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NASA Cooperative Agreement No. NCC2-5024

Effects of Humidity Swings on Adsorption Columns for Air Revitalization: Modeling and Experiments

SUMMARY OF RESEARCH (Final Report)
Period Covered: 1/16/94 - 1/15/97

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Summary of Research

Introduction

Air purification systems are necessary to provide clean air in the closed environments aboard spacecraft. Trace contaminants are removed using adsorption. One major factor concerning the removal of trace contaminants is relative humidity. Water can reduce adsorption capacity and, due to constant fluctuations, its presence is difficult to incorporate into adsorption column designs.

This report summarizes research performed under NCC2-5024, a Joint Research Interchange between the NASA-Ames Research Center and the University of Virginia. The purpose of the research was to allow for better design techniques in trace contaminant adsorption systems, especially for feeds with water present. Experiments and mathematical modeling research on effects of humidity swings on adsorption columns for air revitalization were carried out by Mr. W. Scot Appel, a graduate student in the Department of Chemical Engineering at the University of Virginia, under the joint active direction of Prof. M. Douglas LeVan of the University of Virginia and Dr. John E. Finn of the NASA-Ames Research Center. Mr. Appel divided his time between the NASA-Ames Research Center and the University of Virginia. His work is continuing and he is expected to receive his Ph.D. in January, 1998.

Summary

The goal of this research was to develop a dynamic model which can predict the effect of humidity swings on activated carbon adsorption beds used to remove trace contaminants from the atmosphere in spacecraft. Specifically, the model was to be incorporated into a computer simulation to predict contaminant concentrations exiting the bed as a function of time after a humidity swing occurs. Predicted breakthrough curves were to be compared to experimentally measured results. In all respects the research was successful.

The two major aspects of this research were the mathematical model and the experiments. Experiments were conducted by Mr. Appel using a fixed-bed apparatus at NASA-Ames Research Center during the summers of 1994 and 1995 and during the first 8 months of 1996. Mr. Appel conducted most of his mathematical modeling work at the University of Virginia. The simulation code was used to predict breakthrough curves using adsorption equilibrium correlations developed previously by M. D. LeVan's research group at the University of Virginia.. These predictions were compared with the experimental measurements, and this led to improvements in both the simulation code and the apparatus.

The research is continuing. Mr. Appel in recent months has been measuring new adsorption equilibrium data for incorporation into the model and has been working on a rigorous method for species grouping to allow accurate simplification of the simulation code. Mr. Appel is scheduled to spend the summer of 1997 at the NASA-Ames Research Center prior to returning the Vanderbilt University, to which M. D. LeVan moved in January, 1997. There, Mr. Appel will complete his Ph.D. dissertation for the University of Virginia with a January, 1998 degree anticipated.

Publications and Presentations

Appel, W. S., "Simulation of Humidity Effects on Trace Contaminant Adsorption," M.S. thesis, University of Virginia, August 1995.

Appel, W. S., LeVan, M. D., and Finn, J. E., "Effects of Humidity Fluctuations on Adsorption Columns Used for Air Purification in Closed Environments," SAE Technical Paper Series, #961358 (ISSN 0148-7191), 1996, 5 pp. Presented at the 26th International Conference on Environmental Systems, Monterey, California, July 1996.

Appel, W. S., LeVan, M. D., and Finn, J. E., "Effects of Humidity on Activated Carbon Adsorption Columns used for Air Purification," Symposium on Fundamentals of Adsorption and Ion Exchange, AIChE 1996 Annual Meeting, Chicago, Illinois, November 1996.

Appel, W. S., Ph.D. dissertation, University of Virginia, in progress.

Other publications will result from this research.

