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DEVELOPMENT OF AN IN-LINE FILTER TO PREVENT INTRUSION OF NO₂ TOXIC VAPORS INTO A/C SYSTEMS

by

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ABSTRACT

The hypergolic propellant nitrogen tetroxide (N₂O₄ or NTO) is routinely used in spacecraft launched at Kennedy Space Center (KSC) and Cape Canaveral Air Station (CCAS). In the case of a catastrophic failure of the spacecraft, there would be a release of the unspent propellant in the form of a toxic cloud. Inhalation of this material at downwind concentrations which may be as high as 20 parts per million (ppm) for 30 minutes in duration, may produce irritation to the eyes, nose and respiratory tract.

Studies at both KSC and CCAS have shown that the indoor concentrations of N_2O_4 during a toxic release may range from 1 to 15 ppm and depend on the air change rate (ACR) for a particular building and whether or not the air conditioning (A/C) system has been shut down or left in an operating mode.

This project was initiated in order to assess how current A/C systems could be easily modified to prevent personnel from being exposed to toxic vapors. A sample system has been constructed to test the ability of several types of filter material to capture the N_2O_4 vapors prior to their infiltration into the A/C system. Test results will be presented which compare the efficiencies of standard A/C filters, water wash systems, and chemically impregnated filter material in taking toxic vapors out of the incoming air stream.

INTRODUCTION

The Air Infiltration Studies completed in both KSC and CCAS facilities were initiated to determine the sheltering effectiveness of a variety of structures in the event of a release of toxic materials such as hypergols from a Titan launch abort. The facilities selected were intended to be representative of the structures at KSC/CCAS with respect to location, facility size, materials of construction, and number of employees occupying the structure. During the KSC/CCAS studies, sulfur hexafluoride (SF₆), a nontoxic, invisible, and odorless gas, was used as the tracer gas. The Tracer Gas Decay Technique was used to determine the air changes per hour (ACH) for a building per ASTM E-741-93 "Standard Test Method for Determining Air Changes in a Single Zone by Means of a Tracer Gas Dilution". Infrared (IR) gas analyzer instruments calibrated for SF₆ were used for all testing. Results of the studies showed that existing heating and air conditioning systems (HVAC) were a major factor in the effectiveness of a shelter. The air exchanges per hour for buildings varied widely depending on the HVAC system, but correlated well with the outside air intake from the HVAC design specifications. It was recommended that in the case of contigency, the exhaust systems should be secured in order to further lower the air exchanges per hour. The study presented in this paper was undertaken to examine the possibility of using a filter in-line with or in place of the existing A/C filters which would decrease the incoming NO₂ concentration to acceptable levels and further protect personnel.

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HARDWARE

The testing of air conditioning (A/C) coils and potential filter material was completed in the Toxic Vapor Detection (TVD) lab, complex 34, CCAS. The basic test system, shown in figure 1, was fabricated inside of a certified fume hood running at approximately 1000 cubic feet per minute (CFM). The dew point of the incoming air stream was measured using a General Eastern Model 1211H dew point sensor. The velocity of the air within the polyvinylchloride (PVC) sections of piping was monitored by an Alnor CompuFlow Model 8525 Thermoanemometer. Generation of NO₂ concentrations between 40 to 50 ppm was accomplished by allowing an undiluted vapor sample of NO₂ to mix with the incoming air. The resulting air/NO₂ sample was homogenized using an 18 inch section of piping downstream of the Alnor Thermoanemometer filled with polypropylene mixing balls. The heat exchangers were manufactured by Super Radiator Coils and were all dimensioned with 3" by 3" openings containing 1, 2, and 4 rows of 3/8" outside diameter (o.d.) copper tubes, respectively. The three different coils were fabricated to test the effects of increasing the surface area of the coil for air contact. Drains were placed both upstream and downstream of the A/C coils in order to catch any moisture which might accumulate for subsequent analysis. The blower used during all testing was a PAR Model 35400-0000, with a capacity of 250 CFM. This blower was run using a DC motor controller operating at 12 volts and 5 amps. The concentration of NO₂ generated within the testing assembly was monitored using Energetics Sciences Incorporated (ESI) electrochemical cell analyzers and a DIONEX Ion Chromatograph. The ESI analyzers were calibrated prior to the start of A/C coil testing and recalibrated on a monthly basis to assure analyzer integrity. The stability of the DIONEX system was checked using internal standards during each sample run.

