

# Hydrogen Purification in Support of Plasma Pyrolysis of Sabatier Derived Methane

John T. Holtsnider,<sup>1</sup> Richard R. Wheeler, Jr.<sup>2</sup> and Ross H. Dewberry<sup>3</sup>  
*Umpqua Research Company, Myrtle Creek, OR, 97457*

Morgan B. Abney<sup>4</sup> and Zachary W. Greenwood<sup>5</sup>  
*NASA – Marshall Space Flight Center, Huntsville, AL, 35812*

The use of microwave regenerative sorption media for purification of hydrogen has been studied. The Sabatier Assembly recovers oxygen from carbon dioxide while consuming hydrogen and producing methane and water. The Plasma Pyrolysis Assembly (PPA) is being developed to recover most of the hydrogen from the methane. Acetylene and smaller amounts of other hydrocarbons are produced as byproducts of PPA operation. The present project is directed toward purifying the hydrogen product gas using sorption media and subsequently thermally regenerating the media using microwave power. The penetrative nature of microwave heating is utilized to efficiently drive gas desorption from the physical sorbents. Microwave heating drives off captured contaminants from a sorbent bed (which is held at relative vacuum) during regeneration. A series of molecular sieves, activated carbons and high surface area forms of alumina and silica were evaluated as candidate sorbent materials. Additionally, water vapor removal with the use of silica gel was evaluated. As a result of this research, hydrogen recovery from Sabatier methane is improved, thereby further closing the air-loop. Such increases in efficiency are necessary for crewed deep space exploration missions.

## Nomenclature

<i>AC</i>	=	Activated Carbon
<i>CH<sub>4</sub></i>	=	Methane
<i>cm</i>	=	Centimeter
<i>CRA</i>	=	Carbon dioxide Reduction Assembly
<i>g</i>	=	Gram
<i>H<sub>2</sub></i>	=	Hydrogen
<i>L</i>	=	Liter
<i>MFC</i>	=	Mass Flow Controller
<i>mL</i>	=	Milliliter
<i>mol sieve</i>	=	Molecular Sieve
<i>Mol%</i>	=	Mole Percentage
<i>MSFC</i>	=	Marshall Space Flight Center
<i>NASA</i>	=	National Aeronautics and Space Administration
<i>OGA</i>	=	Oxygen Generation Assembly
<i>PPA</i>	=	Plasma Pyrolysis Assembly
<i>QMS</i>	=	Quadrupole Mass Spectrometer
<i>sccm</i>	=	Standard Cubic Centimeters Per Minute

---

<sup>1</sup> Senior Research Scientist, R&D Division, [holtsnider@urcmail.net](mailto:holtsnider@urcmail.net), 125 Volunteer Way/P.O. Box 609.

<sup>2</sup> Senior Research Engineer, R&D Division, [rwheeler@urcmail.net](mailto:rwheeler@urcmail.net), 125 Volunteer Way/P.O. Box 609.

<sup>3</sup> Junior Scientist, R&D Division, 125 Volunteer Way/P.O. Box 609.

<sup>4</sup> Aerospace Engineer, ECLSS Development Branch, NASA-MSFC/ES62.

<sup>5</sup> Aerospace Engineer, ECLSS Development Branch, NASA-MSFC/ES62..

## I. Introduction

THIS paper summarizes the results of a Phase I SBIR development effort to purify hydrogen produced by the Plasma Pyrolysis Assembly (PPA). A selection of potential sorbent materials were screened for their effectiveness for purifying hydrogen from an ersatz gas mixture representative of the PPA effluent. The sorbent materials evaluated included several molecular sieves (mol sieves), activated carbons and high surface area forms of silica and alumina. Sorbent capacities were measured over temperatures ranging from 20°C to -78.5°C to determine if the added sorption capacities at reduced temperatures would justify the added energy expenditure required for active cooling. A survey of the data revealed that the use of molecular sieve 13X at 20°C is the most desirable option. Sorption media was regenerated by thermal desorption of the acetylene and other contaminants. Initial desorption testing was accomplished with the use of resistive heating. Once the most suitable sorbent material had been identified, the efficacy of microwave heating was evaluated. Results of microwave testing are recorded in the final report, but will not be included in this paper. Implementation of microwave desorption techniques is part of an on-going Phase 3 sub-scale development effort. The use of microwave power for bed regeneration offers several advantages over conventional thermal regeneration using resistive heating elements.<sup>1-8</sup> The benefits of utilizing microwaves include: 1) The entire volume of the bed is heated in unison. 2) Heat is distributed more uniformly. 3) The sorption media is selectively heated so little microwave power is lost to the surroundings. In conclusion, H<sub>2</sub> purification coupled with microwave dielectric heating for efficient thermal desorption of the contaminants from the media is an attractive approach to meeting NASA's needs.

## II. Background

The Sabatier reaction is used for the recovery of water from carbon dioxide, by reduction with hydrogen. During the process, half of the hydrogen is lost as methane. To recover this valuable resource, the PPA was developed to extract H<sub>2</sub> from CH<sub>4</sub> produced by the Carbon dioxide Reduction Assembly (CRA). The PPA was designed to selectively generate gas-phase products, primarily hydrogen and acetylene with minor quantities of ethylene, unreacted methane, and other hydrocarbons. The project was directed toward purifying the H<sub>2</sub> with the use of sorption media. Once purified, some of the H<sub>2</sub> will be returned to the PPA and the remainder will be passed to the CRA to augment H<sub>2</sub> supplied from water electrolysis which takes place in the Oxygen Generation Assembly (OGA).

## III. Experimental

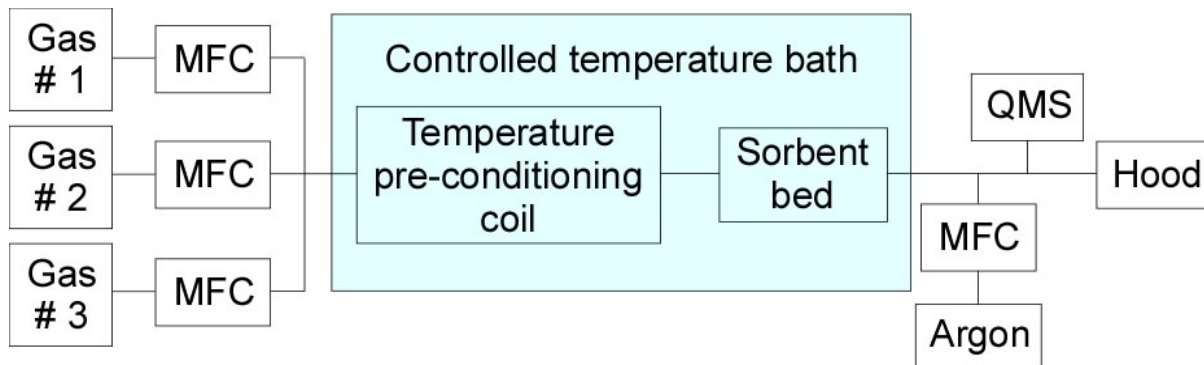
High surface area sorbent materials have the proven capacity to hold many times their equivalent ideal gas density for a given temperature and volume.<sup>9</sup> Six activated carbons (ACs) were selected for evaluation. ACs from differing source materials and prepared in different ways can display profoundly different sorption characteristics so a variety of ACs were appraised. Separation of acetylene from the PPA effluent presented a unique challenge. The PPA effluent is composed primarily of H<sub>2</sub> (~90%), acetylene (~7%), unreacted methane (~2%) and water (~1%) but also contains low concentrations of carbon monoxide,<sup>10</sup> ethylene, ethane and other hydrocarbons. Hydrogen, which makes up the bulk of the PPA effluent stream, is recycled back to the PPA influent either directly via a split stream or indirectly by way of the Sabatier reactor (as it operates in hydrogen rich mode) depending on the final system configuration. Acetylene, which makes up a relatively high proportion of the PPA effluent and with its relatively low hydrogen to carbon ratio of 1/1 is the primary target for the sorption media. Removal of ethylene and ethane, which are present at much lower concentrations, are of less importance. If methane is not removed by the sorption media the impact on CRA performance will be negligible based on independent testing performed at Marshall Space Flight Center which demonstrated that up to 15% methane in the CRA feed results in no significant decrease in CRA efficiency.<sup>11</sup> Carbon monoxide that is not captured by the sorbent will be reduced when reintroduced to the Sabatier, thereby keeping the steady-state level in the PPA low. Water generally competes for sites on sorption media, reducing the effective holding capacity of target compounds such as acetylene. As such, water removal may be beneficial. This may be accomplished by increasing the size of the sorption bed or by adding a second bed tailored for water removal.

