Apr 27th, 2:00 PM - 5:00 PM

Paper Session I-C - Multifunctional Air Revitalization Systems

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MULTIFUNCTIONAL AIR REVITALIZATION SYSTEMS:
Combined CO₂ - Trace Contaminant Removal Using Solid Amines
Scott R Johnson, George G Garrard, Shirley M Mitchell

ABSTRACT
The end goal in developing air revitalization systems is improved performance and enhanced capability to enable long-duration interplanetary life support. The evolution of current and near-term techniques is the most likely path to achieve future systems in which consumables are regenerated to effect weight and cost savings. Regenerative solid amine sorbents are now in use in the Space Shuttle Extended Duration Orbiter (EDO); currently, the solid amine performs only the carbon dioxide (CO₂) removal function. Testing was conducted on solid amines to better understand the behavior during CO₂ adsorption and the influences of trace contaminant gases. Tests were conducted, beginning in 1991, using Thermogravimetric Analysis (TGA) system and on a sorbent column linked to a mass spectrometer and a gas chromatograph to ascertain the ability of the solid amine to remove CO₂ and trace contaminants.

Solid amine adsorption and desorption test data were obtained for trace contaminants representing corrosive and reactive compounds typical of space cabin atmospheres. Test results show that the solid amine has the ability to regeneratively remove trace contaminants, although some highly corrosive gases bond irreversibly. The TGA system proved to be a rapid, versatile method to screen trace contaminants for effects on solid amine; the column system provided more realistic conditions and analysis of off-gas products. Both analysis tools have provided initial capability to assess regenerative air revitalization techniques that may then be combined to create a multifunctional, closed-loop atmosphere purification system.

INTRODUCTION
The long-term goal in characterizing air revitalization sorbents is to improve systems performance and enhance capability. A TGA system developed in 1991 was used to measure weight changes resulting from the adsorption and desorption of CO₂ and corrosive contaminants on solid amine air revitalization sorbents. Several contaminants were analyzed for adsorption and desorption characteristics and their relative influence on the ability of the sorbents to adsorb and desorb carbon dioxide. The testing showed the TGA system was capable of screening trace contaminants such as fuels, oxidizers and other corrosive materials for their behavior on solid amine sorbents. This testing also indicated the need for an additional method to obtain more quantitative data on the dynamics of gas adsorption and desorption. Such a test bed was assembled and its use complemented that of the TGA test bed built and operated in 1991.

Until 1992, lithium hydroxide (LiOH) and charcoal cartridges were used in the environmental control and life support system (ECLSS) of the Space Shuttle to adsorb CO₂ and other impurities (trace contaminants) from the crew compartment. This is a non-regenerative method; once the LiOH is used, it is removed and replaced with a new cartridge. To satisfy longer mission duration requirements, Hamilton Standard developed a regenerative solid amine CO₂ removal system. This solid amine, designated Hamilton Standard - material C (HS-C), is a polyethyleneimine/ acrylic material (polyamine) capable of retaining carbon dioxide, water, and other contaminants. HS-C+, an improved version of HS-C, has a liquid phase coating to enhance adsorption and desorption performance.

The TGA method was investigated and evaluated for screening the behavior of CO₂ and trace contaminants with HS-C solid amine sorbent during 1991. Based on the results of this work, TGA was shown to be a useful tool for studying the adsorption and desorption behavior of sorbents with CO₂ and contaminants. The TGA with the gas/vacuum system provided a means of measuring weight changes resulting from both the adsorption and desorption of gases and vapors under various conditions. The sample size involved and conditions of exposure made it possible to determine the maximum capacity of a sorbent for CO₂ and other contaminants with a minimum adsorption gradient through the sample.

While the TGA system was used successfully to screen trace contaminants and compare the behavior of solid amine sorbents, it had limitations in
providing information necessary to support long

term environmental studies. Therefore, it was

necessary to build and operate a bench scale sorbent
test system to provide data using actual system
temperatures, flows, and contaminant levels

encountered in spacecraft breathing air. This study

involved building a column test system, establishing
test conditions, evaluating the system for testing the

CO₂ adsorption and desorption behavior of HS-C

(and a modified version: HS-C+), initial testing of

trace contaminants, and identifying future testing

needs.

As the result of the 1991 effort, test data were

obtained on several trace contaminants. These

contaminants represented compounds with different

functional groups and expressed varying adsorption

and desorption characteristics and effects on CO₂.

To prevent damage to the TGA micro-balance due
to corrosive gases such as fuels and oxidizers, the

TGA system was modified. This year-long task

involved the modification and evaluation of the

TGA test method, established new test conditions,

further identified the conditions of adsorption and
desorption, and tested and compared the adsorption

desorption behavior of HS-C and HS-C+.

TEST METHODS & RESULTS

Properties of Sorbent Materials

The solid amine sorbent consists of a solid, porous,
inert substrate material coated with a

polyethyleneimine, \((\text{C}_2\text{H}_5\text{N})_n\). The substrate is made

up of approximately 0.5 mm diameter acrylic ester

microspheres which are combined with the

polyethyleneimine to make up the solid amine

sorbent material. The polyethyleneimine

(designated Dow PEI-18), which has a molecular

weight of 1800, is applied to the substrate using a

proprietary process developed by the Hamilton

Standard Division of United Technologies

Corporation. The final product is designated as

HS-C sorbent material. This material consists of

porous beads with a thin amine coating that provides

a very large surface area for material adsorption.
The HS-C+ sorbent is HS-C that has been coated

with approximately 20 weight percent triethylene
glycol (TEG).

