NITRIC ACID VAPOR REMOVAL BY ACTIVATED, IMPREGNATED CARBONS

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ABSTRACT

Laboratory and industrial workers can be exposed to vapors of nitric acid, especially in accidents, such as spills. Nitric acid can also be a product of incineration for energy production or waste (e.g., CW agent) disposal. Activated carbons containing impregnants for enhancing vapor and gas removal have been tested for effectiveness in removing vapors of nitric acid from air. The nitric acid vapor was generated from concentrated acid solutions and detected by trapping in a water bubbler for pH measurements. Both low and moderate relative humidity conditions were used. All carbons were effective at vapor contact times representative of air-purifying respirator use. One surprising observation was the desorption of low levels of ammonia from impregnated carbons. This was apparently due to residual ammonia from the impregnation processes.

INTRODUCTION

The ASC Whetlerite carbon originally developed for protection against chemical agents has also been used in commercial industrial air-purifying respirator cartridges. A recently-developed chromium-free military carbon, ASZM-TEDA, also has the potential for industrial applications. Besides air-purifying respirator (gas mask) applications, such carbons have potential for air cleaning of effluents from demilitarization and industrial chemical destruction operations. One of the potential effluents from such operations is nitric acid vapor. Therefore, we have studied the effectiveness of these impregnated activated carbons for trapping vapors of nitric acid.

EXPERIMENTAL

The carbons discussed in this report were taken from C2 canisters. The carbon we are calling ASC was from a Canister, Chemical-Biological, Mask, C2 (4240-01-119-2315). The ASZM-TEDA carbon was taken from a Canister, Chemical-Biological, Mask, (ASZM-TEDA), C2A1.

Samples of the carbons from these canisters were packed into a fluorocarbon tube of inner diameter 2.1 cm. Total air flows of 2 L/min passing through these beds consisted of a main air flow plus an acid generator purge flow, each calibrated with an electronic bubble flow meter. Carbon sample weights were scaled to correspond at a testing flow of 2 L/min to the same residence time as the full canister bed weight at 50 L/min. Test beds of ¼ these weights were also tested to observe acid vapor breakthroughs in reasonable test times.

The nitric acid vapors were generated by passing a purge air flow (45 mL/min) through a chamber in which concentrated nitric acid was being stirred. It was found that the acid needed to be "aged" several hours before use in testing or else exceptionally high removal efficiencies would be obtained, likely due to more water and less nitric acid being generated until an azeotropic mixture was reached. The nitric acid output was calibrated before and/or after each test by using an empty tube in place of a test bed.

Nitric acid in bed effluent air or challenge air (empty tube) was measured by continuously passing a part of the effluent air through a bubbler containing 200 mL of water and continuously monitoring the pH of the water. The sampling flow averaged 1.08 ± 0.03 L/min. Tests confirmed that the collection efficiency of the bubbler was 99.8% even after 6 hours of sampling 50 ppm nitric acid vapors. A pH probe immersed in the bubbler allowed continuous pH measurements by a meter that sent the values to a computer for data acquisition at 1 minute intervals. The pH meter and probe were calibrated periodically using standard buffer solutions.

Main air flow was humidified for some tests by passing it through a chamber containing water before mixing it with the acid generator purge air. Relative humidity (RH) and temperature (T) were monitored using a dew point hygrometer upstream of the mixing point. Thermocouple probes upstream and immediately downstream of the test bed allowed measurements of temperature changes in air passing through the bed. At selected times during a test pH, RH, and T were manually recorded in a notebook.

DATA ANALYSIS

The pH measurements taken at 1-min intervals during a test were put into a spreadsheet and converted to acid concentrations in the bubbler. For challenge and desorption concentration calculation the average slope of concentration vs. time over a selected time interval was obtained by linear regression. It was then converted to an average acid vapor concentration using the bubbler water volume and local atmospheric conditions (1 mole/L-min = 6.2×10^6 ppm). Evaporation of the bubbler water was measured to be linear with time and dependent on relative humidity. Corrections were made for these losses in calculating challenge and breakthrough concentrations.