Activated alumina, high surface area silica, and molecular sieves 3A, 4A, 5A, and 13X were evaluated in addition to ACs. Molecular sieves are commonly used for adsorbing small molecules and are promising sorbent candidates. A list of sorbent materials that were selected for evaluation is shown in Table 1.

**Table 1.** Sorbent Materials

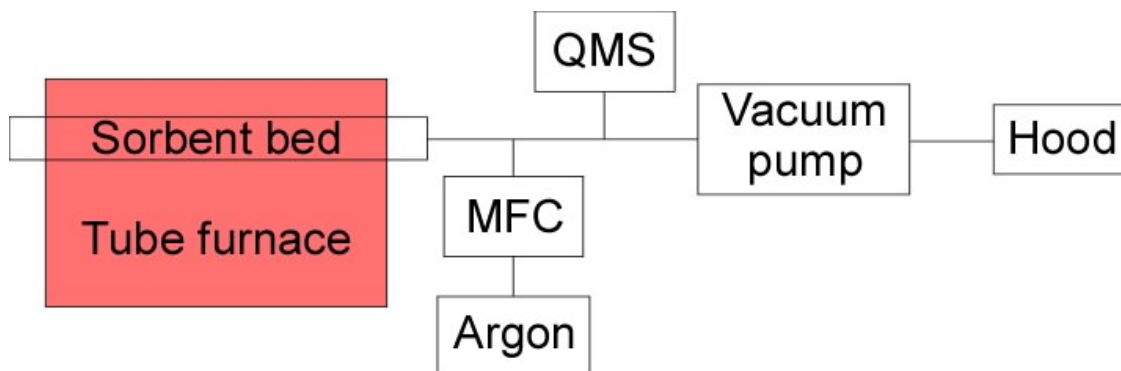
Media #	Sorbent	Size (mm)	Bulk density (g/cm <sup>3</sup> )
1	Kureha BAC G-70R spherical activated carbon	0.3 - 0.5	0.599
2	Schunk FU4652 spherical activated carbon	0.23 - 0.46	0.377
3	General Carbon GC8X305 granular activated carbon	1.6	0.525
4	Calgon APA 12x40 granular activated carbon	0.42 - 1.68	0.371
5	Calgon F600 12x40 granular activated carbon	0.42 - 1.68	0.619
6	Calgon TOG 20x50 granular activated carbon	0.297 - 0.84	0.439
7	GD Sylobead MS 564 CS mol sieve 3A	2.0	0.745
8	GD Sylobead MS 514 mol sieve 4A	2.0	0.738
9	GD Sylobead MS C 522 mol sieve 5A	2.0	0.706
10	GD Sylobead MS 544 mol sieve 13X	2.0	0.652
11	BASF CPN 14x28 alumina	0.59 - 1.19	0.664
12	Fuji Silysia CARIACT Q-30C silica	0.5 - 1.4	0.489

Testing to determine the adsorption capacities of sorbents at various temperatures was conducted using an apparatus represented by the block diagram in Figure 1. The flow rate of each gas was regulated using a dedicated Mass Flow Controller (MFC) for each. The combined gas stream was brought to the desired temperature and passed through a sorbent bed where sorption of one or more of the gases occurred until the sorbent media was saturated. Once saturated, the effluent gas concentration becomes identical to the feed concentration. A controlled flow of argon gas was added to the bed effluent before being analyzed with a Quadrupole Mass Spectrometer (QMS) to identify the gas components. Argon was added to provide a basis for comparison so the gas concentrations could be determined.



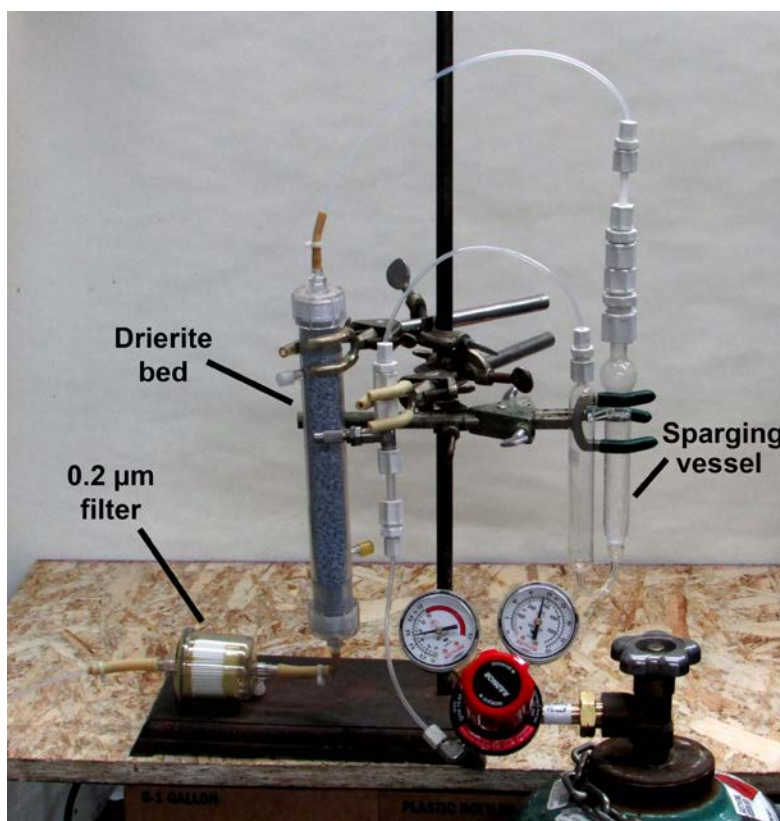
**Figure 1.** Sorption Test Apparatus: Starting at the left, individual gases are regulated using MFCs and combined. The gas mixture is brought to the desired temperature by passing it through a pre-conditioning coil which is submerged in a controlled temperature bath. It then passes through a sorbent bed which is also submerged in the bath. Argon is added to the gas stream before being analyzed by the QMS.

Desorption was accomplished by heating the sorption bed to 250°C while under vacuum. The effluent gas constituents were monitored using the QMS to determine when desorption was complete. Argon was added to the effluent to aid in gas quantitation. A block diagram showing the apparatus used for desorption is shown in Figure 2.



**Figure 2.** Desorption Test Apparatus: With the left side of the sorption bed blocked, it is heated in a tube furnace while under a vacuum. Argon is added to the bed effluent before being analyzed by the QMS.

When acetylene is a component of the gas mixture used during sorption tests, it must first be purified. Acetylene is stored dissolved in acetone within a gas cylinder. AA grade acetylene was used, however even this high grade of acetylene is stored dissolved in acetone. The amount of acetone vapor in the acetylene is reportedly 1% to 2% by volume when the gas cylinder is full and increases to approximately 10% by the time the cylinder is near empty.<sup>12</sup> The acetone can be removed from the gas stream by sparging through water. Figure 3 shows the sparging apparatus that was used. Gas was sparged through 25 mL of water using a sparging vessel with a glass frit. The gas stream was then passed through a 123 cm<sup>3</sup> Drierite bed to remove water vapor that was introduced during the sparging process. Downstream of the Drierite bed was a 0.2 μm filter with 300 cm<sup>2</sup> surface area to remove Drierite fines. Using this apparatus, the concentration of acetone in the gas stream could be decreased to below the level of QMS detection.



**Figure 3.** Acetylene Scrubbing Apparatus: This is used to remove acetone that is present in acetylene that is stored in compressed gas cylinders.

Figure 4 shows the components comprising the housing for a sorption bed. 111 cm<sup>3</sup> of sorption media was housed within a 1 inch OD 316 stainless steel tube with a 0.035 inch wall. Teflon ferrules were used to provide gas-tight seals. Ball valves were located at each end of the bed. The media was constrained to the centermost 10 inches of the 1 inch tube by



**Figure 4.** This image shows a disassembled bed housing.



**Figure 5.** This image shows an expanded view of the screen and spring.

restraining screens. Figure 5 shows an expanded view of a restraining screen with a spring to hold it next to the media with enough force to prevent voids from forming. Before initial use, each was desorbed at 250°C while under a vacuum of less than 10 Torr (13 mbar) for one hour to remove moisture and any other contaminants that may have accumulated on the media during storage. The effluent was monitored using a QMS to confirm that adequate time was allowed to strip contaminants from the media. Additionally, beds were regenerated after each sorption run using the same procedure. QMS data collected during desorption was used to determine the duration of the heating cycle. One hour was adequate for all ACs.