When air is passed through a column packed with
the sorbent material, water and CO₂ are co-adsorbed
onto the sorbent media. The retention of water by

the sorbent is referred to as water loading of the

system. In vacuum, the CO₂ can be desorbed in

order to reactivate the sorbent so it can be reused.

Besides water and CO₂, the material can adsorb
trace vapor contaminants from the spacecraft
breathing air such as hydrocarbons, ketones,

alcohols, aldehydes, mercaptans, halocarbons and a

number of other solvents and inorganic gases. The

addition of TEG to produce HS-C+ enhances the

ability of the HS-C sorbent to adsorb and desorb
gases.

Description: TGA Test Equipment

Testing involved the use of a Thermal Analysis

Instruments, Inc. (TA) 1090 Thermal Analyzer

attached to a TA 951 TGA Module. A schematic of

the TGA system is shown in Figure 1.

![Diagram of TGA test equipment]

FIGURE 1. Simplicity of the TGA allows rapid

screening of sorbents and contaminant gases.

The instrument was programmed to run isothermally

as a function of time and provided a continuous

readout of weight changes and temperature which

was collected by the data system for analysis using

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the TGA program, 2-TGA 02. In addition, the TGA module purge line was modified to accept a gas handling system capable of supplying purge gases and standard gas mixtures at 14.7 psia for adsorption tests. The system could also be operated at pressures of one torr using the vacuum side of the gas handling manifold for desorption tests. The temperatures were programmed and controlled by the thermal analyzer during each test.

Several changes were made in the system to permit tests using corrosive gases/vapors. A gas diffuser was installed such that the test gas was directly introduced to the sorbent sample pan. Also, a water generator was incorporated into the system to provide relative humidities to 40 percent. The main modification involved replacing the furnace tube, that isolates the system within the furnace, and providing a new balance enclosure with a purge port. The purge feature allowed testing with corrosive gases without damaging the TGA balance parts.

**Description: Column Test System**

The Column system, shown schematically in Figure 2, operated in 3 modes:

1. adsorption
2. gas purge desorption
3. vacuum desorption

The system consists of a gas humidifier and contaminant (i.e. CO₂) source plumbed in parallel to a valved proportioning dual flowmeter with exit flow to the sorbent bed followed in series by the analytical instrumentation (a relative humidity sensor, an infrared spectrophotometer, a mass spectrometer, and a gas chromatograph) and a final flowmeter to vent.

The humidifier consists of a water bubbler followed by a silica gel bed to eliminate entrained liquid water in the gas stream. The sorbent bed consists of a three-inch long piece of 0.5 inch O.D. stainless steel tubing (7/16 inch I.D.) which has a 1.75 inch length (or 4.3 milliliter volume) of sorbent contained in it. The bed is placed in a Carle Instruments, Inc. Model 4300 valve oven for temperature control. The infrared spectrophotometer (IR) is a Perkin-Elmer, Inc. Model 1420. A Finnigan, Inc. Model 4500 mass spectrometer (MS) with a valved variable leak direct gas inlet attachment was used. The gas chromatograph (GC) is a Perkin-Elmer, Inc. Model 2B with a gas sample valve and hot wire detector; a J and W 30 meter GSQ Megabore (0.536 mm I.D.) capillary column was used to obtain gas components separation. The humidity sensor monitor is a Vaisala, Inc. Model HMI 32. The MS has a self contained computerized data system; the GC and IR are served by a Perkin-Elmer, Inc. Model 7500 Professional Computer Data System.

**Evaluation of Modified TGA System**

The purpose of this task was to evaluate the modified TGA system and compare results with prior baseline data. Tests were run using 1% CO₂ in dry air at 50 sccm (14.7 psia) to determine the adsorption behavior. Besides the gas flow changes, the sorbent sample size was increased from 20 mg to 30 mg. All the baseline testing for desorption and adsorption was performed at 30°C. The test results showed that the modified system provided results comparable to the previous work; in fact, it appeared to be more accurate due to the larger sample size and a heavier balance pan which reduced buoyancy effects.

**Test Conditions/ Procedures for TGA**

Baseline data for CO₂ adsorption and desorption was obtained and test conditions verified prior to testing the effects of water and trace contaminants. The following test conditions were used except for special effects involving varied water concentrations and varied temperature conditions:

1. TGA in time base and isothermal
2. Gas flow: 50 standard cc/min (sccm)
3. CO₂ content near 1%
4. Contaminant content near 1%
5. 30 mg sorbent sample.
6. Desorption at 1 torr for 2 hours.
7. Test time: maximum weight gain - typically 1 hour
8. Water when involved was near 30 % RH.

Tests consisted of the following procedures. Approximately 30 mg of sorbent were placed on the TGA balance pan, after adjusting the balance to zero, and weighed to the nearest 0.01 mg. The system was closed off and evacuated for two hours or until a stable baseline weight was established at one torr and at the test temperature. The CO₂/matrix
FIGURE 2. A column of sorbent material linked to a mass spec, IR detector, and a gas chromatograph provided gas dynamics and sorbent off-gas data.

gas mixture, or contaminant mixture, was flowed into the TGA system at 50 scm, after isolating the vacuum pump, until the TGA system was at 14.7 psia. After reaching the test pressure, the gas mixture continued to flow while the TGA and thermal analyzer were activated to measure weight changes and record the data. Testing was complete after approximately one hour or when the weight increase had equilibrated.