Appendix: Publications and Presentations

SAE TECHNICAL
PAPER SERIES

961358

Effects of Humidity Fluctuations on Adsorption Columns Used for Air Purification in Closed Environments

W. Scot Appel and M. Douglas LeVan
University of Virginia

John E. Finn
NASA Ames Research Center

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961358

Effects of Humidity Fluctuations on Adsorption Columns Used for Air Purification in Closed Environments

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ABSTRACT

Effects of a cabin-level humidity upset on an activated carbon column used for adsorption of trace compounds from air are examined through a series of experiments and computer simulations. Breakthrough curves measured for dichloromethane in the presence of water indicate that a rapid increase in relative humidity can displace large quantities of dichloromethane from the adsorbed phase resulting in effluent streams containing more than 20 times the feed concentration. Additionally, the breakthrough time for organic compounds is reduced significantly at high relative humidity. Numerical simulation results show favorable qualitative agreement with measured breakthrough curves, yet do not consistently predict accurate water or dichloromethane loadings at all experimental conditions.

INTRODUCTION

Organic species, usually present only at unmeasurable quantities in the earth's atmosphere, may accumulate to health threatening levels in closed environments such as space stations or submarines. Limiting contaminant levels is essential, especially where long term human exposure is involved.

Air revitalization is often achieved by adsorbing organic species on activated carbon. Single species adsorption is easily modeled when adsorption isotherms are available for a specific species on the adsorbent of choice. Often, however, multiple organic compounds must be removed simultaneously in the presence of water. Accurate modeling of such systems is frequently impossible due to the unavailability of multicomponent isotherms describing water/organic coadsorption.

An activated carbon adsorption column meets the requirements of the National Aeronautics and Space Administration for a lightweight and efficient means of controlling trace contaminant levels aboard spacecraft or space stations. Existing Trace Contaminant Control System (TCCS) designs oversize adsorption columns. However, the safety margin obtained through over-sizing is uncertain and may result in considerable expense in terms of both launch costs and logistics penalties. Furthermore, the response of adsorption columns to a cabin-level upset such as a large humidity swing is not well-understood.

Humidity variations may have dramatic effects on a trace contaminant adsorption column and subsequent processors. Significant reductions in the adsorption capacity of activated carbon for some organics at high relative humidity (RH) are well-known. Rapid increases in cabin RH, caused by equipment malfunction for example, could result later in adsorption column effluent streams carrying organic contaminants at sufficiently high levels to damage downstream TCCS components or endanger the crew.

The focus of this paper is the coadsorption of dichloromethane (DCM) and water on activated carbon. This system was chosen both because DCM is a design driver for the TCCS, and because equilibrium data for DCM/water coadsorption are available Breakthrough curves for water and DCM are measured as the RH of the feed stream varies. Computer simulations, developed to model the experimental system, are compared to measured breakthrough curves. Dynamic adsorption simulations are made possible through the work of Taqvi and LeVan [1] who developed adsorption isotherm fits for pure water and DCM/water on BPL activated carbon. This investigation will help quantify the role of water in adsorption processes and applications such as a TCCS.

MATHEMATICAL MODEL

Numerical simulations were used to generate breakthrough curves of DCM and water from an activated carbon adsorption column. The assumption of minimal mass transfer resistances in the dilute system gave rise to a local equilibrium model with constant fluid velocity and no fluid phase accumulation. Adsorption was assumed to occur isothermally for experimental conditions. Additionally, axial dispersion was assumed to be negligible. The material balance, written for each adsorbable component, *i*, is

$$\rho_b \frac{\partial q_i}{\partial t} + \varepsilon' v \frac{\partial c_i}{\partial z} = 0 \qquad i = 1,2 \tag{1}$$

The solution of EQ (1) for $c_i(t,z)$ requires an expression for the adsorption isotherm, $q_i(c_1,c_2)$. Since the shape of breakthrough curves is a strong function of the adsorption isotherm, it is necessary to model adsorption equilibrium data accurately in order to describe the physical system. Pure water isotherms on activated carbon, such as those measured by Rudisill *et al.* [2], are not described well by most models.

Furthermore, isotherms of water/organic mixtures cannot be accurately described by mixing models such as the ideal adsorbed solution theory. The best model currently available to describe the DCM/water system is that developed by Taqvi and LeVan [1].