All mol sieves except 4A required 1.5 to 2 hours to regenerate. Mol sieve 4A required 5 hours to regenerate. It is interesting to note that acetylene breakthrough curves of mol sieve 4A show a very broad breakthrough as compared to the very abrupt breakthroughs seen with all the other media.

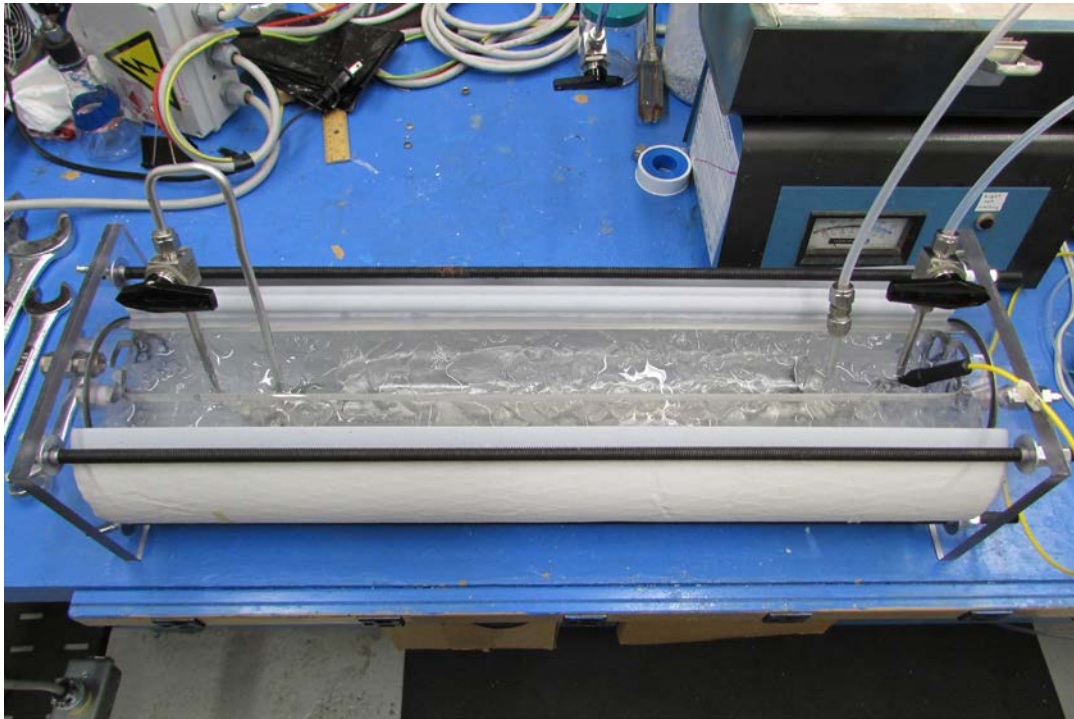
During sorption, the gas temperature was controlled by immersing a temperature conditioning coil (Figure 6) along with the sorbent bed in an appropriate constant temperature bath. A water



**Figure 6.** Temperature conditioning coil used to bring the gas temperature to that of the sorption bed.

bath was used for tests that were performed at 20°C, a water/ice bath was used for testing at 0°C, an ethylene glycol/ethanol/dry ice bath was used for -70°C testing, and an ethanol/dry ice bath was used for -78.5°C testing. A 6 inch spiral of ¼ inch aluminum tubing was used as the conditioning coil to bring (by heating or cooling) the gas to the desired temperature before entering the sorbent bed. In Figure 7 the conditioning coil and sorption bed are shown submerged in a water/ice bath during 0°C testing.

Beds were regenerated by thermal desorption at 250°C in a tube furnace while held in a relative vacuum to below 10 Torr (13 mbar). The tube furnace has a 12 inch heated zone so only the centermost 10 inches of each bed was filled with sorption media to ensure that all of the media would be heated to the prescribed temperature. The gases eluted during regeneration were monitored with the QMS to determine when desorption was complete. A sorbent bed placed in a tube furnace for regeneration is shown in Figure 8.



**Figure 7.** Temperature conditioning coil and sorption bed are submerged in an ice bath during 0°C sorption testing.



**Figure 8.** Thermal desorption is accomplished by heating in a tube furnace to 250°C while in a relative vacuum of <10 Torr (13 mbar).

#### IV. Results and Discussion

Separation of acetylene from the PPA effluent was the ultimate goal. As such, an acetylene gas concentration representative of the PPA effluent was used to evaluate each media shown in Table 1. Acetone was removed from the acetylene using the apparatus shown in Figure 3. Hydrogen is the primary gas in the PPA effluent so it was used as a diluent. Breakthrough curves were generated by passing a 7% mixture of acetylene in hydrogen through the beds. The acetylene flow rate was 8.76 sccm and the hydrogen flow rate was 116 sccm resulting in a total flow of 125 sccm. The total PPA effluent flow resulting from a single crew member is 2130 sccm,<sup>10</sup> which is approximately 17 times the flow used to gather the data presented here. As the gas mixture passed through a sorbent bed, acetylene was adsorbed, leaving behind a relatively pure stream of hydrogen as the effluent.

##### A. Screening Activated Carbons Based on Their Acetylene Sorption Capacities

Initially each of the ACs were evaluated at 20°C and 0°C to screen for those with the highest capacity. The three displaying the highest loading capacity were selected for further testing. They were tested at -78.5°C in a dry ice-ethanol bath. Additionally, they were tested using a gas mixture containing 2% methane in addition to the acetylene and hydrogen.

The QMS was used to monitor the concentrations of hydrogen, acetylene, methane, acetone, water, oxygen and argon. Acetone and water were monitored to confirm that the acetylene scrubbing apparatus was performing satisfactorily. Oxygen was monitored to confirm the absence of air in the system. Argon was monitored because it was added to the bed effluent to serve as a basis for comparison so the other gases could be quantified. Figure 9 shows the acetylene loading on each of the ACs at 20°C.

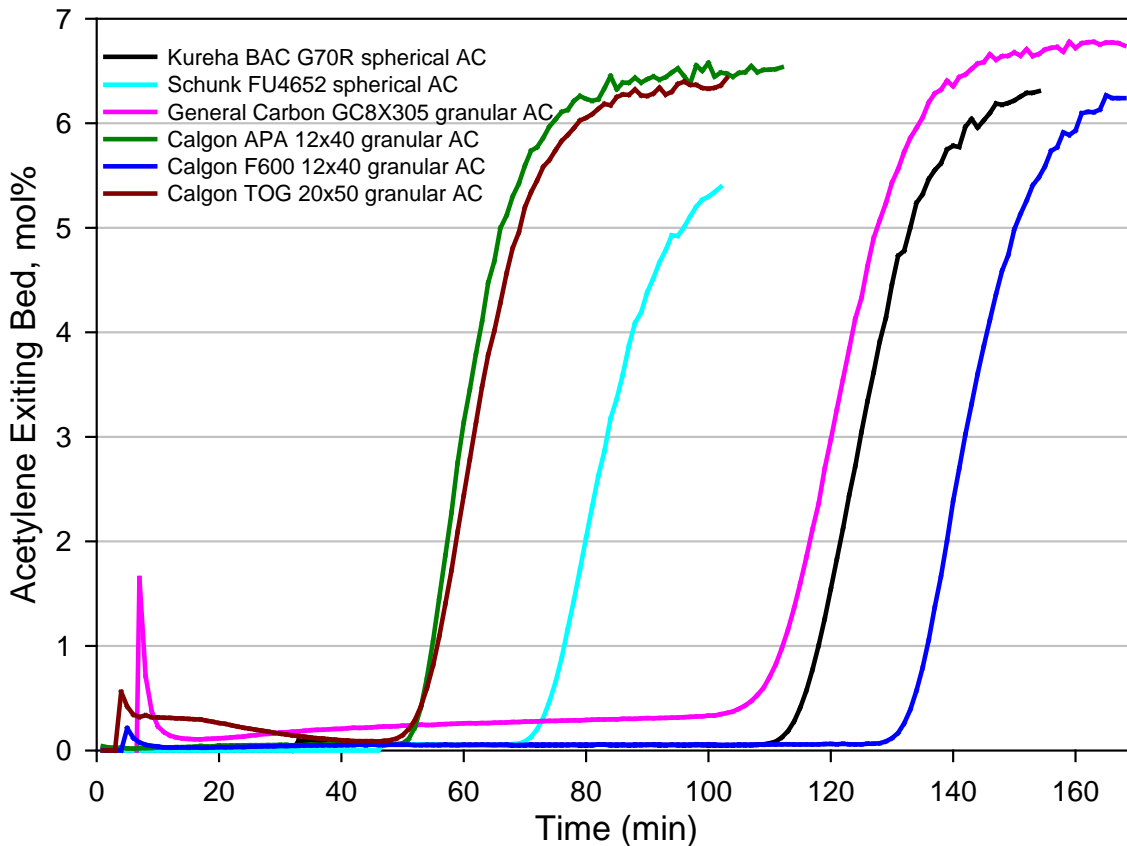


Figure 9. Breakthrough curves for 7% acetylene on activated carbons at 20°C.

