CHEMISORPTION OF ARSINE ON ACTIVATED, IMPREGNATED CARBON ADSORBENTS

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Abstract

This work discusses an ongoing investigation to characterize microporous adsorbents that affect the removal of arsine from air. One aspect of this work was to develop a test system for generating, transport and detection of arsine gas appropriate for adsorbent breakthrough measurements at part-per-billion (ppb) concentrations. Preliminary adsorption data is provided showing the effect of arsine feed concentration, sorbent bed depth, superficial airflow velocity and relative humidity on breakthrough time and capacity on ASZM-T adsorbent. The results of these data are interpreted as a means to propose a standard test method.

Introduction

Arsine is a highly toxic, high vapor pressure chemical that is widely used in the manufacture of semiconductors. Improved respiratory protection is needed for personnel working in environments where arsine is present due to increasingly lower permissible exposure limits promulgated by OSHA and the USACHPPM. A primary form of protection from arsine exposure is filtration of the chemical by reactive adsorption. For over five decades activated carbons containing metal salts have been the material of choice for arsine removal for both occupational and military applications. In the early 1940's, arsine removal was shown by Rowlinson and in Conant's report to be particularly effective with oxides of copper and silver. In this work, arsine performance data for a adsorbent product known as ASZM-T is reported. This material is an activated carbon impregnated with copper (A), silver (S), zinc (Z), molybdenum (M) and triethylenediamine (T). At low to moderate relative humidities, arsine reacts predominantly in stoichiometric proportions with copper and progressively catalytic with silver at higher relative humidities. The emergence of newer classes of sorbents, such as nanoporous metal organic frameworks (MOF) and other porous polymers, may present new challenges in characterizing the materials activity for chemical removal. In the case of arsine, state of the art instrumentation and system controls are needed to accurately measure the reaction process. The objective of this work is to establish a methodology for evaluating the adsorption dynamics of arsine in microporous materials over a wide range of test conditions.

Test Apparatus

Figure 1 shows a schematic diagram of the arsine test system. The design of the system provides for 100 percent of the gas mixture to pass through the adsorbent test cell as a means to minimize the mass of arsine consumed per test. Arsine concentrations are generated from compressed cylinders containing 4% arsine (by volume) in nitrogen (Matheson Tri-Gas) and mixed with compressed air. The initial concentration of arsine is noteworthy as arsine's flashpoint is 5.8% (volume) thus this lowered concentration, further mitigates the concern for possible material ignition. Feed concentrations are acquired by balancing gas mixture proportions using mass flow controllers (Tylan).

Diluent air was humidified prior to mixing with arsine using a saturator cell of water suspended in a temperature controlled water bath. The humidity of the system was monitored with a Dewstar chilled mirror dewpoint hygrometer. Temperatures were taken at various locations including pre- and post- sample with T-type thermocouples. Data acquisition, readout and data storage was processed with National Instruments Labview products.

