that the two adsorber design has a definite advantage in the case of HCN and CNC1. For Phosgene the improvement in total operating time is only

marginal. The adsorbers were assumed to operate at the same superficial adsorption air velocity of 17 cm/sec.

The deactivation data obtained for the three chemicals were compiled along with the data obtained for Styrene and DMMP and plotted as capacity vs cycle number as shown in figure 1. It is presumed that the deactivation is due to accumulation of strongly adsorbed species in the pores. For light inert gases such as oxygen or nitrogen only weak physisorption takes place and the desorption process is completely reversible.

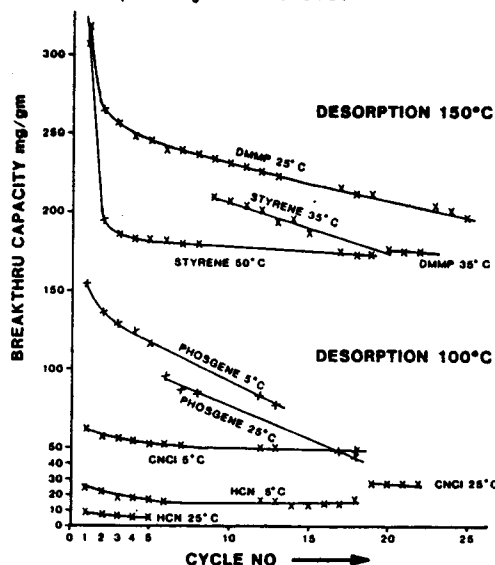


Figure 1. Deactivation data.

References

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- Note: The abstract "Capacity Decay of Regenerated Carbon Air Filters" by A.H. Weiss, K. Gürüz, and D. Guo is in the Proceedings of the 16th Biennial Conference on Carbon, July 18-23, 1983, San Diego.