Figure 10 shows the acetylene loading at 0°C. The three ACs that were selected for testing at -78.5°C were Kureha BAC G-70R spherical AC (media #1), General Carbon GC8X305 granular AC (media #3) and Calgon F600 12x40 granular AC (media #5).

Temperature plays an important role in determining loading capacity as indicated by the acetylene sorption at 20°C, 0°C and -78.5°C shown in the three plots of Figure 11 in which the same time scale is used for each plot. Loading capacity is determined by summing the amount of acetylene that entered the sorbent

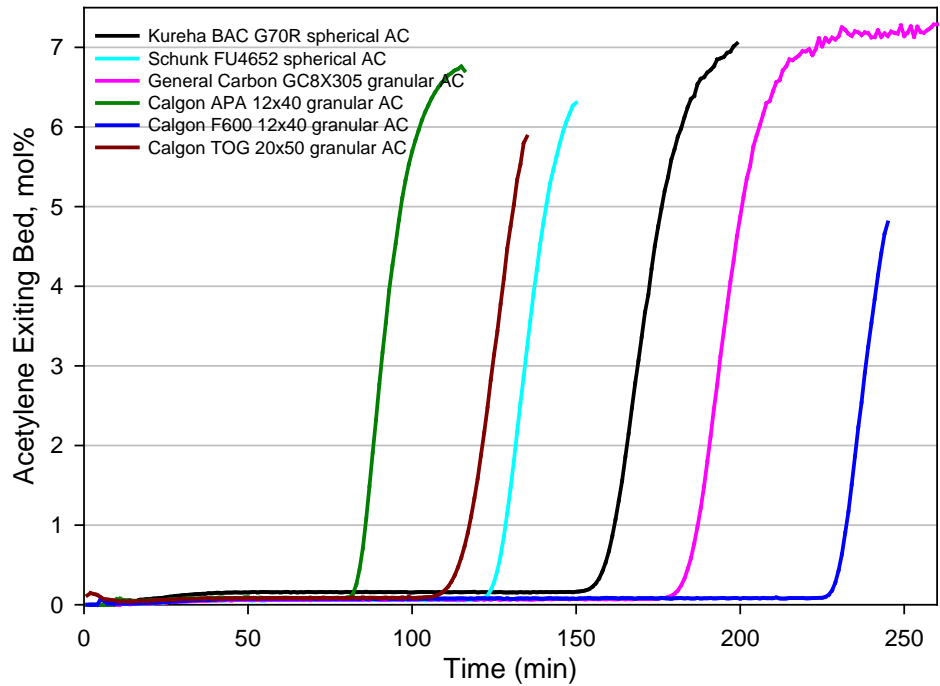


Figure 10. Breakthrough curves for 7% acetylene on activated carbons at 0°C.

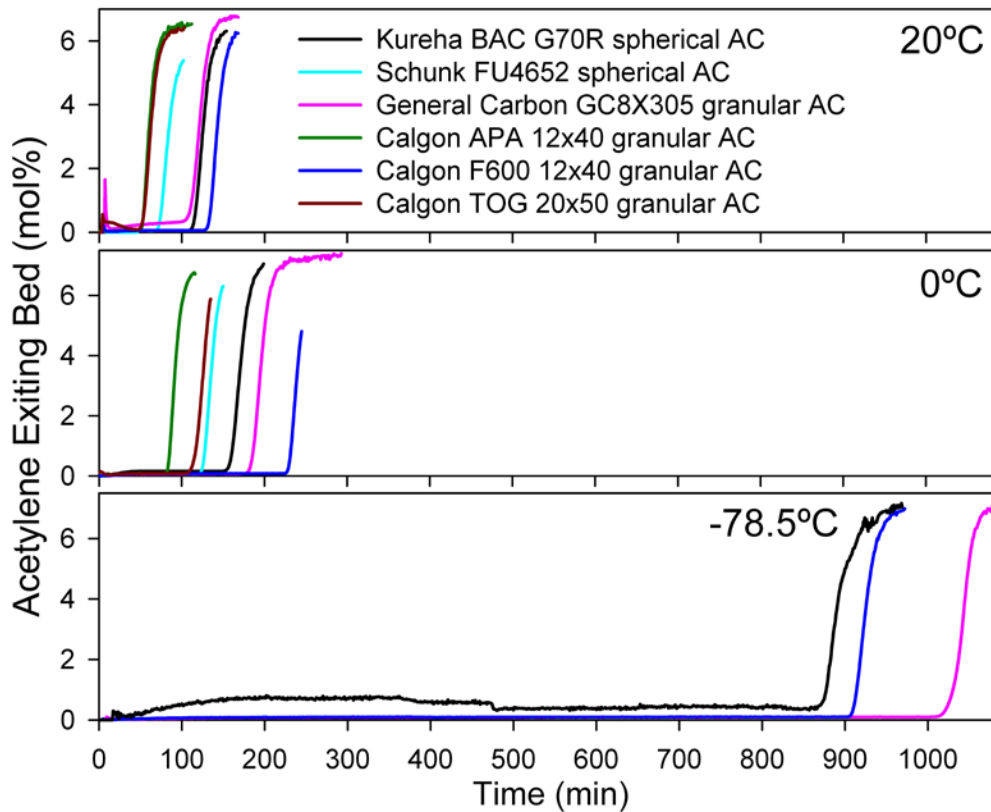
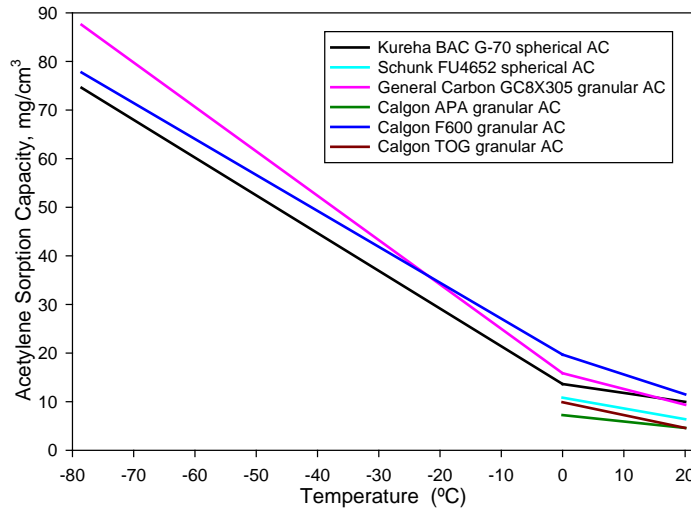


Figure 11. Breakthrough curves for 7% acetylene at 20°C (top), 0°C (middle) and -78.5°C (bottom). All curves use the same time scale to aid in a visual comparison.



bed until the time of 10% breakthrough. Compared to the acetylene sorption capacity at 20°C, Media #3 has 1.7 times the capacity when at 0°C and 9.3 times the capacity when at -78.5°C. Figure 12 shows the loading capacities as a function of temperature.