In the case of using a corrosive gas or vapor, the mixture was introduced through the corrosive gas inlet tube shown in Figure 1. Desorption tests were performed following adsorption test runs to show typically the weight loss after CO₂ adsorption. This was accomplished by turning off the CO₂ mixture, closing off the system and slowly starting the evacuation procedure without physically disturbing the sample.

HS-C: Adsorption/Desorption Processes in TGA

All previous testing was performed using 1.0% CO₂, a relatively high concentration, and no information was obtained to show the adsorption behavior at concentrations lower than 0.5 percent. All prior testing was completed showing the effects of vacuum on desorption during initial activation of the HS-C and following contaminant and CO₂ exposure. No testing was performed to show the effects of a gas purge as compared to vacuum. In all cases the contaminant exposure was followed by CO₂ adsorption; therefore, no data were obtained on what effects purging CO₂ saturated HS-C with selected contaminant mixtures might have on adsorption and desorption. And finally, as a result of the previous testing at only one temperature (30°C), it was felt that obtaining test data at
different temperatures would provide valuable information on the adsorption behavior of contaminants. The following tests were performed:

Test 1. Adsorption tests using CO\textsubscript{2} concentrations from 0.01 to 1.0%.

Test 2. Desorption tests to compare vacuum with nitrogen gas purge.

Test 3. Effects of previously adsorbed CO\textsubscript{2} on trace contaminant adsorption.

Test 4. Show adsorption behavior for CO\textsubscript{2} and several trace contaminants (methanol, acetone and benzene) as a function of temperature.

Test 1. Adsorption tests using CO\textsubscript{2} concentrations from 0.01 to 1.0 percent. The results of Test 1 showed the HS-C capacity (weight of CO\textsubscript{2} adsorbed) using 0.06 to 1.0 volume percent CO\textsubscript{2} concentrations ranged from 2.6 to 2.9 weight percent, respectively. The weight adsorbed starts falling off rapidly below concentrations of 0.05 volume percent. This would indicate that lower CO\textsubscript{2} concentrations (near 0.1 percent) could be used for the testing under these moisture conditions. However, there is some advantage to using the higher concentration (close to 1%) because of effects from purging and displacement of gases in the volume of the balance when making system changes.

Test 2. Desorption tests to compare vacuum with nitrogen gas purge. The results of the desorption testing show a significant difference in the rate of desorption for vacuum and purge gas conditions. This testing was performed in an open TGA pan and may not directly reflect the behavior of purging the HS-C material in a column. Information on the latter condition would have to be obtained using the column test bed system.

Test 3. Tests for effects of previously adsorbed CO\textsubscript{2} on trace contaminant adsorption. In the cases where methanol and benzene were used after CO\textsubscript{2} exposure, there was little change in the weight of adsorbed material after switching the gas flow from CO\textsubscript{2} to the 1.0% contaminant mixture. It cannot be determined exactly what is occurring since only the weight is known. It is possible that no contaminant is being adsorbed or that the CO\textsubscript{2} is being displaced. This can only be determined by performing a test whereby the effluent of the system can be analyzed quantitatively for specific materials, such as with the column test bed system. However, with methanol and benzene, the condition did not affect subsequent desorption and CO\textsubscript{2} adsorption behavior; CO\textsubscript{2} adsorption met baseline conditions and all the materials were totally desorbed. For acetone, it was obvious that acetone was being adsorbed, and it affected the capacity of HS-C for CO\textsubscript{2} to some extent. Again, as previously found with acetone, the acetone probably reacts with the HS-C to inhibit CO\textsubscript{2} adsorption and cannot be desorbed.

Test 4. Show adsorption behavior for CO\textsubscript{2} and several trace contaminants (methanol, acetone and benzene) as a function of temperature. In most cases the maximum amount of contaminant that can be adsorbed by the HS-C is in equilibrium at some temperature, with concentration constant (1.0 %). Any obvious non-linear relationship between the amount of material adsorbed versus temperature reflects some difference in the behavior of a particular contaminant. It could be due to the influence of water, reaction with the HS-C or a physical property of the contaminant itself. Therefore, it is felt that this type of testing at different temperatures is valuable in identifying the possible reasons for material behavior. It also provides additional information on the capacity of HS-C for the trace contaminants at different temperatures.

**HS-C Contaminant Testing in TGA**

The contaminant materials were tested using a contaminant concentration of 1% and the same conditions described above. One percent was used since this testing involved obtaining the weight of contaminant adsorbed when the HS-C was saturated. Tests were performed in two ways with respect to running the contaminant mixtures. All the testing involved desorption to activate the HS-C, flowing the one percent contaminant mixture and final desorption of the HS-C. In the case of sulfur dioxide and nitrogen dioxide it was necessary to perform separate runs for each exposure time because of the reactive nature of the materials involved. The results for the ammonia and hydrazines could be obtained in a single run.

During the above testing all the contaminant mixtures were introduced through the corrosive gas/vapor inlet and all the tests were performed with a relatively dry environment. Runs were performed until equilibrium was reached or, in the case of SO\textsubscript{2} and NO\textsubscript{2}, a value was obtained for each exposure...
time. For the latter materials, equilibrium was reached at the longest exposure time shown in the tables below.