RESULTS

Full bed equivalent carbon weights (as defined above, 4.52 g for the ASC and 4.70 g for the ASZM-TEDA) were first tested for nitric acid vapor removal from air. No acid was observed in the effluent air from the beds even after 24 hours. Figure 1 shows two tests with ASC carbon, 40 ppm nitric acid vapor, and 69% relative humidity air.

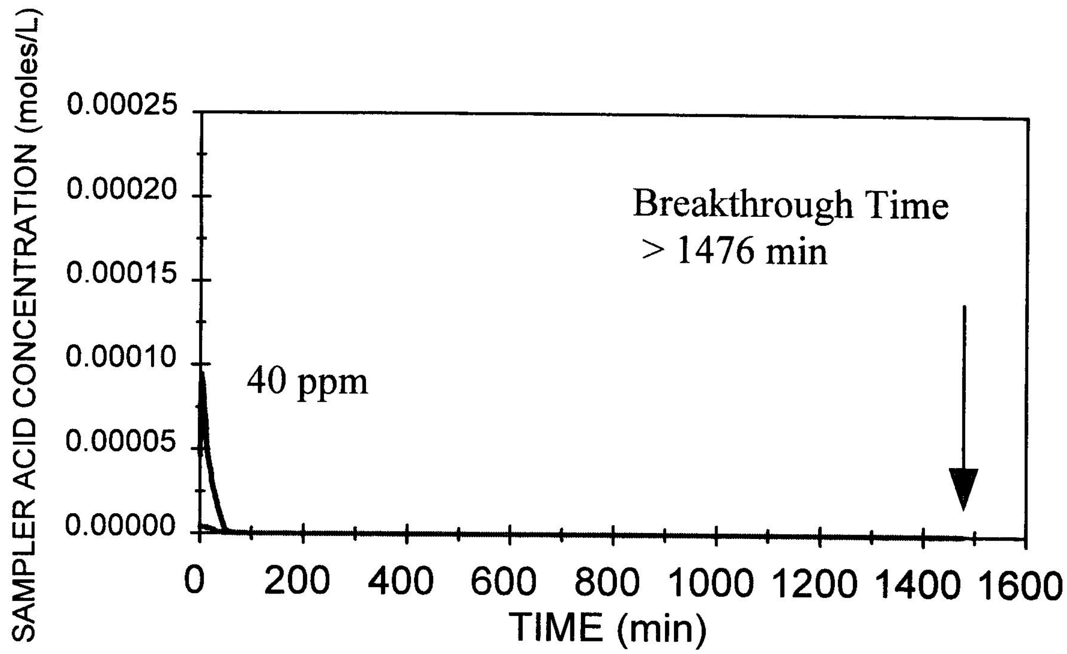

Figure 1. Full equivalent bed ASC carbon tests at 69% relative humidity with acid challenge.

Quarter bed equivalents were used for other tests to get measurable breakthroughs. Figures 2 and 3 show breakthrough curves for ASC and ASZM-TEDA, respectively.

Sampler water was initially slightly acidic (pH = 5-6), even though it had been distilled and boiled before use to remove carbon dioxide. Figures 1-3 show that at the beginning of the acid breakthrough tests the acidity of the sampler water actually <u>decreased</u>. This occurred at both low (10-13%) and moderate (60-70 %) relative humidities, both with and without acid vapor challenge to the bed. However, using an unimpregnated carbon did not produce this effect.

Further tests were done to explore this effect. Figures 3-6 show examples of the acid concentration decreases for humid and dry air and both activated carbons. The results shown were obtained with full bed equivalents of carbons taken from freshly opened canisters.