RESULTS

Initial Tests (Standard A/C Coils)

The initial task of the A/C coil study was to examine the potential removal efficiency of the coils using humid air flowing at 500 feet per min (ft/min) across 1,2 or 4 coil heat exchangers. The measured flow path lengths for the 1,2, and 4 coil heat exchangers are 1,2, and 3.5 inches, respectively. During testing, the coil temperatures were held below the dew point of the inlet air so that a water film would form on the surfaces of the individual coils.

There are two factors in gas/liquid scrubbers that have to be considered when one is computing the efficiency of a scrubber system. The first factor is the residence time. This time must be long enough for the interaction between the reacting gas (NO2) and the scrubbing liquid (H2O) to occur. The second factor is the calculated ratio of the scrubber liquor mass flow (L) to the total gas mass flow (G), and is represented by L/G. The scrubber liquor mass flow rate for typical oxidizer scrubbers is the product of the liquid pumping rate (50 gallons per minute gal/min) and the density of the scrubber liquor (10.6 pounds per gallon, lb/gal). The calculated mass flow rate for the oxidizer scrubbers is the product of the volumetric flow rate in standard cubic feet per minute (scfm) times the standard density of the nitrogen carrier gas, 0.078 pounds per standard cubic foot (lb/scf). The data presented in table 1 is a summary of the efficiency of a typical oxidizer scrubber. The oxidizer scrubber towers are 30 inches in diameter with approximately 4 feet of packing and the scrubbers have four towers connected in series. The scrubber liquor, 25% sodium hydroxide (NaOH), is pumped at a total of 200 gallons per minute (gal/min) with an equal split in all four towers. The data displayed in table I was taken with a constant pumping rate in the scrubber while the total gas flow rate through the scrubber was varied. In the case of the standard A/C coils, where humidified outside air is used to deposit a water film on the heat exchanger coils, the liquid mass flow can be approximated as the difference between the mass of the water vapor in the incoming humidified air and the mass of saturated water which can be found at a known coil temperature (table 2).

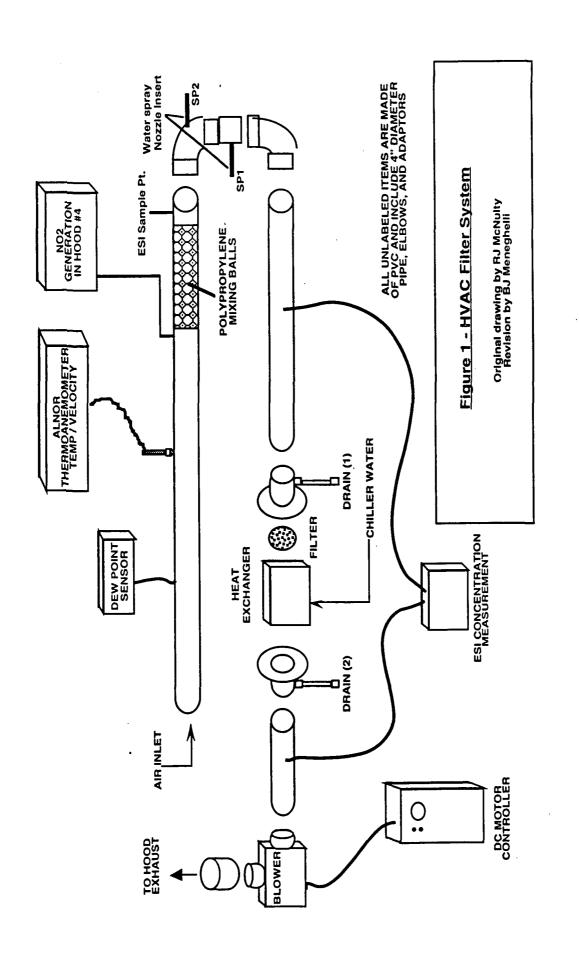


Table 1. Summary of Flow Rate vs. Efficiency, Residence Time, and L/G Ratio

Total Flow Rate	Packing Depth	Gas Velocity	Residence Time	Efficiency ⁽¹⁾	L/G
scfm ⁽¹⁾	ft	ft/min	min		Ratio ⁽¹⁾
108	16	22.0	0.73	100	61
202	16	41.2	0.39	94.2	32
215	. 16	43.8	0.37	92.2	31
308	1 6	62.8	0.25	81.7	21
408	16	83.2	0.19	72.9	16
508	1 6	103.5	0.15	70.6	1 3