Sulfur Dioxide (SO₂) Contaminant: The results of the SO₂ exposure testing are presented in Table 1. This material has a significant effect on CO₂ adsorption during exposure times over 30 minutes at the concentration used with very little material desorbed. This was expected because of the strong acid formed and reactions with traces of adsorbed water.

Nitrogen dioxide (NO₂) Contaminant: The NO₂ behaved similar to the SO₂ with respect to adsorption and damaging effects but to a greater extent. The results of the NO₂ testing are presented in Table 2 showing a large reduction in CO₂ adsorption and little material desorbed with only a 30 minute exposure.

TABLE 1.

<table>
<thead>
<tr>
<th>SULFUR DIOXIDE Percent (g x 10⁻²/g HS-C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exposure time (minutes)</td>
</tr>
<tr>
<td>SO₂ adsorbed</td>
</tr>
<tr>
<td>CO₂ adsorbed(2)</td>
</tr>
<tr>
<td>% desorbed(3)</td>
</tr>
</tbody>
</table>

(1) Equilibrium reached for SO₂ desorption.
(2) CO₂ adsorbed following adsorption of SO₂.
(3) Percent of adsorbed material desorbed.

Ammonia (NH₃) Contaminant: Some of the material could not be totally desorbed. It would appear that NH₃ may even enhance the adsorption of CO₂. Tests were performed using one percent contaminant vapor followed by CO₂ in dry air. Results show that the HS-C material has a low affinity for this contaminant, with little effect on CO₂ adsorption. Testing with NH₃ shows that 0.17 x 10⁻² g/g of HS-C is adsorbed. When the NH₃ vapor exposure was followed by CO₂, the capacity for CO₂ was 3.36 x 10⁻² g/g of HS-C as compared to an average baseline result of 3.0 x 10⁻² without NH₃. A typical TGA curve is shown in Figure 3. Different amounts of water loading will also affect NH₃ adsorption. The results are also tabulated in Table 3.

Hydrazine (N₂H₄) Contaminant: Test results show that the HS-C material has a low affinity for this contaminant, with little effect on CO₂ adsorption. A typical TGA curve is shown in Figure 4. The results are also tabulated in Table 3.

FIGURE 3. Ammonia enhances CO₂ absorption, but does not completely desorb.

FIGURE 4. Hydrazine does not markedly effect CO₂ absorption, but does not completely desorb.

TABLE 2.

<table>
<thead>
<tr>
<th>NITROGEN DIOXIDE Percent (g x 10⁻²/g HS-C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exposure time (minute)</td>
</tr>
<tr>
<td>NO₂ adsorbed</td>
</tr>
<tr>
<td>CO₂ adsorbed(2)</td>
</tr>
<tr>
<td>% desorbed(3)</td>
</tr>
</tbody>
</table>

(1) Equilibrium reached for NO₂ adsorption.
(2) CO₂ adsorbed following adsorption of NO₂.
(3) Percent of adsorbed material desorbed.
Some of the material could not be totally desorbed. Tests were performed using one percent contaminant vapor followed by CO₂ in dry air. Testing with hydrazine shows that 0.15 × 10⁻² g/g of HS-C is adsorbed. When the hydrazine vapor exposure was followed by CO₂, the capacity for CO₂ was 2.92 × 10⁻² g/g of HS-C as compared to baseline results of 3.0 × 10⁻² without hydrazine.

Monomethylhydrazine Contaminant (CH₃N₂H₃): Tests were performed using one percent contaminant vapor followed by CO₂ in dry air. Results with monomethylhydrazine (MMH) showed that 1.11 × 10⁻² g/g of HS-C is adsorbed. When the MMH vapor exposure was followed by CO₂, the capacity for CO₂ was 2.88 × 10⁻² g/g of HS-C as compared to baseline results of 3.0 × 10⁻² without MMH. A typical TGA curve is shown in Figure 5. The results are also tabulated in Table 3.

![Figure 5](image)

**FIGURE 5.** MMH effects are similar to Hydrazine

### Table 3.

<table>
<thead>
<tr>
<th>Contaminant Type</th>
<th>Percent (g x 10⁻²/g HS-C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>3.0</td>
</tr>
<tr>
<td>NH₃</td>
<td>3.4</td>
</tr>
<tr>
<td>N₂H₄</td>
<td>2.9</td>
</tr>
<tr>
<td>CH₃N₂H₃</td>
<td>2.9</td>
</tr>
</tbody>
</table>

(1) % of adsorbed material subsequently desorbed

HS-C and HS-C+ Water Adsorption Behavior in TGA

Due to the modifications of HS-C by the supplier to produce HS-C+, considered to be more efficient for regenerable systems, interest turned to comparing the two materials. It was decided to characterize the HS-C+ material for CO₂ capacity and the effects of trace contaminants. At the same time, it provided an opportunity to use the TGA system with the added factor of water loading. The latter involved a relative humidity of approximately 33 percent instead of the relative dry conditions used previously. Previous testing has shown that water loading greatly influences the capacity of these sorbents for CO₂. Under relative dry conditions, ppm range typical of dry nitrogen, HS-C and HS-C+ have an average baseline CO₂ capacity close to 3.0 and 2.7 percent, respectively. With water loading using 33 percent relative humidity the capacities are 2.5 and 2.0 percent, respectively.