Arsine effluent concentrations were monitored with a Zellweger/Honeywell CM4 detector, which employs a colorimetric sensor tape configured on a cassette wheel. Reactions of arsine with the tape material causes a stain commensurate with the concentration of the arsine. The color intensity is read by an optical detection system in the concentration range of 50-500 ppb.
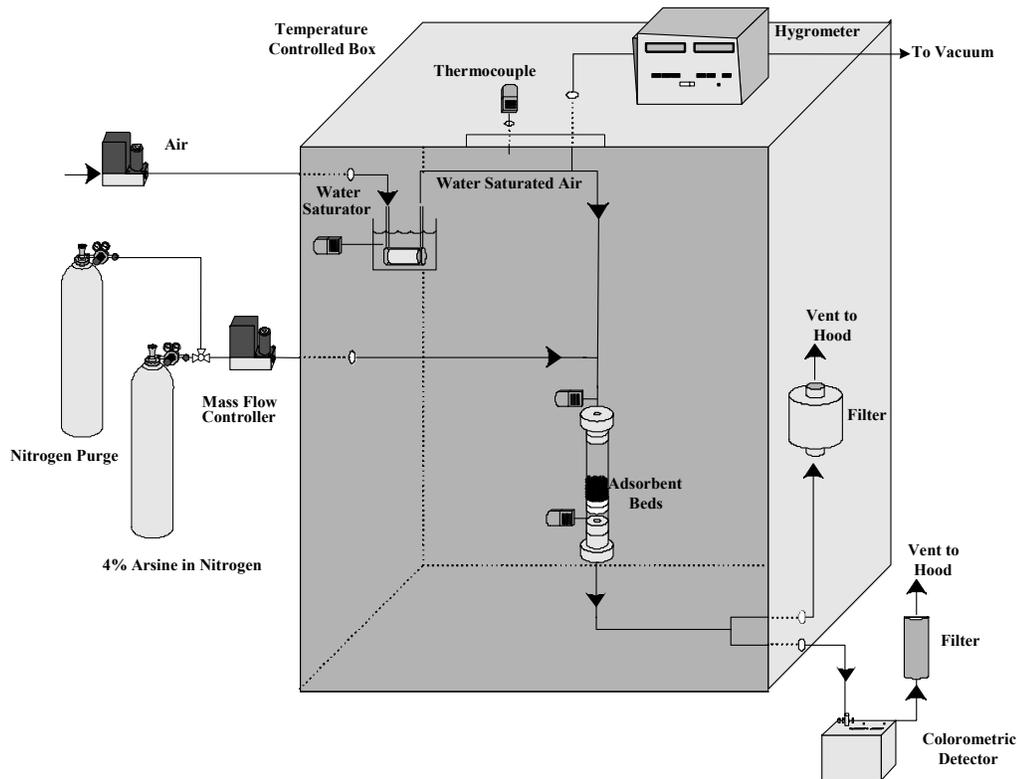
Figure 1. Arsine Test System for Adsorbent Breakthrough Measurements.

Results and Discussion

The test conditions evaluated in this work are shown in Table 1. These conditions are typical of test beds used in developing adsorbent performance correlations and for certification purposes. The desired test characteristics focus primarily on time to breakthrough, airflow velocity, adsorbent bed depth, relative humidity and in the case of a reactive chemical, bed temperature.

Table 1. Test Conditions and Performance Characteristics.

Test Conditions:

Feed Concentration (mg/m3):	1000 – 10,000
Effluent Concentration (mg/m3):	0.2 mg/m^3 = 63 ppb
Pre-Humidification (% RH):	50 to 80
Test Relative Humidity (% RH):	15 to 80
AR – As Received Moisture	maximum 3% by weight
Airflow Velocity (cm/s):	5.9 to 9.6
Adsorbent Bed Depth (cm):	1 to 2

Desired Test Characteristics:

Breakthrough Time:	30 to 60 min
Airflow Velocity:	6.0 to 10 cm/s
Test Relative Humidity:	50 to 80% RH
Bed Temperature Rise:	less than 20 C

During the initial phase of testing it became clear that high feed concentrations and relative humidities affected the CM4 detector's ability to distinguish between arsine and water concentrations. Feed concentrations of 10,000 mg/m^3 at 80-80 (preequilibrated-test RH) humidity conditions resulted in water condensation in the sample tube and temperature increases approaching 70 C at the adsorbent sample bed. The CM4 arsine detector has an upper humidity limit of 80% RH, so when

condensation was observed during a test, the test was stopped to limit potential damage to the analyzer and/or false positive results. It was confirmed at relative humidities above 80% RH that the CM4 detector provided a false response to arsine. In addition, the analyzer has an upper temperature limit of 40C but, temperature data from the effluent sample line proved that the line was adequate to dissipate excess heat upstream of the CM4 detector.