Taqvi and LeVan fit the experimental data of Rudisill *et al.* [2] and Eissmann and LeVan [3] to a virial model which accounts for the heterogeneous nature of activated carbon by breaking the surface into hydrophobic and hydrophilic patches, *A* and *B* respectively. The isotherm, valid at 25°C, is written on both patches and recombined to obtain the total loading. The two-component isotherm, written on patch *A*, for DCM and water is given by

$$\begin{aligned} P_d &= q_{d_A} \exp\Big(A_{d_A} + 2B_{dd_A} q_{d_A} + 2B_{dw_A} q_{w_A} \\ &\quad + \tfrac{3}{2} C_{ddd_A} q_{d_A}^2 + 3 C_{ddw_A} q_{d_A} q_{w_A} + \tfrac{3}{2} C_{dww_A} q_{w_A}^2\Big) \\ P_w &= q_{w_A} \exp\Big(A_{w_A} + 2 B_{ww_A} q_{w_A} + 2 B_{dw_A} q_{d_A} \\ &\quad + \tfrac{3}{2} C_{www_A} q_{w_A}^2 + 3 C_{dww_A} q_{d_A} q_{w_A} + \tfrac{3}{2} C_{ddw_A} q_{d_A}^2\Big) \end{aligned} \tag{2}$$

Similarly, a pure component isotherm for water may be written on patch *A* as

$$P_w = q_{w_A} \exp\Big(A_A + 2B_A q_{w_A} + \tfrac{3}{2} C_A q_{w_A}^2\Big) \tag{3}$$

EQs (2) and (3) must also be written on patch B and then combined with EQ (4) to completely define the isotherm.

$$\begin{aligned} q_d &= q_{d_A} + q_{d_B} \\ q_w &= q_{w_A} + q_{w_B} \end{aligned} \tag{4}$$

The total loading of each component is the sum of the loadings on patch *A* and patch *B*. To retain a physical description of the system, component partial pressures must be equal above each patch. Constants for EQs (2) and (3) are given in the appendix.

EXPERIMENTS

An isothermal fixed bed apparatus was used to measure breakthrough curves of water and DCM/water mixtures from an activated carbon adsorption column. The apparatus, shown in Figure 1, feeds an air stream at a desired RH and DCM concentration into an activated carbon bed. The RH is controlled by adjusting the relative flows of a dry air stream and a humid air stream using mass flow controllers. This control method allows RH to be adjusted very rapidly during an experiment. DCM is added to the feed stream as a function of temperature by diffusion through a capillary. The RH and temperature of the combined stream are measured at both the inlet and outlet of the carbon bed. DCM concentration is determined by analyzing samples of the air stream with a flame ionization detector.

The adsorption column is a 0.55 cm I.D. stainless steel tube with a packed length of approximately 5 cm containing ~0.5 g of 40x50 mesh BPL activated carbon. Prior to an experiment, the carbon is regenerated by flowing dry nitrogen at 225°C through the column for over 10 hours. During an experiment, the entire column is submerged in a constant temperature water bath at 25°C to insure isothermal operation. In all experiments, the total flow to the column is held constant at 0.10 L/min to match the superficial velocity in the TCCS.

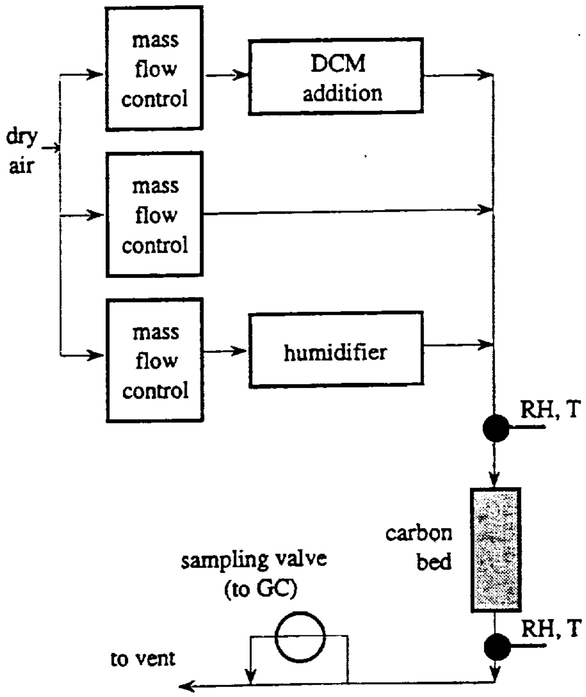

Figure 1. Simplified schematic of isothermal fixed-bed adsorption apparatus.