TGA tests were run at approximately 33 percent relative humidity for both HS-C and HS-C+ and followed by the water mixture with 1.0% CO₂. The relative humidity was generated by flowing wet nitrogen gas through a water saturated silica gel bed. The TGA curves are shown in Figures 6 and 7 for the above tests. The HS-C and HS-C+ adsorbed 1.85 and 1.48 percent water, respectively.

![Figure 6](image)

**FIGURE 6.** HS-C adsorbs 2% by weight of H₂O, but CO₂ absorption is not greatly affected.

In order to further characterize water loading behavior, TGA runs were made using different relative humidity percentages ranging from 15 to 40 percent and the amount of water adsorbed determined at equilibrium. Figure 8 shows curves for water capacity comparing HS-C and HS-C+.
Methanol (CH₃OH) Contaminant: There were no apparent adverse effects on subsequent CO₂ adsorption, after desorption, resulting from this exposure. Test results show that the HS-C+ material has an affinity for this contaminant, with some effect on CO₂ adsorption. All the adsorbed material could be totally desorbed. Tests were performed using one percent contaminant vapor followed by CO₂ in dry air. Results with methyl alcohol showed that 1.0 x 10⁻³ g/g of HS-C+ is adsorbed. When the methyl alcohol vapor exposure was followed by CO₂, the capacity for CO₂ was 1.9 x 10⁻² g/g of HS-C+ as compared to baseline results of 2.7 x 10⁻² without methyl alcohol. A typical TGA curve is shown in Figure 9. The results are also tabulated in Table 4.

Acetone (CH₃COCH₃) Contaminant: Test results show that the HS-C+ material has an affinity for this contaminant, with some effect on CO₂ adsorption. A typical TGA curve is shown in Figure 10.

**HS-C+ TGA Contaminant Tests**

In order to better understand the effects of trace contaminants on CO₂ adsorption and desorption, several of the same materials tested previously using HS-C were repeated using HS-C+. The trace contaminants included methanol, acetone, benzene and Freon 13B1. These tests were run at low water conditions to provide a good comparison with results obtained using HS-C during the FY 1991 effort. All the contaminant tests were run using the same conditions described earlier in this report.

**Methanol (CH₃OH) Contaminant**: There were no apparent adverse effects on subsequent CO₂ adsorption, after desorption, resulting from this exposure. Test results show that the HS-C+ material has an affinity for this contaminant, with some effect on CO₂ adsorption. All the adsorbed material could be totally desorbed. Tests were performed using one percent contaminant vapor followed by CO₂ in dry air. Results with methyl alcohol showed that 1.0 x 10⁻³ g/g of HS-C+ is adsorbed. When the methyl alcohol vapor exposure was followed by CO₂, the capacity for CO₂ was 1.9 x 10⁻² g/g of HS-C+ as compared to baseline results of 2.7 x 10⁻² without methyl alcohol. A typical TGA curve is shown in Figure 9. The results are also tabulated in Table 4.

**Acetone (CH₃COCH₃) Contaminant**: Test results show that the HS-C+ material has an affinity for this contaminant, with some effect on CO₂ adsorption. A typical TGA curve is shown in Figure 10.
All the adsorbed material could be totally desorbed. Tests were performed using one percent contaminant vapor followed by CO₂ in dry air. Results with acetone showed that 1.9 \times 10^{-2} \text{ g/g of HS-C+} is adsorbed. When the acetone vapor exposure was followed by CO₂, the capacity for CO₂ was 1.1 \times 10^{-2} \text{ g/g of HS-C+} as compared to baseline results of 2.7 \times 10^{-2} without acetone. The results are also tabulated in Table 4. There were no apparent adverse effects on subsequent CO₂ adsorption, after desorption, resulting from this exposure. This differed from previous testing with HS-C where acetone appeared to have a damaging effect on the substrate.

Benzene (C₆H₅) Contaminant: Test results show that the HS-C+ material has some affinity for this contaminant, with only a slight effect on CO₂ adsorption. All the adsorbed material could be totally desorbed. Tests were performed using one percent contaminant vapor followed by CO₂ in dry air. Results with benzene showed that 0.9 \times 10^{-2} \text{ g/g of HS-C+} is adsorbed. When the benzene vapor exposure was followed by CO₂, the capacity for CO₂ was 2.3 \times 10^{-2} \text{ g/g of HS-C+} as compared to baseline results of 2.7 \times 10^{-2} without benzene. A typical TGA curve is shown in Figure 11. The results are also tabulated in Table 4. There were no apparent adverse effects on subsequent CO₂ adsorption, after desorption, resulting from this exposure.

Freon 13B1 (Trifluorobromomethane) Contaminant: Test results show that the HS-C+ material has some affinity for this contaminant, with only a slight effect on CO₂ adsorption. All the adsorbed material could be totally desorbed. Tests were performed using one percent contaminant vapor followed by CO₂ in dry air. Results with Freon 13B1 showed that 0.7 \times 10^{-2} \text{ g/g of HS-C+} is adsorbed. When the Freon vapor exposure was followed by CO₂, the capacity for CO₂ was 2.4 \times 10^{-2} \text{ g/g of HS-C+} as compared to baseline results of 2.7 \times 10^{-2} without Freon. A typical TGA curve is shown in Figure 12. The results are also tabulated in Table 4. There were no apparent adverse effects on subsequent CO₂ adsorption, after desorption, resulting from this exposure.