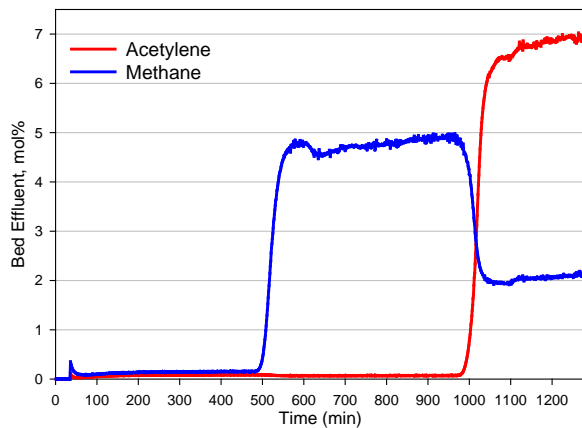


**Figure 12.** Acetylene sorption vs. temperature on activated carbons.

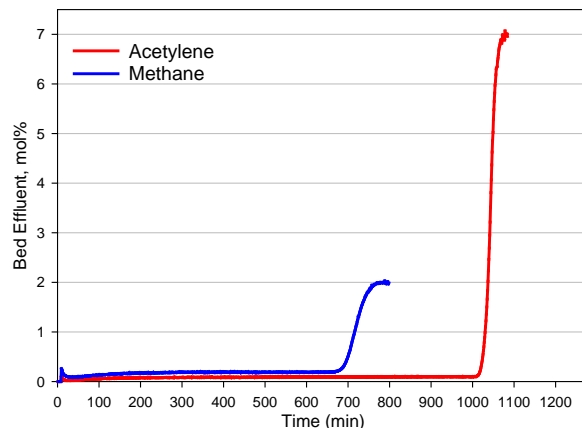
### B. Methane Sorption on Activated Carbons

To observe the effect of combining methane with the feed gas, a mixture containing 7% acetylene and 2% methane diluted in hydrogen was used to generate breakthrough curves with media #3 and media #5. These were compared to breakthrough curves generated with acetylene and methane (diluted with hydrogen) run separately. These comparisons were made using data generated at -78.5°C. Figures 13 and 14 show respectively, breakthrough curves for media #3 with acetylene and methane combined with hydrogen, and with acetylene and methane run independently. Figures 15 and 16 show the results of the same set of tests while using media #5.

Note that when all gases are combined, methane breaks through earlier and the concentration rises to almost 5 mol% and then drops to 2 mol%, the concentration of the feed, once acetylene breaks through. This phenomena is consistent with sorption displacement theory<sup>13,14</sup> i.e. the methane that initially loads on the media is displaced by

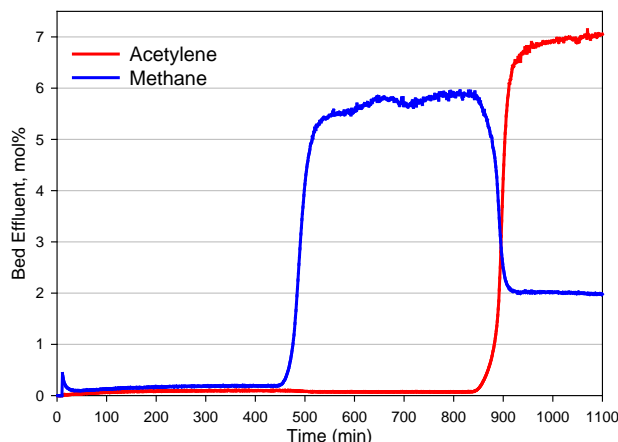


**Figure 13.** Media #3 at -78.5°C with combined acetylene and methane diluted into hydrogen.

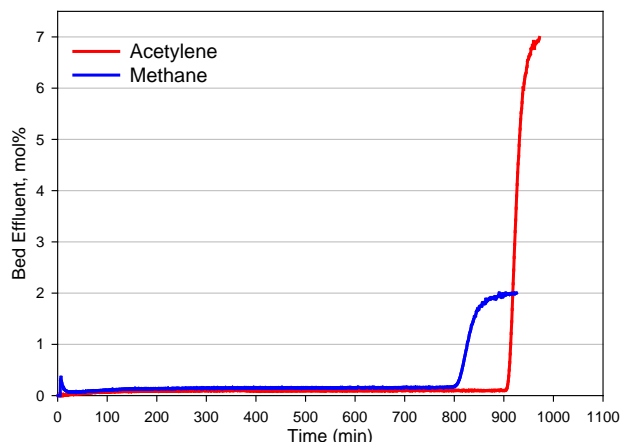


**Figure 14.** Media #3 at -78.5°C with acetylene in hydrogen and methane in hydrogen run independently.

acetylene until most of the methane binding sites are occupied by acetylene. Once the media is saturated with acetylene, both the methane and acetylene concentrations in the effluent approach the feed concentrations.



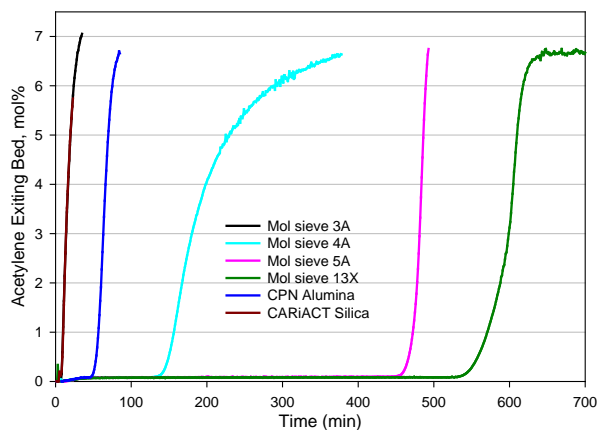
**Figure 15.** Media #5 at  $-78.5^{\circ}\text{C}$  with combined acetylene and methane diluted into hydrogen.



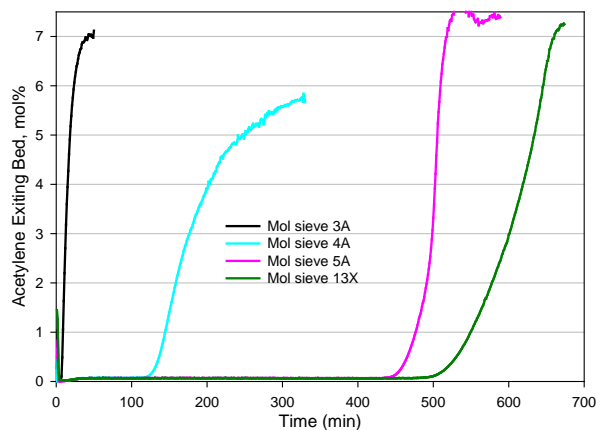
**Figure 16.** Media #5 at  $-78.5^{\circ}\text{C}$  with acetylene in hydrogen and methane in hydrogen run independently.

### C. Evaluation of Molecular Sieves, Activated Alumina and Silica

The mol sieves, activated alumina and porous silica (collectively referred to as non-AC sorption media) were evaluated next. These included molecular sieves 3A, 4A, 5A and 13X as well as high surface area forms of alumina and silica. As with the ACs, the non-AC sorption media were initially screened for acetylene loading capacity using 7% acetylene in hydrogen at  $20^{\circ}\text{C}$ . The results are shown in Figure 17.