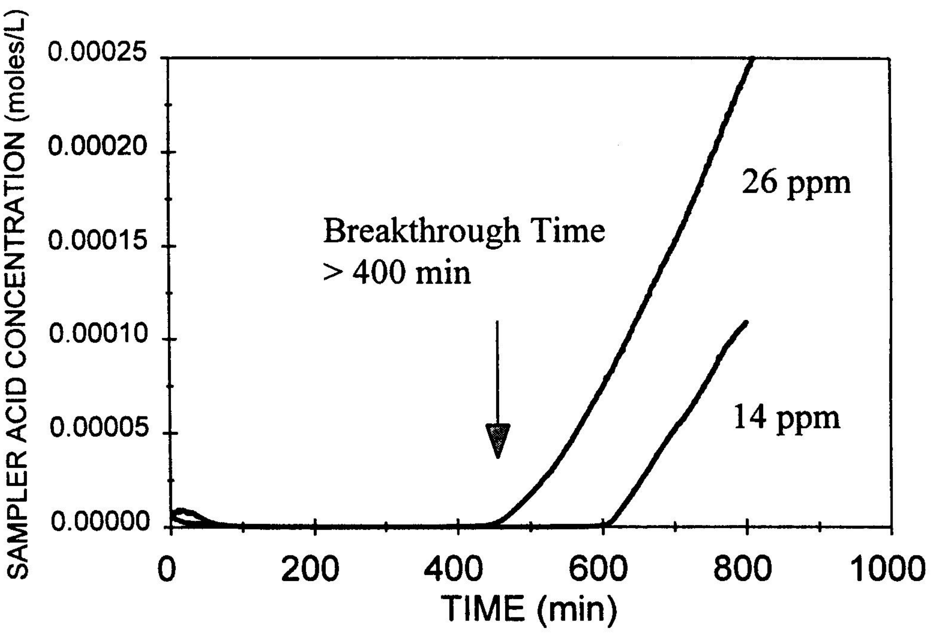

Figure 2. ASC quarter bed equivalent breakthrough curves at 69% RH with acid challenge.

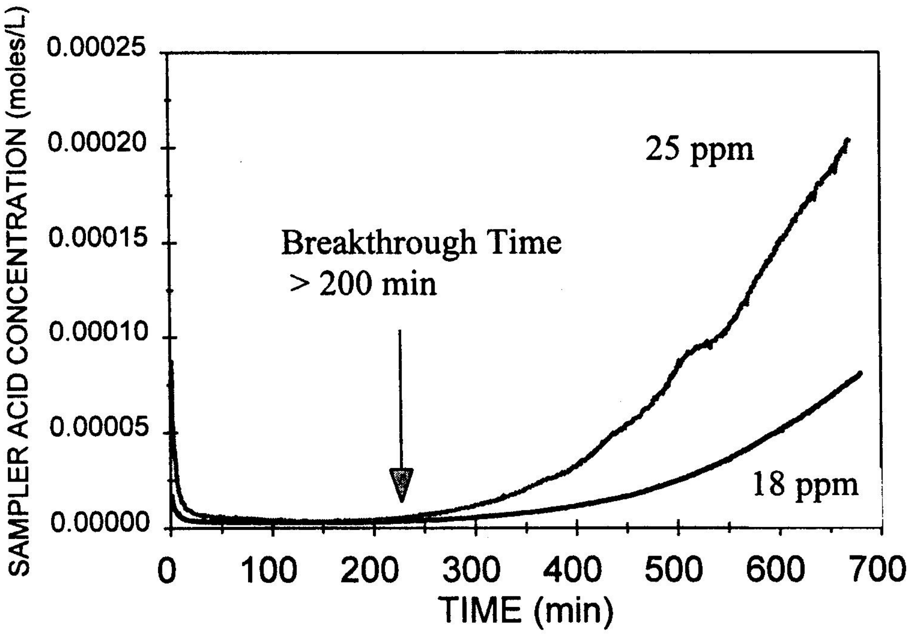

Figure 3. ASZM-TEDA quarter bed equivalent breakthrough curves at 69% RH with acid challenge.