RESULTS AND DISCUSSION

ISOTHERMS - Equilibrium isotherms give considerable insight into the breakthrough behavior of adsorbed species. Experiments were limited in scope to adsorption dynamics, and no isotherms were recorded. However, in order to better understand water and DCM breakthrough curves, adsorption isotherms are presented in Figures 2 and 3. The isotherms shown represent fits to experimental data which were developed by Taqvi and LeVan [1].

Figure 2 shows a graphical representation of the pure water isotherm fit of Taqvi and LeVan [1] along with experimental data reported by Rudisill *et al.* [2]. The most dramatic feature of the water isotherm is the increase in loading which occurs between about 40% RH to 60% RH. The volume of water adsorbed increases rapidly as RH rises, resulting in a decrease in the available pore space for the adsorption of organics such as DCM.

Figure 3 illustrates the extent to which DCM loading is influenced by water adsorption when DCM vapor concentration is held constant. For example, the Taqvi-LeVan model predicts a decrease in DCM loading of over 20 times between 25% RH and 75% RH at a DCM concentration of 3 ppm. The obvious drop in adsorption capacity for DCM at high RH leads to the possibility of column effluent streams which are highly concentrated with DCM following a rise in feed RH. Moreover, the reduced capacity will cause faster organic breakthrough times and will substantially decrease the operational time of an adsorption column.

BREAKTHROUGH CURVES - A dimensionless time equal to the number of superficial bed volumes of gas passed into the bed was used to analyze both experimental and simulation results. Volumetric flow rate, *F*, was taken at standard conditions, and dimensionless time was calculated from:

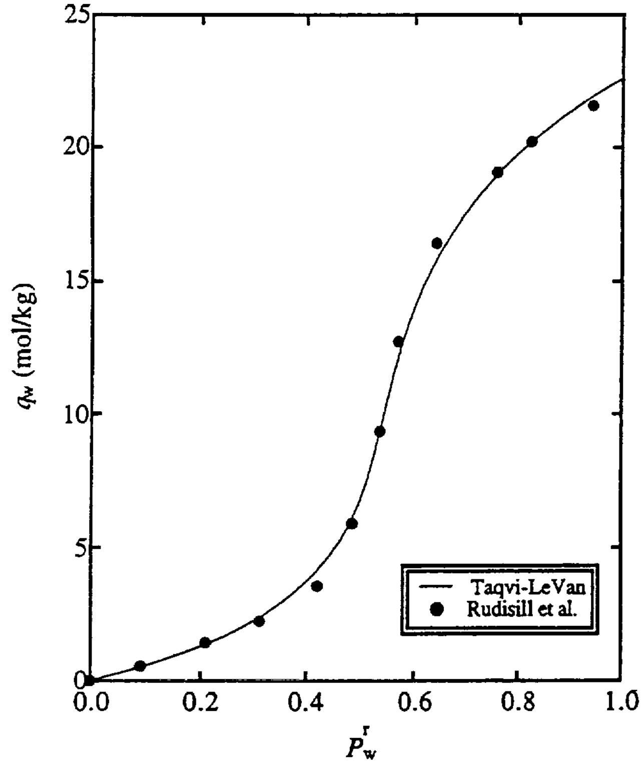

Figure 2. Water isotherm at 25°C on BPL activated carbon. Experimental data of Rudisill *et al.* and virial fit of Taqvi. (P^s_w= 3.1714 kPa)

