Sorbent Structural Testing on Carbon Dioxide Removal Sorbents for Advanced Exploration Systems

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Long term space missions require carbon dioxide removal systems that can function with minimal downtime required for maintenance, low power consumption and maximum efficiency for CO_2 removal. A major component of such a system are the sorbents used for the CO_2 and desiccant beds. Sorbents must not only have adequate CO_2 and H_2O removal properties, but they must have the mechanical strength to prevent structural breakdown due to pressure and temperature changes during operation and regeneration, as well as resistance to breakdown due to moisture in the system from cabin air. As part of the studies used to select future CO_2 sorbent materials, mechanical tests are performed on various zeolite sorbents to determine mechanical performance while dry and at various humidified states. Tests include single pellet crush, bulk crush and attrition tests. We have established a protocol for testing sorbents under dry and humid conditions, and previously tested the sorbents used on the International Space Station carbon dioxide removal assembly. This paper reports on the testing of a series of commercial sorbents considered as candidates for use on future exploration missions.

Nomenclature

MSFC	=	Marshall Space Flight Center
ISS	=	International Space Station
CDRA	=	Carbon Dioxide Removal Assembly
MTF	=	Mechanical Test Facility
HCS	=	Humidity Conditioning Test Stand
AES	=	Advanced Exploration Systems
LSSP	=	Life Support Systems Project
HST	=	Hydrothermal Stability Test

I. Introduction

The Carbon Dioxide Removal Assembly (CDRA) was installed on the ISS in early 2001 and has provided the bulk of the CO_2 removal function for the ISS. The CDRA consists of moisture removal sorbent beds, packed with silica gel and a 13X zeolite, upstream of zeolite 5A packed CO_2 removal beds. The moisture removal beds are required for removing moisture from the CDRA incoming air stream so that maximum CO_2 removal will occur in the CO_2 beds. A recent issue concerning the operation of the CDRA was the detection of moisture in the CDRA air stream, downstream of the CO_2 removal beds. Though the source of the moisture has not, at this time, been resolved, the issue of possible moisture contamination, and mechanical and performance degradation, of the CO_2 removal sorbents became important. A test program was therefore begun to understand the structural effects of moisture on selected sorbents considered for use on ISS and future spacecraft.

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Zeolites currently used for capture of CO_2 are agglomerates of zeolite crystals and (typically) clay binder. The roughly cubic crystals (approximately 2 µm per side) are bound into spherical or cylindrical pellets (approximately 2 mm in diameter in the CDRA application). Pelletization with clay binder is required to reduce flow resistance through the fixed bed. An open structure inside the pellet is required to maximize CO_2 mass transfer into the pellet.

However, this open composite structure tends to have low resistance to attrition and is may be weakened by humidity and/or large temperature excursions. The pellet fragments resulting from attrition can migrate to the mesh screen retaining the sorbent, partially blocking the flow path and increasing differential pressure. Blower speed can be increased to regain the flow rate required for CO_2 removal performance, but at the cost of additional power. When screen blockage and the resulting flow restriction increases above equipment limits, replacement of the fixed bed or cleaning of the retention screen is required. The current ISS CDRA design includes features for screen cleaning, however this requires considerable crew time which is highly undesirable. For future spacecraft, the vehicle architecture may not allow easy access to equipment as on the ISS, such that maintenance may become even less desirable.

A test program to screen, characterize and to understand the structural effects of moisture on selected sorbents has been undertaken as part of the Advanced Exploration Systems Life Support Systems Project (AES LSSP). Simple tests to screen existing and emerging sorbents for structural stability and working capacity can quickly identify sorbents with the highest potential. More detailed structural stability testing may then be conducted on selected sorbents. Previous work in the area of sorbent screening included pellet and bulk crush and attrition testing of selected sorbents[1,2,3,7] and in a Hydrothermal Stability Test[5,6], which simulates the CDRA bed operation while subjected to various humidity levels. The HST testing is still ongoing..

Dust production and sorbent fracturing are undesirable for packed bed applications on long term missions. Recognizing the mechanisms for dust production and sorbent fracturing are important factors when selecting sorbent materials. As noted in earlier works[1,2,3,7], crush strength differs between dry and humidified sorbents. In order to provide a comprehensive comparison between candidate sorbents, evaluation of bulk and pellet crush strength and attrition characteristics are necessary under both dry and humid conditions. A Humidity Conditioning Test Stand (HCS) was developed to enable conditioning the samples to differing humidities. The HCS supports these efforts to provide insight to the influence of adsorbed water on the structural integrity of sorbents. All of the tests discussed in this paper were performed at approximately -90°C dewpoint and at sorbent conditioned dewpoints of -21°C and -14°C (7.25E-05, 0.7, and 1.38 mmHg inlet vapor pressure, respectively). Sorbent candidates included in this study include zeolites Grace Davison Grades 522 5A and Grade 544 13X, BASF 5A and 13X, and Honeywell UOP APG-III and VSA-10. Also tested is a sorbent currently used in ISS CDRA, Allied Signal Research and Technology ASRT 2005 5A zeolite, and a previous version, ASRT 1995, for comparison. These tests continue the investigations begun in References 1 and 2. Table 1 lists the sorbents selected for test.