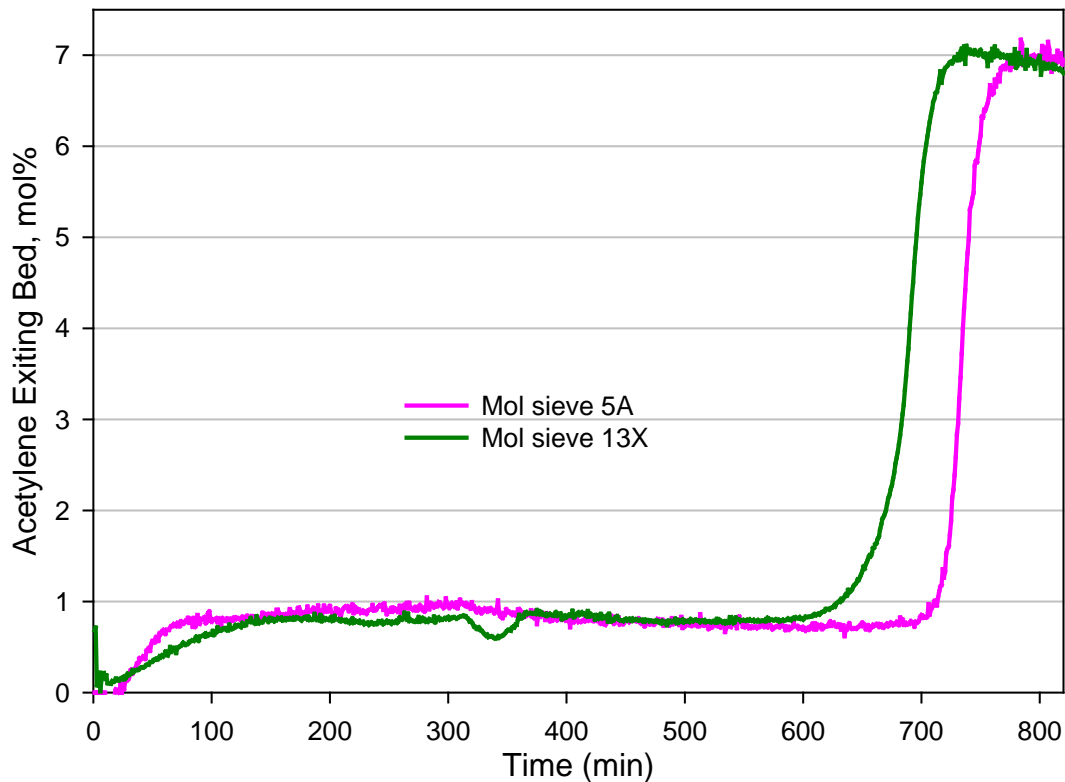


**Figure 17.** Sorption of 7% acetylene in  $\text{H}_2$  at  $20^{\circ}\text{C}$  on non-AC media.



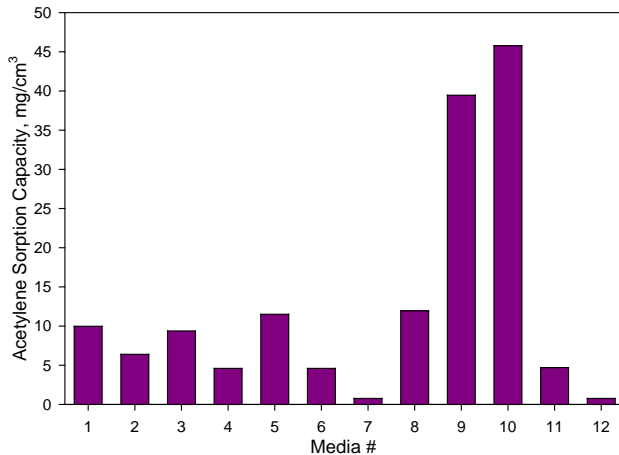
**Figure 18.** Sorption of 7% acetylene in  $\text{H}_2$  at  $0^{\circ}\text{C}$  on mol sieves.

Mol sieve 3A and CARiACT silica break through immediately (the curves are superimposed over each other). The alumina displays some sorption capacity but not enough to warrant further investigation. Mol sieve 4A, previously evaluated by NASA for  $\text{H}_2$  purification,<sup>15</sup> displays an intermediate sorption capacity. Its breakthrough is much more gradual than what was observed with the other media. Molecular sieves 5A and 13X show significantly higher loading capacities than the other media while at  $20^{\circ}\text{C}$ . To determine the dependence of temperature on sorption capacity of mol sieves, breakthrough curves were generated for acetylene on each mol sieve at  $0^{\circ}\text{C}$ , and for mol sieves 5A and 13X at  $-78.5^{\circ}\text{C}$ , shown in Figures 18 and 19 respectively. As can be seen, there was no significant change in capacity when the temperature was decreased from  $20^{\circ}\text{C}$  to  $0^{\circ}\text{C}$  and only a moderate improvement when the temperature was further decreased to  $-78.5^{\circ}\text{C}$ . This is in stark contrast to the temperature dependence observed with the ACs.

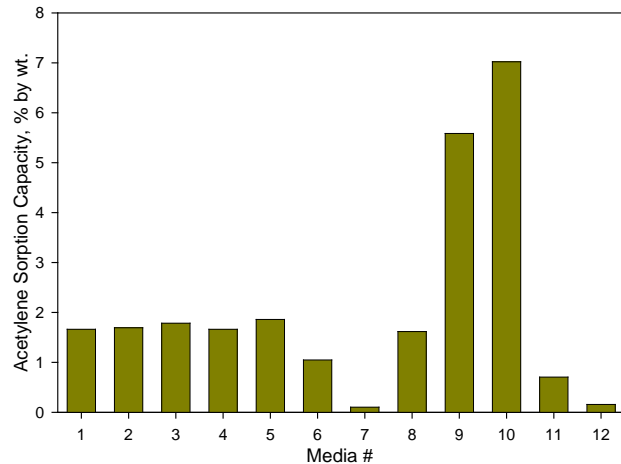


**Figure 19.** Sorption of 7% acetylene in H<sub>2</sub> at -78.5°C on mol sieves 5A & 13X.

The best sorbent for acetylene at 20°C is mol sieve 13X with a capacity of 47.9 mg/cm<sup>3</sup>. However, at -78.5°C, media #3 (General Carbon GC8X305 granular activated carbon) has a capacity of 87.5 mg/cm<sup>3</sup>, almost twice that of mol sieve 13X at 20°C. Although media #3 performs better at -78.5°C, unless the cold of space can be utilized to



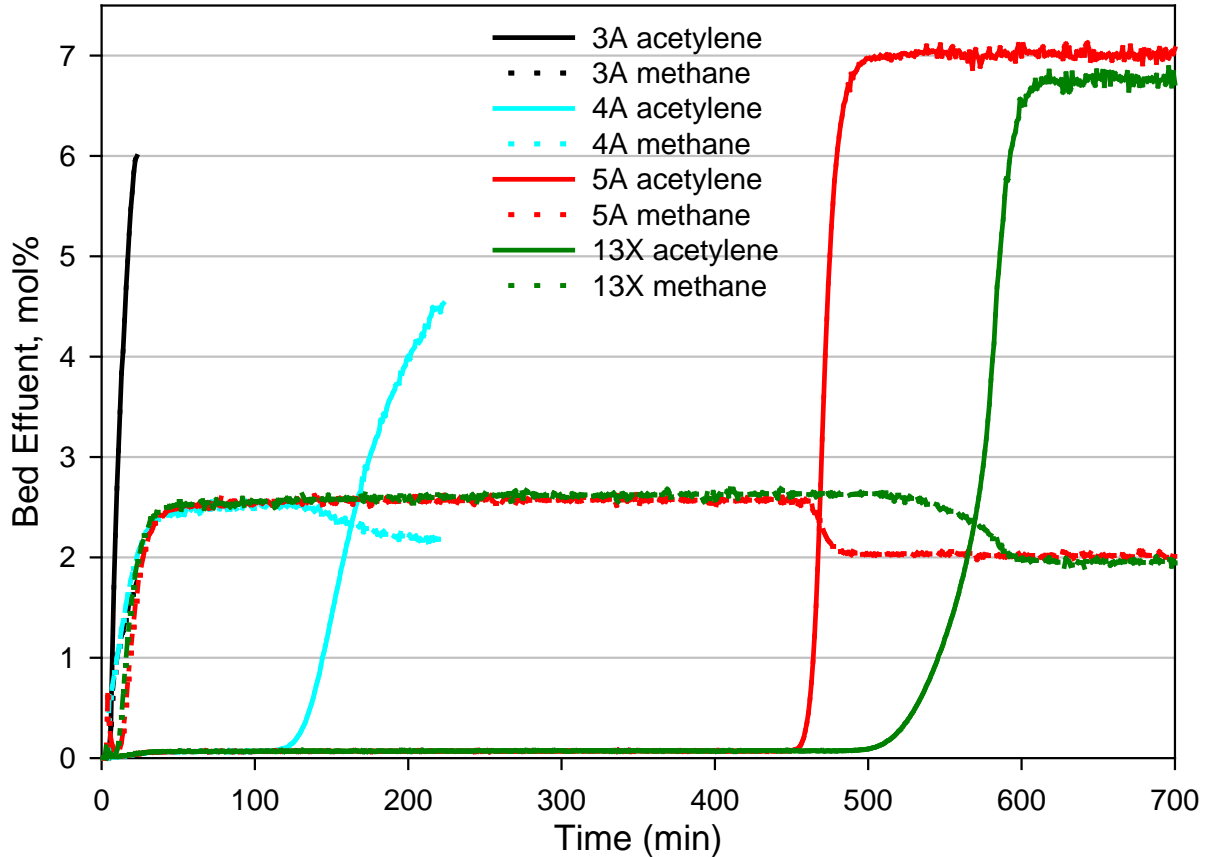
**Figure 20.** Sorption capacity based on bed volume.