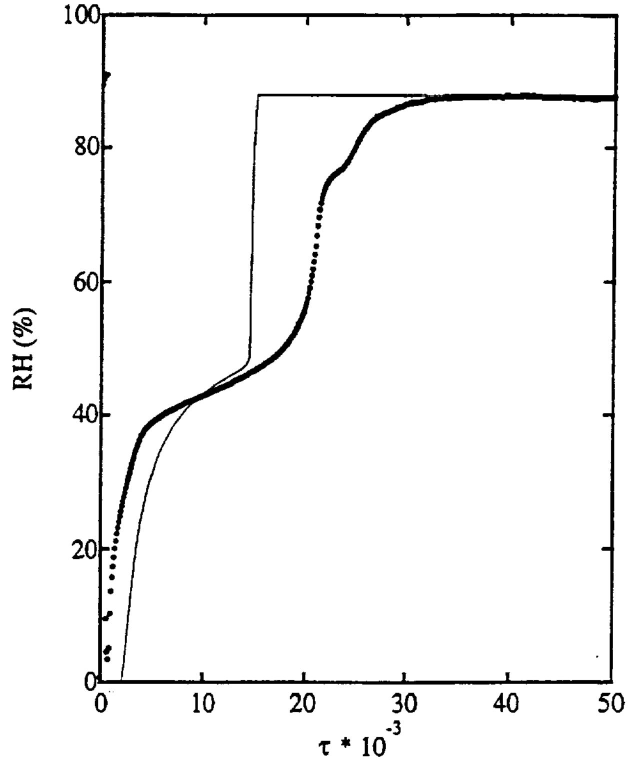

Figure 4. Breakthrough curve for water on BPL activated carbon at 25°C. Air stream at 88% relative humidity fed to an initially dry column. Solid line indicates model prediction.

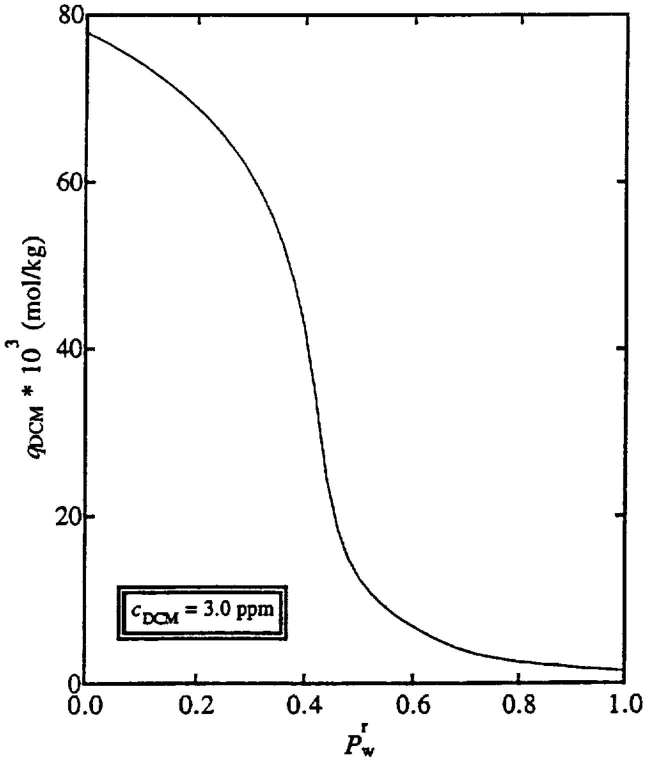

Figure 3. Variation of dichloromethane loading on BPL activated carbon at 25°C with reduced water pressure. Curve given by Taqvi-LeVan isotherm of EQ (2). (P^s_w= 3.1714 kPa)

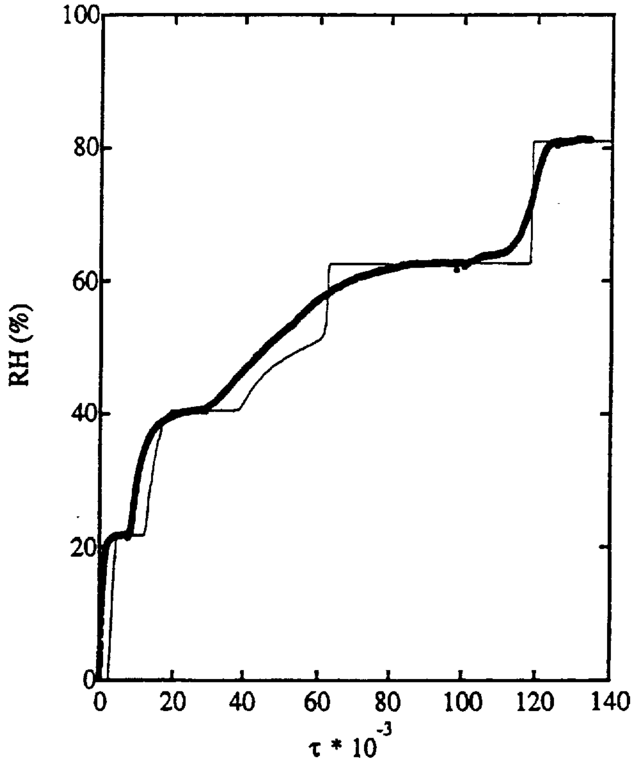

Figure 5. Water breakthrough on BPL activated carbon at 25°C following step changes in relative humidity. Solid line indicates model predictions.