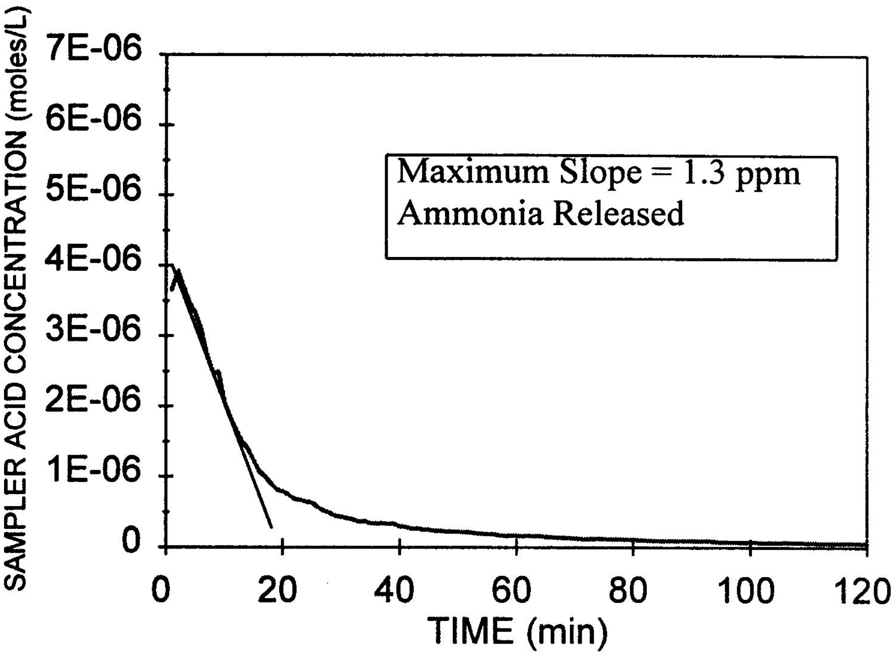

Figure 4. Full equivalent bed ASC carbon dry (11% RH) air purge with no acid challenge.

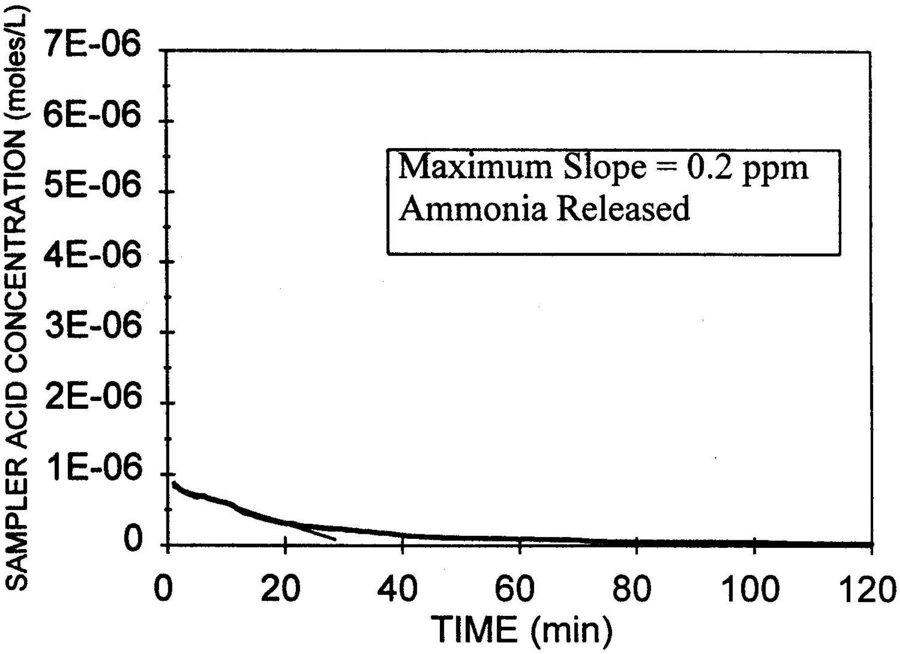

Figure 5. Full equivalent bed ASC carbon humid (67% RH) air purge with no acid challenge.