**Figure 21.** Sorption capacity based on bed mass.

lower the bed temperature, it probably will not be cost effective to lower the temperature enough to increase its capacity beyond that of mol sieve 13X. A comparison of sorption capacity at 20°C based on bed volume for each media listed in Table 1 is shown in Figure 20.

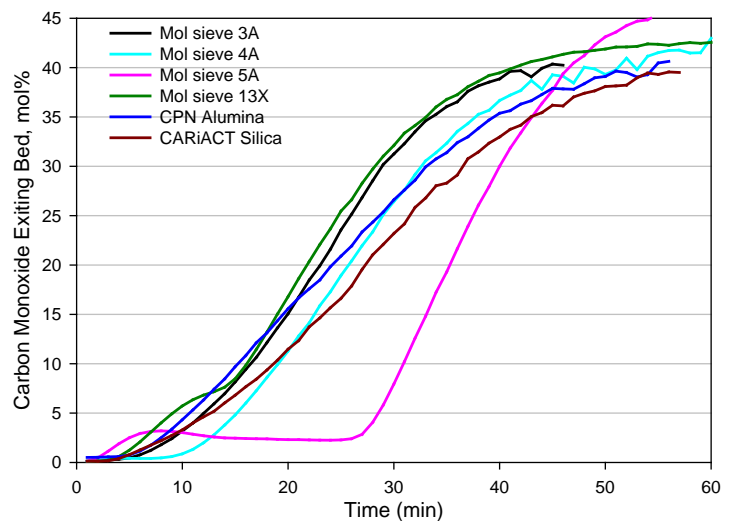
Since the bulk density of each media is different, it is useful to also compare sorption capacities based on bed mass. Figure 21 shows loading capacities at 20°C as percent by weight. 20°C breakthrough data was gathered for each of the mol sieves when fed a mixture of 7% acetylene and 2% methane in hydrogen. See Figure 22.



**Figure 22.** Breakthrough curves using a combined feed gas containing 7% acetylene and 2% methane diluted into hydrogen at 20°C.

All the mol sieves show a very low capacity for methane, a property that is highly desirable for this project. The acetylene loading capacities are nearly identical to those seen when methane is not a component of the gas mixture. The best sorbent, mol sieve 13X, shows a loading capacity of 45.8 mg/cm<sup>3</sup>. This compares favorably to the loading capacity of mol sieve 4A, the acetylene sorbent previously evaluated by NASA for purifying hydrogen from the PPA. Mol sieve 4A evaluated under the same conditions as mol sieve 13X displayed an acetylene capacity of only 11.9 mg/cm<sup>3</sup>. The use of mol sieve 13X in place of mol sieve 4A results in almost a four fold improvement in capacity. Furthermore, we have witnessed that regeneration of a mol sieve 13X bed can be accomplished in approximately one third the time as a mol sieve 4A bed, resulting in significant energy savings.

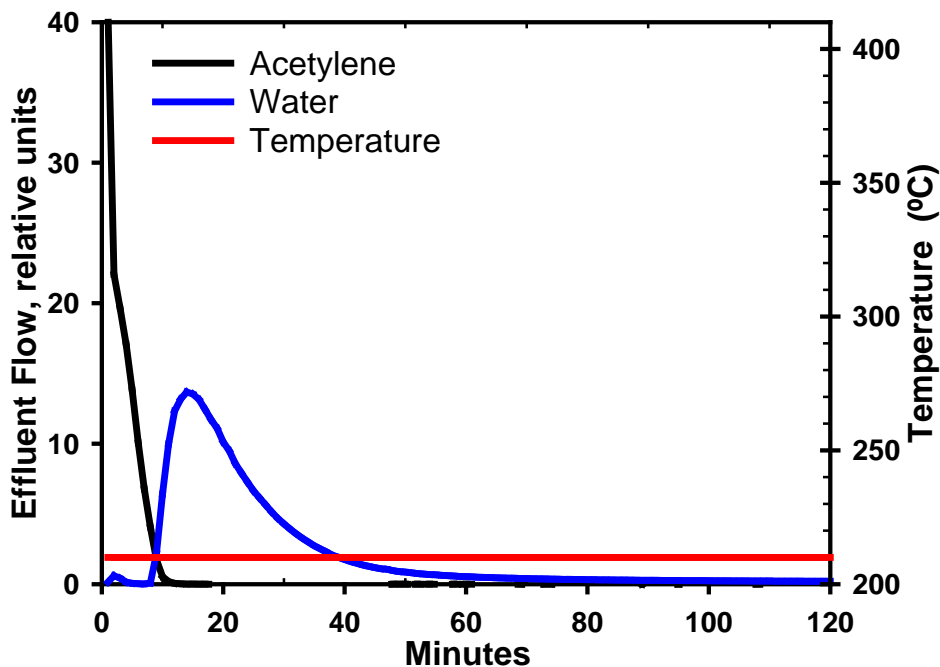
Breakthrough curves for carbon monoxide (a minor component of the PPA effluent) were generated using each mol sieve, alumina and silica at 20°C. The feed contained 42% CO and the total flow was 137 scfm. The results are shown in Figure 23. None of the media tested displayed a significant carbon monoxide capacity. As a result, carbon



**Figure 23.** Sorption of a 42% CO stream.

monoxide will not be separated from the hydrogen stream. This should not seriously impact downstream processes.

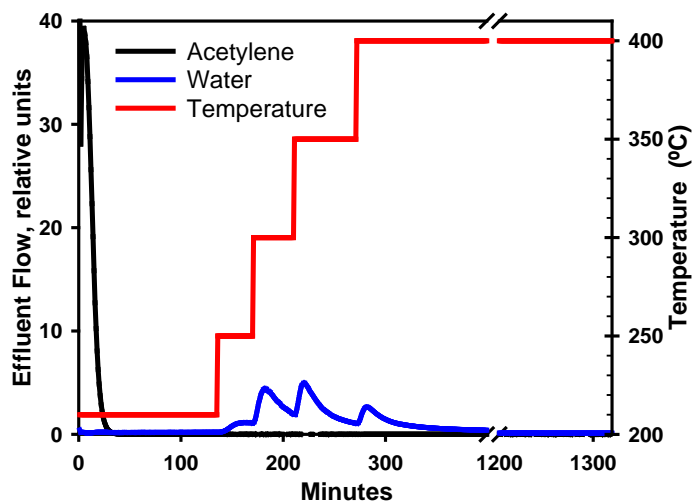
Since water vapor will be in the PPA effluent, a silica gel bed will be used to remove it from the gas stream to prevent water accumulation on the mol sieve 13X. A 111 cm<sup>3</sup> bed of silica gel (Grace Davison SYLOBEAD SG B 127) successfully removed water vapor from a gas mixture representative of PPA effluent. Regeneration was accomplished at 210°C. Refer to Figure 24.



**Figure 24.** Thermal desorption of water from mol sieve 13X at 210°C under a relative vacuum of <10 Torr (13 mbar).

#### D. Multiple Cycles of Sorption and Desorption using Molecular Sieve 13X

A series of six sorption/desorption cycles were performed at 20°C on mol sieve 13X to confirm that the sorption capacity doesn't change with use. The bed contained 111 cm<sup>3</sup> of mol sieve 13X. The gas stream was representative of PPA effluent with water vapor previously removed with silica gel. The flow rate was 125 sccm and consisted of hydrogen adulterated with 7% acetylene, 2% methane and 0.2% ethylene. Regeneration was performed at 210°C at <10 Torr (13 mbar). After 5 cycles the sorption capacity for acetylene had declined by 20% indicating that an unknown contaminant (other than hydrogen, acetylene, methane or ethylene) was being sorbed by the media and wasn't being desorbed. The most likely contaminant is water even though we avoided adding it to the feed stream. To rejuvenate the bed, regeneration was performed with the temperature increased stepwise to 400°C



**Figure 25.** Removal of water from mol sieve 13X at significantly elevated temperatures.

while monitoring the water vapor. See Figure 25.