Table 2. L/G Ratio for 1, 2, and 4 Coil Heat Exchangers

Heat Exchanger	Air Weight	Water Content	Water Content	Water Weight	L/G
		Inlet	Outlet		Ratio
	lb/min_	lb/min	lb/min	lb/min	
1 Coil	3.52	0.0490	0.0183	0.0307	0.0087
1 Coil	3.52	0.0490	0.0282	0.0208	0.0059
1 Coil	3.52	0.0571	0.0197	0.0374	0.0106
1 Coil	3.52	0.0486	0.0183	0.0303	0.0086
2 Coil	3.52	0.0476	0.0282	0.0194	0.0055
2 Coil	3.52	0.0553	0.0197	0.0356	0.0101
2 Coil	3.52	0.0645	0.0211	0.0433	0.0123
4 Coil	3.52	0.0472	0.0335	0.0137	0.0039
4 Coil	3.52	0.0677	0.0388	0.0289	0.0082
4 Coil	3.52	0.0641	0.0187	0.0455	0.0129
4 Coil	3.52	0.0553	0.0211	0.0342	0.0097

During testing of the A/C coils, there was no measurable decrease in the concentration of NO₂ when a nominal 50 ppm concentration sample was passed through the 1,2, or 4 coil exchangers as measured by the ESI electrochemical analyzers. This implies that the efficiencies for these tests would be zero. A summary of the heat exchanger efficiency studies can be found in table 3.

Table 3. Efficiency Study with 1, 2, and 4 Coil Heat Exchangers

	Gas Velocity	Heat Exchanger	Path Length	Residence Time	Efficiency
	ft/min		f t	min_	
Γ	500	1 Coil	0.08	0.00017	0
1	500	2 Coil	0.17	0.00033	0
L	500	4 Coil	0.29	0.00058	0

The data presented in tables 2 and 3 clearly show that the residence times and L/G ratios are too low to produce any measurable change in the NO₂ concentration by using the A/C coils alone. In comparison, the residence times for NO₂ in the hypergolic scrubber study shown in table 1 are 1000 times longer than the residence times found in the A/C coil study presented in table 3. In addition, similar differences were found with the L/G ratio for the scrubber study (table 1) as compared with the A/C coil study (table 2). These large differences suggest that the path length for any solid adsorbent filter media to be tested must be large in order to achieve an efficiency of 90% or greater (2).

Water Spray Testing

Hollow Cone Spray Nozzle

In an attempt to increase the gas residence time within a "scrubber" system, a hollow cone spray nozzle (UNIJET Spray Tip, TN1) was procurred and placed into the test assembly. The inlet water pressure to this nizzle was set for 100 psig. At this pressure the nozzle is designed to deliver water droplets with a size range of 60 to 70 microns. This droplet size was chosen in an attempt to maximize the ability of the water spray to mix with the NO₂ in the vapor sample. The first test point for the water spray system was downstream of the polypropylene mixing balls at a point perpendicular to the air flow. This position is designated as SP1 on figure 1. The flow of the spray head was measured to be 1.0 gallons per hour (GPH). No decrease in the NO₂ concentration was observed when comparing the output values from two independent ESI analyzers positioned upstream and downstream from the injection point of the water spray. Subsequently, the water spray injection point was moved to SP2 on figure 1. This sample point was chosen since the water spray flow would be countercurrent to the air flow, affording more contact time between the scrubber liquor. H₂O, and the air stream. This countercurrent orientation of the scrubber liquor and air stream is consistent with typical scrubbers. In conjuction with the movement of the water spray injection nozzle to SP2, the concentration of NO2 in an integrated water sample, measured as nitrate and nitrite, was done using ion chromatography (IC). The nitrite and nitrate found in solution are the result of both NO2 and N2O4 dissolving in water to form nitrous and nitric acid. During subsequent testing of the water spray method, the ESI electrochemical analyzers were used to monitor the relative concentration of the NO2, while depending on the results of the IC for the analytical concentrations.