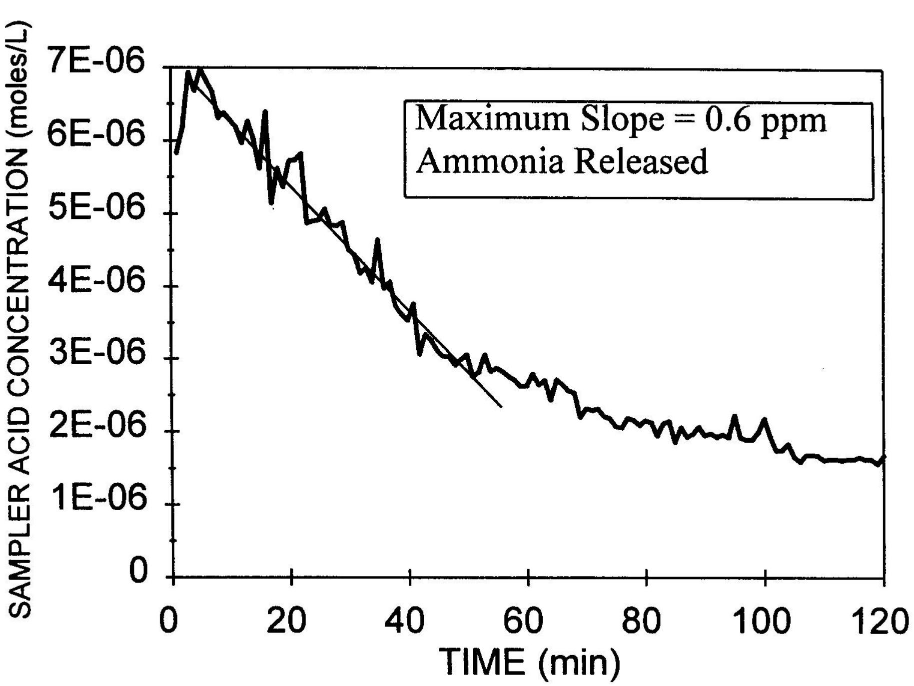

Figure 6. Full equivalent bed ASZM-TEDA carbon humid (66% RH) air purge with no acid challenge.

DISCUSSION AND CONCLUSIONS

Figures 1-3 show that the ASC and ASZM-TEDA carbons are highly effective in removing nitric acid vapors for long times. Similar experiments with an unimpregnated carbon have also shown such effectiveness, so that some of the capacity can be attributed to reactions with the carbons and/or their impurities. We saw no nitric acid desorption after adsorption and stopping the acid challenge.

We attributed the observed decreases in sampler water acidity mentioned above to ammonia or some organic amine desorbing from the respirator cartridge carbons. Ammonia salts are used in the ASC and ASZM-TEDA formulations to enhance the carbon reactivity. Recently, in response to Army requirements to eliminate chromium from military canister carbon an organic amine, triethylenediamine (TEDA), has been used as one of the impregnants.

A mass spectrometric study of the effluent from the carbons was done to identify the basic effluent. Because of background problems, it was necessary to use helium, rather than air as the carrier gas. Also, a short, heated inlet line ending immediately downstream of the test bed was the only way to avoid ammonia line losses. However, clear signals at mass peaks 15, 16, and 16, corresponding to the fractionation pattern of ammonia, were observed. We saw no significant mass peaks corresponding to other compounds up to and including mass 112 (TEDA).

Maximum concentrations of ammonia in the effluents can be calculated from the maximum rates of acid decrease in the effluent sampler water (negative slopes in Figures 3-6). For full bed equivalents of these carbons at an air flow corresponding to a breathing rate of 50 L/min, the maximum ammonia release observed from these two carbons was 1.3 ppm. This is well below the ammonia TLV of 25 ppm.

The presence of ammonium salts on and release of ammonia from the two impregnated, activated carbons probably enhance their effectiveness in removing nitric acid from air.

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