After performing this rejuvenation, a 6<sup>th</sup> sorption was performed. The acetylene sorption capacity of the mol sieve 13X returned nearly to what it was originally. See Figure 26. This suggests that even though 210°C is adequate to remove acetylene from mol sieve 13X occasional regenerations at a higher temperature will be necessary to remove water vapor that gradually accumulates.

Due to its impressive performance, mol sieve 13X was selected for hydrogen purification. The bed size needed to process the PPA effluent for 4 hours and scaled for a single crewmember is approximated as follows:

Approximately 350 sccm of methane is processed by the PPA per crewmember. Following 4 hours of PPA use, the PPA goes offline while it undergoes a 45 minute carbon burn-off process. Therefore 4.75 hours of methane needs to be processed during 4 hours of operation. If the PPA were 100% efficient, 54 g of acetylene would result. Mol sieve 13X has a capacity of 45.8 mg/cm<sup>3</sup> so a bed capable of removing the acetylene for 4 hours needs to be 1.2 L. The media has a bulk density of 0.652 g/cm<sup>3</sup> so the bed mass would be 782 g.

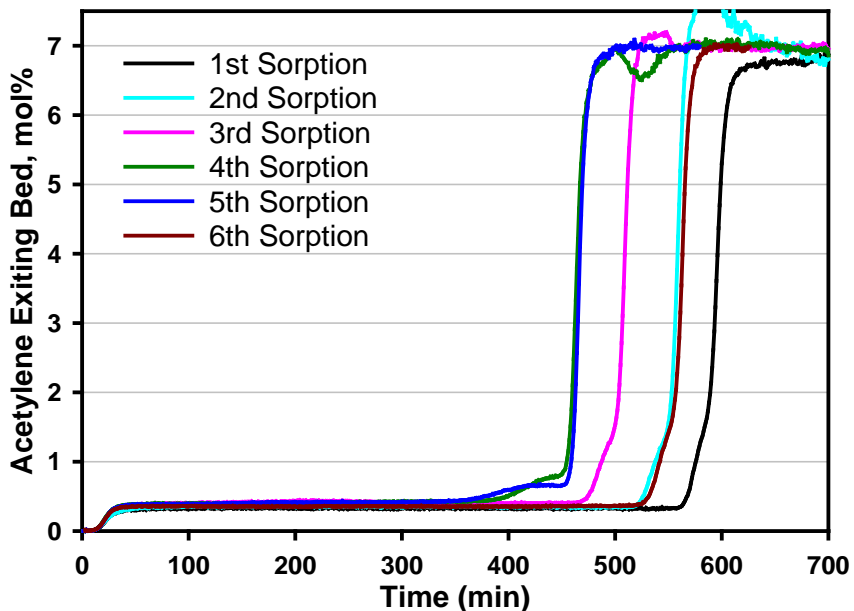


Figure 26. Successive sorptions of ersatz PPA effluent on mol sieve 13X.

## V. Conclusion

To summarize, six activated carbons were evaluated, two spherical and four granular. The activated carbons were produced under different conditions and thus displayed different sorption properties. Four molecular sieves were evaluated, 3A, 4A, 5A and 13X, all obtained from Grace Davison. High surface area forms of alumina and silica were evaluated, BASF CPN 14x28 alumina and Fuji Silycia CARIACT Q-30C silica. Silica gel from Grace Davison was used for water removal. Breakthrough curves were generated by passing gas mixtures through 111 cm<sup>3</sup> sorbent beds until the compounds in the influent gas mix appeared in the effluent. The breakthrough curves were used to determine the sorption capacities of each sorbate on each sorbent at several temperatures. The sorbates that were evaluated for the hydrogen purification portion of this project were acetylene, methane, ethylene and carbon monoxide.

The best sorbent to be used for hydrogen purification is molecular sieve 13X. This material displays 4 times the capacity of molecular sieve 4A, the sorbent previously considered for acetylene removal from hydrogen. The most probable implementation resulting from the Phase I research will be to use silica gel to remove water vapor and molecular sieve 13X to remove acetylene, ethylene and related hydrocarbons, while allowing hydrogen and methane to pass through. Thermal regeneration of silica gel and mol sieve 13X, loaded with target sorbate contaminants, has been demonstrated. Microwave heating of sorbent material has been shown to be feasible. The longevity of the mol sieve 13X media has been demonstrated with repeated cycles of sorption and desorption.

These exciting results document the success of sorbent based hydrogen purification coupled with microwave desorption of the sorbent media. When scaled to accommodate a crew of at least four the system will become an indispensable component of the air revitalization system.

## Acknowledgments

The National Aeronautics and Space Administration's Marshall Space Flight Center, Huntsville, AL supported this work under contract NNX14CM20P.

## References

1. Atwater, J. E., Holtsnider, J. T., and Wheeler, R. R., Jr., Microwave Regenerable Air Purification Device, Final Report, NASA Contract No. NAS2-14374, August 1996.
2. Atwater, J. E., Holtsnider, J. T., Wheeler, R. R., Jr., and Luna, B., Microwave-Powered Thermal Regeneration of Sorbents for CO<sub>2</sub>, Water Vapor and Trace Organic Contaminants, *SAE Technical Paper Series* No. 972430, presented at 27th International Conference on Environmental Systems, Lake Tahoe, NV, July 14-17, 1997.
3. Atwater, J. E., and Wheeler, R. R., Jr., Development and Testing of the Microwave Regenerable Air Purification Technology Demonstrator, Volume 2, Final Report, NASA Contract NAS2-97017, June 1999.
4. Atwater, J. E., and Wheeler, R. R., Jr., A Complex Permittivity Study of Sorbent Materials and Volatile Contaminants, Volume 1, Final Report, NASA Contract NAS2-97017, June 1999.
5. Wheeler, R. R., Jr., Atwater, J. E., Akse, J. R., Holtsnider, J. T., and Luna, B., Development and Testing of a Microwave Powered Regenerable Air Purification Technology Demonstrator, SAE 2002-01-2403, presented at 32nd International Conference on Environmental Systems, San Antonio, TX, July 2002.
6. Atwater, J. E., and Wheeler, R. R., Jr., Complex Permittivities and Dielectric Relaxation of Granular Activated Carbons at Microwave Frequencies between 0.2 and 26 GHz, *Carbon*, 41 (9), 1801-1807, 2003.
7. Atwater, J. E., and Wheeler, R. R., Jr., Temperature Dependent Complex Permittivities of Graphitized Carbon Blacks at Microwave Frequencies Between 0.2 and 26 GHz, *J. Mater. Sci.* 39, 151-157, 2004..
8. Atwater, J. E., and Wheeler, R. R., Jr., Microwave Permittivity and Dielectric Relaxation of a High Surface Area Activated Carbon, *Appl. Phys. A* 79, 125-129, 2004.
9. Ma, Y. H., Sun, W., Bhandarkar, M., and Wang, J., Adsorption and Diffusion of Oxygen, Nitrogen, Methane and Argon in Molecular Sieve Carbons, Final Rpt., Prepared for United States Air Force, Contract USAFSAM-TR-89-32, April 1990.
10. Mansell, M. J., Abney, M. B., and Miller, L. A., Influence of Oxygenated Compounds on Reaction Products in a Microwave Plasma Methane Pyrolysis Assembly for Post-Processing of Sabatier Methane, AIAA 2011-5035, presented at the 41<sup>st</sup> International Conference on Environmental Systems, Portland, OR, July 2011.
11. Abney, Morgan B. at NASA-MSFC, personal communication, June 2012.
12. Hyman, Michael R., and Arp, Daniel J., Quantification and Removal of Some Contaminating Gases from Acetylene Used to Study Gas-Utilizing Enzymes and Microorganisms, *Applied and Environmental Microbiology*, vol 53, No. 2, 1987, p 298-303.
13. Rees, L. V. C., Adsorbent Materials: Their Structure, Properties and Characterization, from the *Proceedings of the 5<sup>th</sup> BOC Priestley Conference in Birmingham*, Sept. 19<sup>th</sup>-21<sup>st</sup> 1989.
14. Harland, C. E., *Ion Exchange*, published by The Royal Society of Chemistry, 1994.
15. Abney, M. B., Miller, L. A., and Barton, K., Evaluation of Sorbents for Acetylene Separation in Atmosphere Revitalization Loop Closure, AIAA Paper No. 2011-5057, presented at the 41<sup>st</sup> International Conference on Environmental Systems, Portland, OR, 2011.