Arsine feed concentrations were evaluated between 1,000 and 7,5000 mg/m^3 in an attempt to determine the concentration that best reflects optimal bed temperatures and breakthrough times. Figure 2 shows the effect of arsine feed concentration on bed temperature rise and breakthrough time. At 7,5000 mg/m^3 the adsorbent bed temperature increased to about 70 C with a breakthrough time of 60 min. Under these high temperature conditions there is concern that further oxidation could occur that would accelerate the temperature rise in the adsorbent bed. It was determined that a feed concentration of 4000 mg/m^3 was optimum to maintain the temperature of the adsorbent test bed below 50 C, while providing a breakthrough time in the range of 80 min.
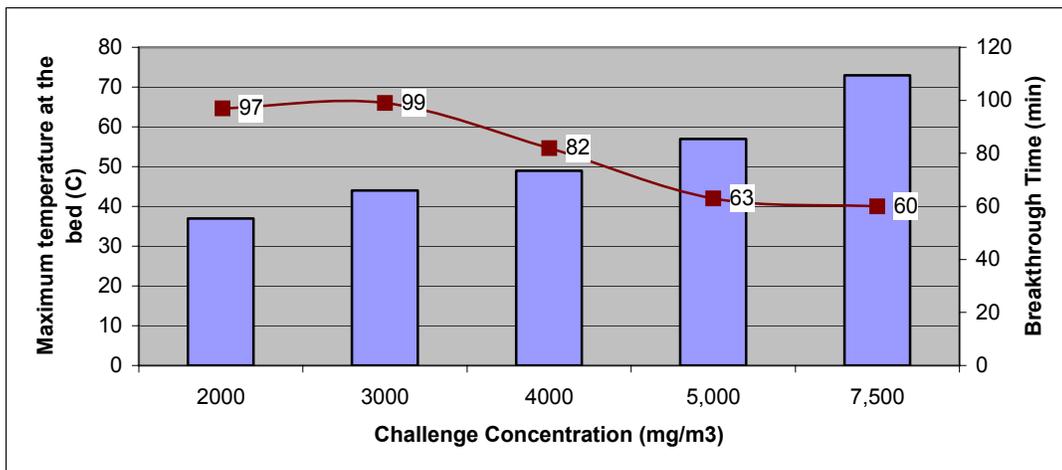

Figure 2. Effect of Arsine Concentration on Sample Bed Temperature and Breakthrough Time.
Sorbent: ASZM-T, Humidity : AR-80, Bed Depth : 2 cm, Velocity : 9.6 cm/sec

In addition to the variables of concentration and humidity, bed depth and airflow velocity were evaluated to determine their effect on breakthrough time. Typical bed depth and flow conditions were set such that the residence time in the adsorbent test bed was between 0.2 and 0.3 s, reflecting standard filter bed design criteria. Bed depths of 1 to 2 cm and airflow velocities from 6 to 10 cm/s were evaluated in this work.

Figures 3 and 4 show the effect of bed depth and airflow velocity on arsine breakthrough time. At 2 cm the arsine breakthrough time was about 100 min, but when the bed depth was reduced to 1 cm the breakthrough time decreased to about 10 min. The data for the shallower bed (1 cm) demonstrates a dominant kinetic effect that is far less than the arsine capacity of the 2 cm bed (Figure 3). Additional bed depths between 0.5 and 1 cm are needed to identify the critical bed depth for a given set of airflow velocities.