The results for the trace contaminant testing for HS-C+ and HS-C are summarized in Tables 4 and 5, respectively. The HS-C+ material with the TEG coating has a lower capacity for CO₂ and trace contaminants than HS-C.

**TABLE 4.**

<table>
<thead>
<tr>
<th>Contaminant Type</th>
<th>Contaminant Adsorbed</th>
<th>CO₂ Adsorbed</th>
<th>Not Desorbed</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂ baseline</td>
<td>2.7</td>
<td></td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Methanol</td>
<td>1.9</td>
<td>1.9</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Acetone</td>
<td>1.1</td>
<td>1.1</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Benzene</td>
<td>2.3</td>
<td>2.3</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Freon 13B1</td>
<td>2.4</td>
<td>2.4</td>
<td>&lt;0.01</td>
</tr>
</tbody>
</table>

**EVALUATION OF THE COLUMN TEST SYSTEM**

Two tests (Nos. 1 and 2) were performed with an HS-C sorbent column (1.236 grams) under...
TABLE 5.
HS-C ADSORPTION - DESORPTION RESULTS
CONTAMINANT FOLLOWED BY CO₂
( g x 10⁻²/g of HS-C)

<table>
<thead>
<tr>
<th>Contaminant Type</th>
<th>Contaminant Absorbed</th>
<th>CO₂ Absorbed</th>
<th>Not Desorbed</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂ baseline</td>
<td>3.0</td>
<td>&lt;0.01</td>
<td></td>
</tr>
<tr>
<td>Methanol</td>
<td>2.3</td>
<td>2.3</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Acetone</td>
<td>0.9</td>
<td>1.5</td>
<td></td>
</tr>
<tr>
<td>Benzene</td>
<td>3.0</td>
<td>&lt;0.01</td>
<td></td>
</tr>
<tr>
<td>Freon 13B1</td>
<td>0.9</td>
<td>3.2</td>
<td>&lt;0.01</td>
</tr>
</tbody>
</table>

essentially the same conditions for TGA CO₂ adsorption to evaluate the column system. See Figure 13 for tabulated test conditions of column desorption and CO₂ adsorption and results. The system functioned well and sorption was reproducible (1.8 ± .05 x 10⁻² gram CO₂/gram HS-C) for two tests; the results compared well with the HS-C supplier and other investigators data including prior TGA data. Tests were conducted to determine the effects of bed temperature and the relative humidity of the adsorption gas upon the CO₂ sorption capacity of the HS-C column, and the length of time required for desorption/regeneration. Tests 3 and 5 versus Tests 4 and 6 data show that more than five hours of gas purge are required for complete desorption; Test 7 versus Test 6 data indicate that 15 to 17 hours of gas purge is sufficient for complete desorption of the HS-C column. In addition, the data indicate that varying the relative humidity (RH) from 60 to 80 percent has no effect on sorbent column capacity, but capacity is reduced by 10 to 20 percent when humidity is lowered to 1 to 2 percent RH. Column temperature was varied from a nominal of 25°C to 35°C in tests 7 through 9; data show no effect on CO₂ adsorption capacity at 35°C and 30°C, but a reduction of 20 to 25 percent at 25°C.

Comparison of HS-C and HS-C+ on the Column System

This series of tests compared HS-C with HS-C+ at temperatures of 30°C and nominal relative humidities of 2 and 60 percent (See Figure 13). HS-C and HS-C+ capacity at 30°C and 60 percent RH was the same (2.2 x 10⁻² gram CO₂/gram sorbent), but unlike the HS-C, the lower gas humidity did not decrease the HS-C+ capacity.

Subsequently, a test was performed on both HS-C and HS-C+ which was intended to simulate spacecraft usage conditions where a regenerative sorbent system is cycled between adsorption and desorption. Results are shown in Figure 14.

FIGURE 13. HS-C & HSC+ COLUMN TESTS

<table>
<thead>
<tr>
<th>TEST</th>
<th>HS-C BED DRY GN₂ REGENERATION</th>
<th>HS-C BED SORPTION</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>TIME (HRS)</td>
<td>TEMP deg C</td>
</tr>
<tr>
<td>1</td>
<td>24</td>
<td>35</td>
</tr>
<tr>
<td>2</td>
<td>18</td>
<td>35</td>
</tr>
<tr>
<td>3</td>
<td>5</td>
<td>35</td>
</tr>
<tr>
<td>4</td>
<td>17</td>
<td>35</td>
</tr>
<tr>
<td>5</td>
<td>5.3</td>
<td>35</td>
</tr>
<tr>
<td>6</td>
<td>15.6</td>
<td>35</td>
</tr>
<tr>
<td>7</td>
<td>456</td>
<td>34.4</td>
</tr>
<tr>
<td>8</td>
<td>18.8</td>
<td>25</td>
</tr>
<tr>
<td>9</td>
<td>93</td>
<td>30</td>
</tr>
<tr>
<td>HS-C+</td>
<td>16.5</td>
<td>27</td>
</tr>
<tr>
<td>HS-C+</td>
<td>21</td>
<td>30</td>
</tr>
</tbody>
</table>

HS-C Column = 1.236 grams
HS-C+ Column = 1.80 grams
A gas flow of 75 milliliters/minute of one percent by volume CO₂ and 34 percent RH at 24°C was used for the adsorption cycles. Desorption was accomplished by a 10⁻³ to 10⁻⁶ torr vacuum source on the mass spec. A bed temperature of 30 plus-or-minus 1°C was maintained and 11-minute cycles were used. Breakthrough occurred for the HS-C on cycle 3 and CO₂ adsorption continued at a level reduced by 13 to 27 percent up to test termination at 40 cycles. No breakthrough occurred on the HS-C+ bed during the 40 cycles, and after 10 cycles of operation HS-C+ removed 10 to 20 percent more CO₂ than did HS-C per cycle. The HS-C+ sorbent was clearly superior for CO₂ removal from breathing air under these simulated spacecraft conditions.