$$\tau = \frac{Ft}{V} \qquad (5)$$

Water - Breakthrough curves measured for water on BPL activated carbon at 25°C along with results from numerical simulations using the Taqvi-LeVan isotherm of EQ (3) are shown in Figures 4 and 5. The experimental breakthrough curve shown in Figure 4 was obtained by passing an air stream at 88% RH through a regenerated carbon bed. The overall shape of the experimental curve is predicted well; however, some quantitative differences are present. Most significantly, the isotherm model given by EQ (3) under-predicts the equilibrium water loading which is observed experimentally, resulting in an anticipated breakthrough time considerably faster than the measured time.

Breakthrough curves, recorded as inlet RH was successively increased in increments of 20% beginning from a dry column and ending at 80% RH, are shown in Figure 5. Evident in both Figures 2 and 5, the largest increase in water loading occurs between 40% RH and 60% RH. In Figure 2, this is represented by the steep slope of the isotherm. The same trend is indicated in Figure 5 by the gradual slope of the breakthrough curve as relatively large quantities (compared to the other RH steps) of water are adsorbed. This region, usually near 50% RH, is a defining characteristic of the water isotherm, and is very important when considering the coadsorption of water and organics.

DCM/Water - In Figures 6 and 7, numerical simulations incorporating the DCM/water isotherm of EQ (2) are shown along with experimental measurements. Prediction of qualitative trends in the breakthrough curves is favorable; yet, the model appears to exaggerate the dependence of DCM loading on RH.

Figure 6 was obtained using an activated carbon bed initially in equilibrium with an air stream at 25°C and 25% RH containing ~3 ppm DCM. The breakthrough curves were generated when the RH of the feed stream was increased from 25% to 75%. By far the most important effect of the humidity swing is the displacement of DCM from the adsorbed phase. As water is adsorbed, particularly in the region near 50% RH to 70% RH, DCM desorbs from the bed resulting in a maximum effluent stream concentration of over 60 ppm. This represents a concentration approximately 20 times larger than the feed concentration.

The experiment represented in Figure 7 illustrates the effect that small changes in RH can have on DCM loading. The experiment proceeds by first feeding an air stream containing ~3 ppm DCM to a regenerated carbon bed. Following the breakthrough of dry DCM, the RH of the feed stream is increased in increments of 20%. The column effluent stream is allowed to break through completely prior to each subsequent humidity step. As the RH is increased through 40%, the effect on DCM loading is inconsequential; however, as the RH is increased further, larger quantities of DCM desorb from the column. This effect reiterates that DCM loading is a strong function of RH near 50%.

Contaminant Control - The above results indicate that relative humidity can have a significant effect on activated carbon adsorption columns used for removal of trace organic contaminants from air streams. Moreover, Figure 7 demonstrates one difficulty which may be encountered when attempting to control contaminant concentrations in closed environments wherein RH levels exceed 50%.