Figure 4 shows the effect of airflow velocity from 5.9 to 9.6 cm/s for a 1 cm test bed of ASZM-T adsorbent. At the lowest airflow velocity (5.9 cm/s) the breakthrough time was about 100 min. A 50 percent increase in airflow velocity from 5.9 to 9.6 cm/s, the breakthrough time decreased to about 30 min, indicating a rapidly increasing mass transfer zone. These results were anticipated since the residence times ranged far below the minimum value of 0.2 s for typical adsorbent bed designs.
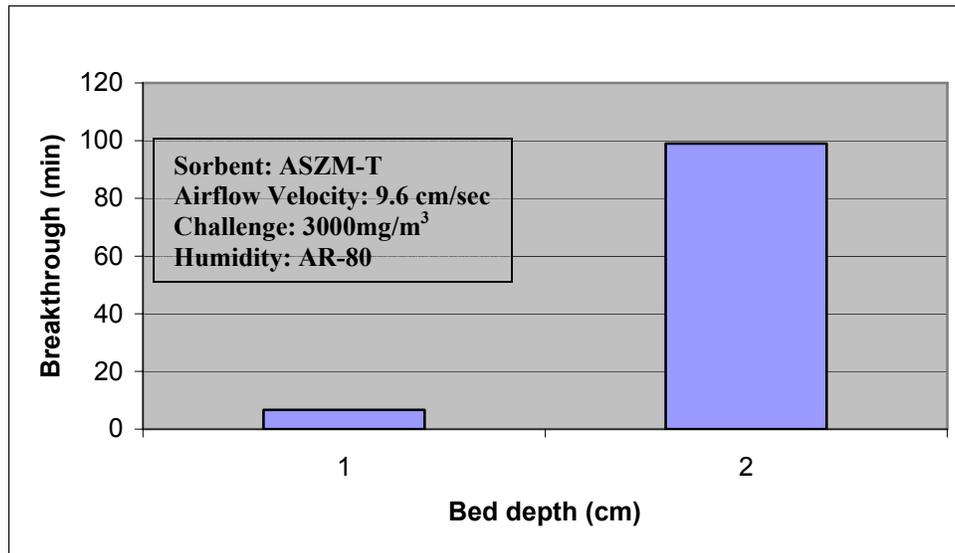
Figure 3. Effect of Bed Depth on Breakthrough Time of Arsine Challenge at 3,000mg/m^3.
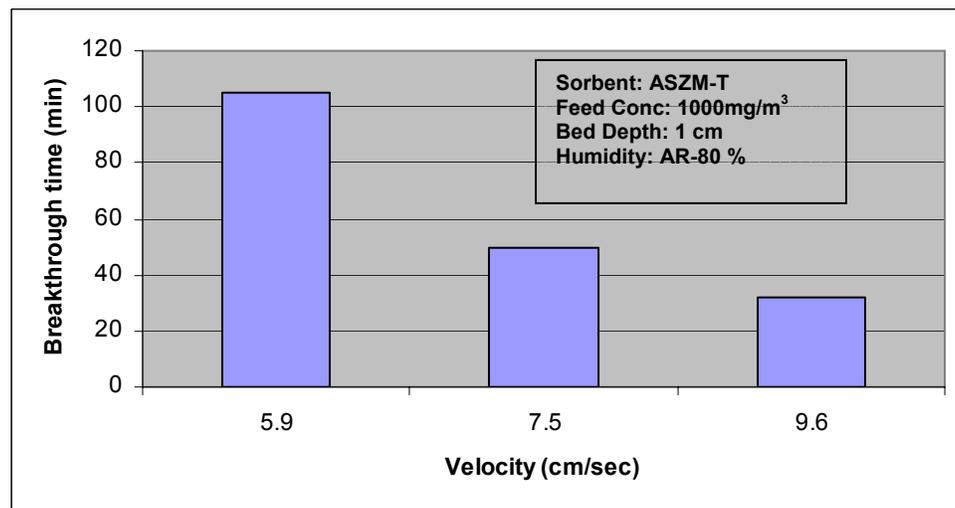

Figure 4. Effect of Velocity on Breakthrough Time of Arsine on ASZM-T Carbon.

Summary and Conclusions

- A test system for conducting arsine breakthrough on test beds of adsorbent was developed. The test system incorporates electronic flow control , humidification and a colorimetric optical detector to monitor effluent arsine concentrations.
- Preliminary data has been measured reflecting the breakthrough dynamics of a reference adsorbent ASZM-T. This data and information has resulted in a proposed test methodology for conducting arsine breakthrough for reference and newly developed adsorbents.

Although additional test parameters are required to develop a further understanding of the arsine removal process, a standardized test is proposed. Under these conditions the desired target characteristics shown in Table 1 are obtained.

Preliminary Standard Test Conditions:

Feed Concentration: 4000 mg/m^3
Effluent Concentration: 0.2 mg/m^3

Pre-Humidification:	As Received
Test Humidification:	60-80 RH
Bed Depth:	2.0 cm
Airflow Velocity:	6.0 to 10 cm/s

Future Work

While much has been done to determine optimal test conditions of arsine removal by ASZM-T, the mechanisms of removal have not been completed. Planned work will result in understanding the empirical relationships of various metal salts impregnated on ASZM-T and other newly developed porous reactive adsorbents for comparison to the work of Haacke and others.

References

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