IC Instrumentation and Methodology

The Ion Chromatograph used for analysis of water samples was a DIONEX LC20 IC System. The setup parameters for the system during operation are listed in table 4. A QC sample with a concentration of 500 nanograms/milliliter (ng/ml) of sodium nitrite (NaNO₂) was analyzed prior to quantifying any samples from the A/C coil test system as an internal check of the instrument stability.

IC ParameterDescriptionDetectorED40 Conductivity DetectorPumpGP40 Gradient PumpEluent1.8 mM Na2CO3/1.7mM NaHCO3TemperatureAmbientSample loop100 microliters (ul)Pressure1000 pounds per square inch gauge (PSIG)

Table 4. DIONEX IC System Parameters

12" PVC Test Bed

A secondary test section of PVC was constructed using a 4 ft section of 12" i.d. PVC in place of the 4" i.d. PVC used during previous testing. Two water flow configurations, shown in figure 2, were used during the testing. A water sample was collected for 10 minutes from the labeled drainage points and analyzed by IC for each of the water flow configurations.

4" PVC/Polypropylene Ball Test Bed

The third configuration used during the testing of the water spray is shown in figure 3. The 50" section of PVC is filled with polypropylene balls in a manner similar to the mixing section illustrated in figure 1. The water spray is again pointed down with the air flowing in a countercurrent direction to maximize the contact area between the air stream and scrubber liquor.

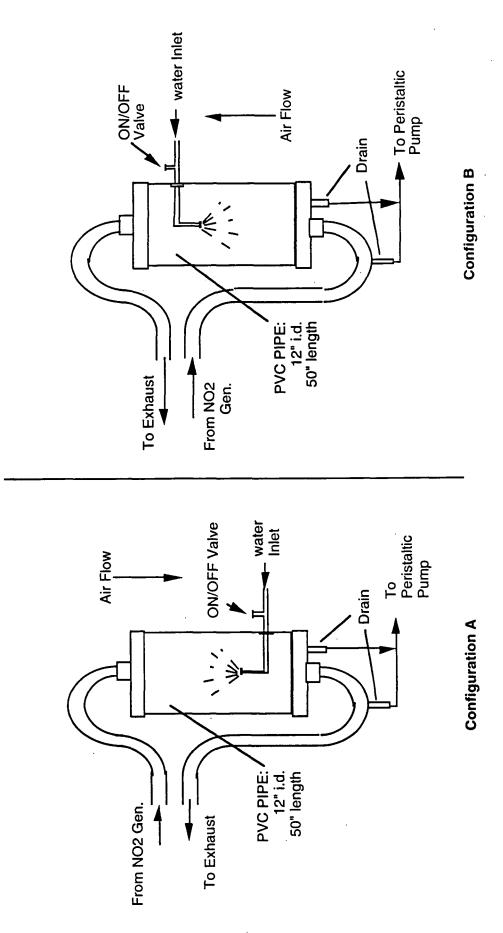


Figure 2. Water Spray Test Configurations (12" PVC)

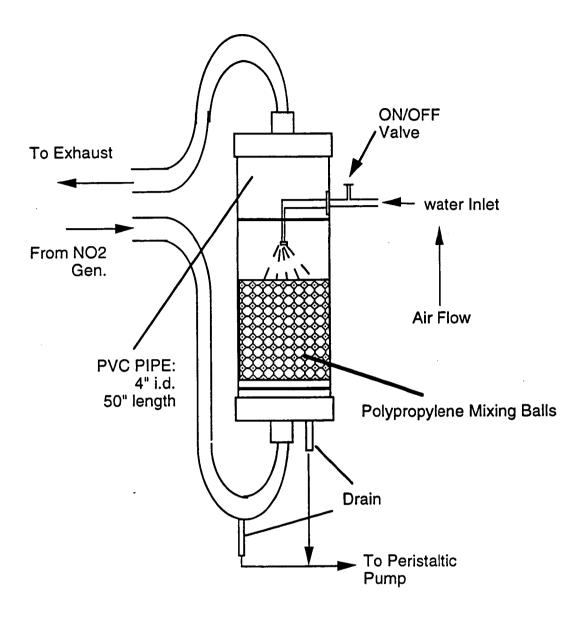


Figure 3. Water Spray Test Configuration (4" PVC)

Results

The data collected during the testing of the hollow cone water spray nozzle is summarized in table 5. Note that the L/G ratios for all of the water testing are quite low compared to the typical ratios for standard scrubber systems shown in table 2. At the measured air flow of 500 linear feet per minute (lfm) the calculated residence time for any sample within the water spray area is very short and precludes obtaining a high percentage of NO₂ dropout.