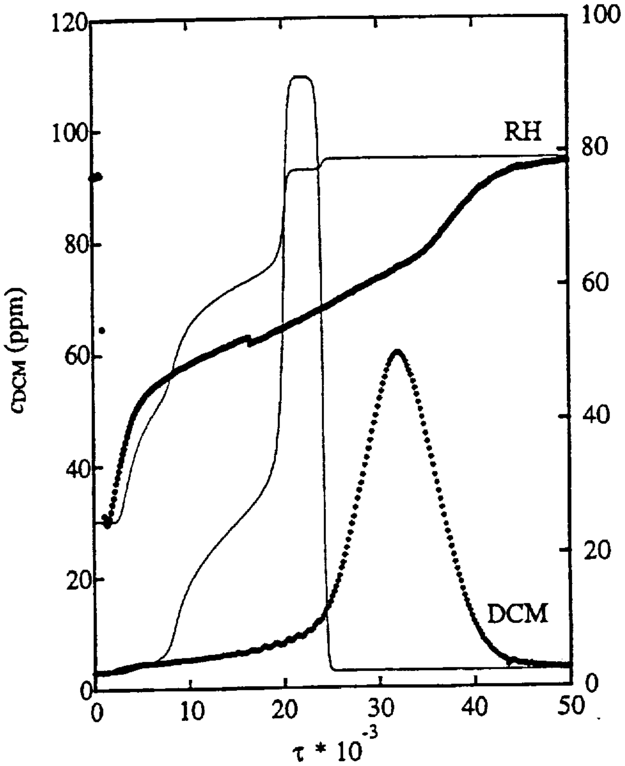

Figure 6. Breakthrough curves for water and dichloromethane on BPL activated carbon at 25°C following a step change in relative humidity from 25% to 75%. Column initially in equilibrium with 3 ppm DCM and 25% RH. Solid lines indicate model predictions.

Although the effect of water on DCM adsorption is clear, it is difficult to extrapolate these results directly to more complex systems containing many contaminants. Water/organic interactions can vary widely with the compounds considered. Furthermore, consideration of additional contaminants necessitates the investigation of organic/organic interactions. Currently, research and modeling work is ongoing to explore humidity effects on systems containing multiple organic compounds.

CONCLUSIONS

An isothermal adsorption column was used to measure breakthrough curves for water and dichloromethane/water mixtures at 25°C on BPL activated carbon. Additionally, numerical simulations incorporating isotherms based on the virial model were compared to experimental results.

Rapid increases in RH levels were shown to significantly reduce the capacity of BPL activated carbon to adsorb DCM. Furthermore, the decline in DCM loading resulted in column effluent streams containing concentrations of over 60 ppm DCM, a value 20 times larger than the feed concentration. Highly elevated contaminant levels represent a potential hazard to both downstream equipment and personnel.

Humidity effects should be considered carefully when designing adsorption columns for trace contaminant control. Research is continuing in order to better understand the role of humidity in the operation activated carbon beds for air revitalization and related applications.