The maximum length of cycle time for which CO₂ breakthrough did not occur on the HS-C+ column was determined to be 20 minutes with desorption at high vacuum (0.01 to 0.2 torr across the sorbent column after 20 minute pumpdown). At low vacuum (0.3 torr at bed head after 20 minute pumpdown) breakthrough occurred at 18.5 minutes and 6 percent by weight less CO₂ was removed compared to high vacuum.

**HS-C Column Testing with Acetone Contaminant**

The objectives of this testing were:
1. Determine if acetone, or dimethylketone (DMK), was irreversibly adsorbed on the HS-C sorbent
2. Determine if DMK adsorption reduced HS-C capacity for CO₂

See Figure 15 for tabulated test information including HS-C bed desorption/regeneration conditions and bed adsorption conditions plus resultant data. Adsorption was performed at a temperature of 30 ± 1°C and humidity for the tests ranged from 24 to 41 percent RH. Adsorption data is given for both column desorption/regeneration methods: vacuum and gas purge.

Test No. 10 was run as a base for CO₂ adsorption to allow comparison in the later tests. Test No. 11 indicates that 5.5 hours of vacuum desorption removes approximately 80 percent of adsorbed CO₂. Test No. 12 was run as a base for DMK sorption; DMK breakthrough on the bed occurred after only approximately 50 percent of the amount of CO₂ sorbed (1.5 x 10⁻² gram DMK/gram HS-C versus 2.9X10⁻² gram CO₂/gram HS-C). The DMK was gas purge desorbed and the CO₂ adsorption repeated to determine if the previous DMK sorption would reduce CO₂ capacity; it did not. Test Nos. 14 and 14a were run to see what effect adsorbed DMK would have on subsequent CO₂ adsorption. The adsorbed DMK reduced CO₂ capacity approximately 10 percent. Test Nos. 15, 15a, and 15b were co-adsorption tests of CO₂ and DMK. After gas purge desorption of the bed in test No. 15, co-adsorption of CO₂ and DMK gave the same capacity for each as when they were run separately. Test No. 15a indicates that 2 hours of vacuum desorbs 90+ percent of the sorbed DMK but only approximately 60 percent of the CO₂. Seventy hours of vacuum (No. 15b) desorbed all of the DMK and approximately 87 percent of the CO₂.
FIGURE 15.

<table>
<thead>
<tr>
<th>TEST #</th>
<th>HS-C COLUMN(1) DRY GN₂ REGENERATION</th>
<th>HS-C BED ADSORPTION</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>TIME (HRS)</td>
<td>TEMP (deg C)</td>
</tr>
<tr>
<td>10</td>
<td>40</td>
<td>30</td>
</tr>
<tr>
<td>11</td>
<td>5.5 hours vacuum to 100 microns</td>
<td>75.5</td>
</tr>
<tr>
<td>12</td>
<td>18</td>
<td>30</td>
</tr>
<tr>
<td>13</td>
<td>89</td>
<td>30</td>
</tr>
<tr>
<td>14</td>
<td>20</td>
<td>30</td>
</tr>
<tr>
<td>14a</td>
<td>No regeneration after DMK</td>
<td>76.0</td>
</tr>
<tr>
<td>15a(3)</td>
<td>46</td>
<td>30</td>
</tr>
<tr>
<td>15a(3)</td>
<td>2 hours vacuum to 20 microns</td>
<td>76.0</td>
</tr>
<tr>
<td>15b(3)</td>
<td>70 hours vacuum to 13 microns</td>
<td>76.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(1) 1.62 g HS-C, 0.5" OD, 7/16" ID, SS 316 tube 1.75" long
(2) DMK: Dimethylketone or acetone
(3) Co-adsorption of acetone and carbon dioxide

SUMMARY OF RESULTS

The tasks performed in 1992 were designed to establish the conditions for thermogravimetric analysis of sorbents in the presence of water vapor, corrosive trace contaminants and effects of variable concentration and temperature. A second test system, using a column of sorbent material linked to a mass spectrometer and a gas chromatograph, called the column test system, was also built. These test systems, the TGA and the column, were used to compare the HS-C solid amine sorbent with the modified version designated HS-C+. The tests:

- Related adsorption behavior for several trace contaminants as a function of temperature
- Compared baseline carbon dioxide and water adsorption capacity: HS-C versus HS-C+
- Determined the adsorption and desorption characteristics and effects on the carbon dioxide capacity of HS-C for the following contaminants:
  1. Sulfur dioxide
  2. Nitrogen dioxide
  3. Ammonia
  4. Hydrazine
  5. Monomethylhydrazine
Established the adsorption and desorption characteristics and effects on the CO₂ capacity of HS-C+ sorbent of the following contaminants:

1. Methanol
2. Acetone
3. Benzene
4. Freon-13B1

Compared the results of HS-C+ testing with information obtained during 1991 for the HS-C sorbent.