Pipe Size L/G Water Flow Pipe Mixing %NO₂ Air Flow Residence Time Direction Direction Length (ft) (i.d. in Balls Dropout Ratio (min) inches) 4 Yes 0.93 0.026 Up Down 0.003 1.5 4 0.026 Down 0.008 Yes 1.01 Up 4 0.026 Down 0.075 4.17 12 No 1.72 Up 12 No 2.12 0.026 Up Down 0.075 4.17

Table 5. Hollow Cone Water Spray Nozzle Test Results

Ultrasonic Atomizing Nozzle

Further testing using water as the scrubber medium was continued using an ultrasonic atomizing nozzle (Sono-Tek, Model 8700-48MS). This nozzle is designed to atomize liquid as it comes in contact with the vibrating nozzle atomizing surface. The atomizing nozzle was positioned at SP2 (figure 1) and used to generate a fine mist of water droplets countercurrent to incoming air flow. The mist was intended to provide a potentially larger surface area for interaction with the incoming air sample. Water samples were pumped to the nozzle by means of a Watson Marlow 505S variable speed peristaltic pump fitted with 6 roller pump heads and minicartridges. The minicartridges housed PharmedTM tubing able to dispense water at flows ranging from 1 to 25 sccm. The speed of the pump was fixed at 50 revolutions per minute (rpm). No decrease in the concentration of NO₂ was observed during testing of the ultrasonic nozzle.

Chemical Filter Testing

MSA Canister

The use of chemical filters as potential absorbents of NO₂ was initiated based on the minimal dropout of NO₂ during the water spray testing. An MSA gas mask canister, type GMN-SSW, targeted for respiratory protection against NO₂, was initially tested at a flow of 15 sLpm and found to totally absorb NO₂ from an air stream at a concentration of 40 parts per million (ppm). The canister continued to absorb NO₂ at concentration levels as high as 125 ppm and air flow rates as high as 370 sLpm. The concentration of NO₂ was measured both upstream and downstream of the canister by ESI electrochemical detectors. The canister is composed of soda lime, a mixture of calcium oxide and sodium hydroxide, along with hopcalite. The hopcalite is a mixture of the oxides of copper, cobalt, manganese and silver, designed as a catalyst to convert carbon monoxide to carbon dioxide. The chemical composition of the canister effectively scrubbs out the NO₂ present in the incoming air sample in a manner similar to the 25% NaOH crubber liquor discussed earlier in this paper. The canister is rated as being able to protect against concentrations of NO₂ as high as 2% by volume for up to 12 minutes. During a catastrophic failure of a spacecraft containing NTO, the concentration of levels of toxic material at building sites is projected to be in the 25 to 50 ppm range. This canister could be used as personnel protection for several hours at these low concentration levels.

Charcoal

A secondary test of chemical filters was done using charcoal as the medium. A 12" section of 4" PVC was filled with charcoal and packed at either end with standard A/C filter material and screening to prevent movement of the charcoal during testing. This test bed decreased a 40 ppm vapor sample by 10% compared to an unfilled section of PVC. This is a significant decrease in concentration, but not high enough to consider the charcoal as an effective filter medium.

Conclusions

- 1. Water is not an effective medium for capturing NO₂ toxic vapors in a scrubber-like system at the high flow rates typical of commercial HVAC systems.
- 2. Soda lime based materials are potential filter media for eliminating NO₂ toxic vapors, but further experiments at high linear velocities are required to show feasibility.

Continuing Work

- 1. Testing of soda lime based materials at high linear velocities to show feasibility of filter media.
- 2. Sizing, fabrication and testing of an in-line filter using soda lime based materials as the filter media. The sizing of the filter should approximate one which could be inserted into an existing A/C system.
- 3. Investigation of powder spray techniques as potential methods for removing NO₂ toxic vapors.

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