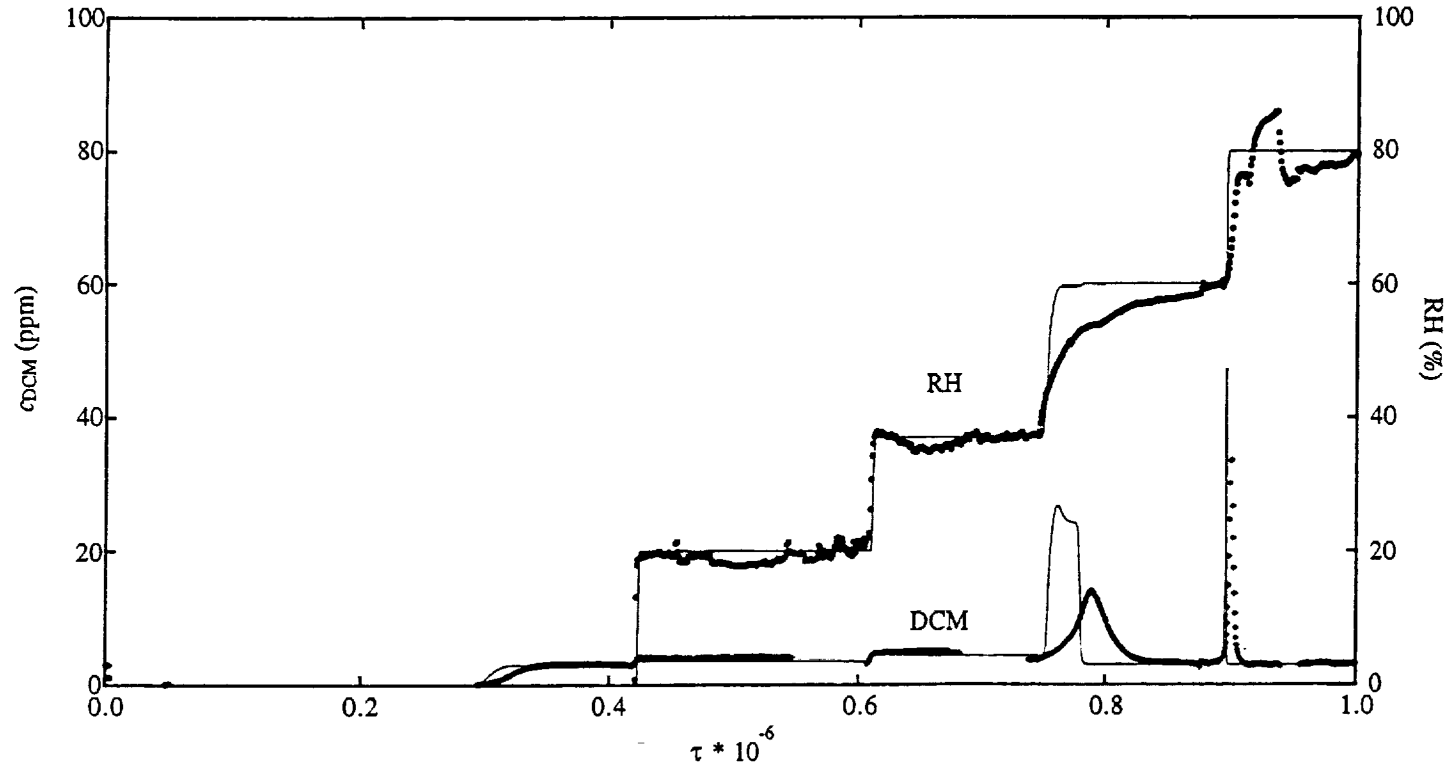

Figure 7. Breakthrough curves for water and dichloromethane on BPL activated carbon at 25°C. Feed air stream contains constant c_{DCM} = 3 ppm; relative humidity is increased incrementally from dry to 80%. Solid lines indicate model predictions.

ACKNOWLEDGEMENT

We are grateful to the National Aeronautics and Space Administration for funding this research.

NOMENCLATURE

A = virial coefficient
B = virial coefficient
c = gas phase concentration of solute, mol / m^3
C = virial coefficient
D = virial coefficient
F = volumetric flow rate, m^3 / s
p = partial pressure of solute, kPa
P_w^r = reduced pressure of water
P_w^s = saturation pressure of water, kPa
q = adsorbed-phase concentration, mol / kg
t = time, s
v = superficial velocity, m / s
V = volume of bed, m^3
z = axial coordinate, m

Greek Letters

ε' = total bed voidage
ρ_b = bulk density of packing, kg / m^3
τ = dimensionless time

Subscripts

A = patch A
B = patch B
d = dichloromethane
i = solute
w = water

REFERENCES

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APPENDIX

System Parameters

ρ_b, kg/m^3	4.80
ε'	0.7
F, L/min	0.10
V, m^3	1.04e-6

Effects of Humidity on Activated Carbon Adsorption Columns Used for Air Purification

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High relative humidity levels can limit the effectiveness of activated carbon beds used for air purification. The coadsorption of water and organics on activated carbon is a complex problem, and has not been extensively studied; however, experiments have demonstrated that the presence of water reduces the adsorption capacity of certain organic compounds on activated carbon. Carbon beds used to remove organic compounds from air streams are often subjected to fluctuating humidity levels. As the relative humidity of the feed stream increases, the breakthrough time for many organics is expected to decrease, although the extent of this humidity effect can seldom be quantified.

An isothermal fixed bed apparatus is used to measure breakthrough curves for the coadsorption of dichloromethane (DCM) and water on BPL activated carbon at 25 C. Breakthrough curves for trace concentrations of DCM are measured both at constant and varying relative humidity levels. Experimental curves are compared to computer simulations generated from a material balance coupled with a model for the DCM/water multicomponent isotherm. These results aid in the development of criteria for species grouping which can be used to estimate breakthrough time for feed streams containing many organic compounds in addition to water.

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