Capacity of sorbents for CO₂ and several expected spacecraft breeding air contaminants have been determined by TGA. Testing has been performed at several temperatures and relative humidities to define their effect(s) on sorbent capacity. Included was the definition of sorption/vacuum desorption characteristics for contaminants and their subsequent effect upon CO₂ capacity of the sorbent.

The TGA system modifications made for corrosive gas/vapor and water loading tests provided excellent data. These modifications made possible the study of adsorption and desorption behavior of sorbents with CO₂ and trace contaminants under varying conditions of temperature, gas concentrations and water loading. The results reflect the versatility of the TGA system for studying the behavior of sorbent materials in different environments.

Test data were obtained on five trace contaminant materials representing corrosive and reactive compounds for adsorption and desorption characteristics and effects they may have on CO₂ behavior with HS-C. Comparative test data were obtained for both HS-C and HS-C+ to show differences in behavior for water, CO₂ and trace contaminant effects. It was found that HS-C+ behaves differently than HS-C by adsorbing less water, CO₂ and trace contaminant. Test results indicate that HS-C+ exhibits less CO₂ capacity compared with HS-C, but desorbs CO₂ faster than HS-C. Testing has shown that HS-C+ exhibits limited thermal vacuum stability at temperatures above 40°C (104°F). The use of HS-C+ for extended periods of time under these conditions may lead to the loss of the absorptive coating.

However, while the TGA proved to be a fast, inexpensive screening method, it does not represent the dynamic conditions characteristic of spacecraft.

Therefore, a simplified scaled-down version of an on-board spacecraft sorbent bed for breathing air contaminant removal was assembled in the laboratory to reproduce those spacecraft dynamic conditions. Bed temperatures and gas flow per weight of sorbent was kept within the HS-C supplier's recommended ranges.

CO₂ adsorption capacity data for HS-C and HS-C+ for column system and TGA tests agree fairly closely. In contrast, the behavior of acetone on HS-C adsorption capacity as determined by the column system is only 1/3 (1.5 wt. %) of the capacity determined by saturated weight (4.5 wt. %) on the TGA. Also, column tests indicated complete desorption of the acetone by gas purge and little reduction of subsequent CO₂ adsorption capacity even after acetone breakthrough on the bed, whereas TGA data indicated incomplete desorption of the acetone (1.5 wt. % residual) and a marked reduction (0.9 wt. % versus close to 3 % initially) in CO₂ capacity after acetone saturation. Even column data from vacuum desorption, which is the mode of TGA desorption, differs from the TGA data. On the column, acetone is almost completely desorbed after two hours of vacuum, but CO₂ takes more than 70 hours.

The difference between TGA and column test data indicates that column tests should be performed with other contaminants to further check data correlation. In addition, it is possible with the present test system to test co-adsorption of 5 to 10 contaminants at the same time to check synergistic effects.

**SIGNIFICANCE OF RESULTS**

The regenerative CO₂ removal method used in the Shuttle Endeavour is HS-C+. This new solid amine, while tested by the manufacturer, Hamilton Standard, for CO₂ performance, is relatively untested with regard to the effects on the CO₂ removal function by trace contaminants. Tests in 1992 have established performance criteria under the influence of common trace contaminants, in addition, we have enhanced our test facilities and skills which supports our long-term goal of improving air revitalization systems performance and capability. This capability was employed under Shuttle contract funding to answer specific performance questions posed by JSC - Crew and Thermal Systems Division.
Our tests have shown that HS-C+ is more immune than HS-C to poisoning by the trace contaminants selected for this study. This may indicate that the HS-C+ has a longer operational life, and greater capacity for additional function. More testing will be required to definitively characterize HS-C+ and to determine whether this material can perform its primary function of CO$_2$ removal, and remain unaffected by or regeneratively remove trace contaminants.

Testing performed during 1992 has shown the potential of the TGA system in testing sorbents and comparing sorbents such as HS-C and HS-C+. It provided usable information on several of the trace contaminants, especially as a screening tool for looking at the effects of hazardous vapors and materials that may be deleterious to sorbents. It is recommended that the use of the TGA system be continued to further characterize and compare sorbent materials and identify conditions under which they can perform. This would include trace contaminant testing and support to operation of the column test bed system.

The column test bed proved to be a significant asset to understanding gas-sorbent dynamics. This column system more closely simulated actual air revitalization conditions, and revealed aspects of sorbent performance impossible to obtain with the TGA system. The column configuration sorbent bed test system successfully provided data for CO$_2$ sorption on solid amine sorbents HS-C and HS-C+ at temperatures, gas flow, and humidities that were representative of spacecraft breathing air. The system exceeded initially envisioned capability by allowing co-adsorption studies of CO$_2$ and a contaminant (acetone). Further, it is believed that co-adsorption effects of a number of selected contaminants can be tested simultaneously. This would reproduce spacecraft cabin conditions even more realistically. It is felt that these test methods described herein could be used for the characterization of other sorbent materials besides HS-C and HS-C+.

These tests serve a dual function: enhance current operational systems; and lay the groundwork for future, multifunctional air revitalization systems. Future systems must be regenerative to reduce operational cost and resupply. Without regenerative capability, interplanetary life support will be prohibitively costly.

REFERENCES


10. Laboratory Notebook N 00245, pp. 37 through 50.

11. Laboratory Notebook E 00011, pp. 3 through 15, 33 through 40