Name	Manufacturer	Shape	Size	Type
ASRT 2005 5A	Allied Signal Research and Technology	Cylindrical	Varies	Zeolite
ASRT 1995	Allied Signal Research and Technology	Cylindrical	Varies	Zeolite
Grade 544 13X 10A	Grace Davison	Bead	8x12	Zeolite
Grade 522 5A	Grace Davison	Bead	8x12	Zeolite
BASF 13X	BASF	Bead	8x12	Zeolite
BASF 5A	BASF	Bead	8x12	Zeolite
APG-III	Honeywell UOP	Bead	8x12	Zeolite
VSA-10	Honeywell UOP	Bead	8x12	LiX

Table 1. Sorbent Selection

II. Sorbent Humidity Conditioning

A Humidity Conditioning Test Stand (HCS) was developed to humidify sorbent samples at the required dew point for testing. The schematic for the test stand is shown in Figure A1 in the Appendix. A dry N_2 gas and a mixture of water vapor and N_2 gas are combined to produce a humid gas flow at the specified dew point prior to entering the process. The mixed gas flow enters the inlet dew point sensor and by-passes the sample canisters, exiting through an outlet dewpoint sensor. Once the inlet dew point sensor reaches the desired dew point, flow is redirected through the sample canisters. When the outlet dew point is equal to the inlet dew point, conditioning is complete. Typical operation of the HCS ranges from -21°C to 10°C, and typical conditioning duration requires approximately 24 hours at -14°C and 48 hours at -21°C.

III. Sorbent Structural Stability screening

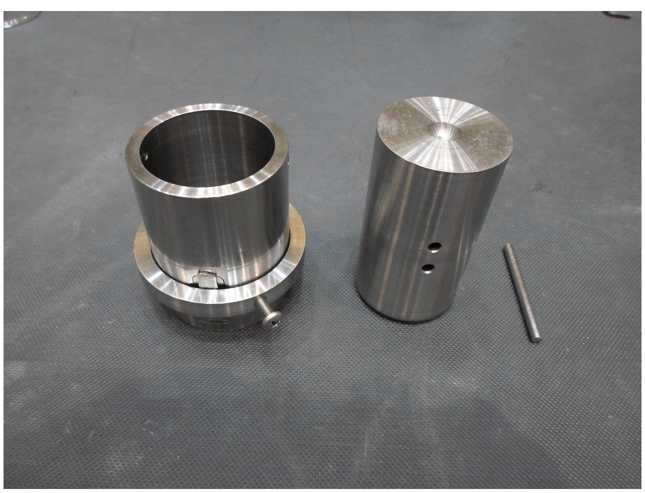
A. Bulk Crush Testing

The bulk crush strength test outlined in ASTM Standard D7084-04, Standard Test Method for Determination of Bulk Crush Strength of Catalysts and Catalyst Carriers (2009), provides a method of evaluating the bulk crush strength of a bed of sorbent to determine the ability of the sorbent material to maintain its physical integrity. The bulk crush test differs from the pellet crush strength by better representing how a load applied to a packed bed can damage the sorbent material. Bulk crush testing of ASRT 1995 and 2005, Grace Davison Grades 522 5A and Grade 544 13X, BASF 5A and 13X, and UOP APG-III and VSA-10 were performed in accordance with the standard, with each sorbent conditioned at -90°C (dry), -21°C, and -14°C dewpoints.

1. Experimental

A Bulk Crush Test Cell was built as per the ASTM Standard, shown in Figure 2. The amount of each sorbent required to fill the test cell was determined pre-test, according to the Standard. Each sorbent tested was activated according to ES62-TCP-SORB-14-001, Test and Checkout Procedure for Sorbent Activation, transferred to a nitrogen-purged glovebox, and the required mass for testing was weighed from the sample. If required for a humidity-conditioned test, the sorbent was conditioned on the Humidity Conditioning Test stand (HCT) to the desired dewpoint and returned to the glovebox. Inside the glovebox, the test cell was packed with the sorbent sample using a snowstorm apparatus. The snowstorm is a cylinder with a mesh of fine wire across the opening that fits in the opening of the test fixture. The wire mesh helps to efficiently distribute the pellets as they are poured into the cell. The use of a snowstorm packing apparatus is a modification to the standard and was used to increase the density of material in the packed cell and to better simulate a bed that was packed using the snowstorm packing method typically used in beds that are prepared for life support processes. The test cell was subjected to various pre-determined crush loads for 30 seconds by MFSC's Mechanical Test Facility's (MTF) Instron 5569 electro-mechanical test frame. The sample was sieved to separate the dust from the remaining pellets. To increase the accuracy of the results, as well as to reduce the impact of the humid environment present at Marshall Space Flight Center, and insure repeatability, the pellets were re-activated using ES62-TCP-SORB-14-001 for the bulk material. The fines were dried by a Quantachrome MasterPrep vacuum degasser. The dry fines were weighed and the dry percent fines calculated.

As per the Standard, three runs were done to produce fines $< 1\%$, and three to produce $> 1\%$ fines. The data points were fitted to a straight line and the fit was used to determine the crush load for 1% fines.



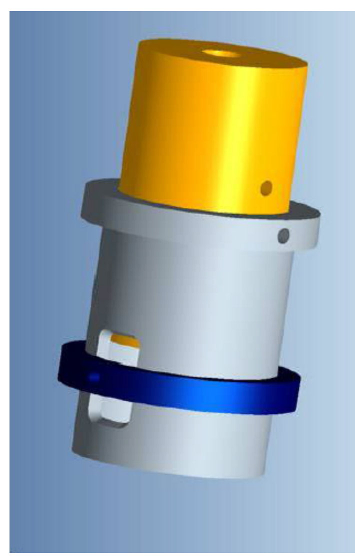


Figure 2. Bulk Crush Strength Test Fixture

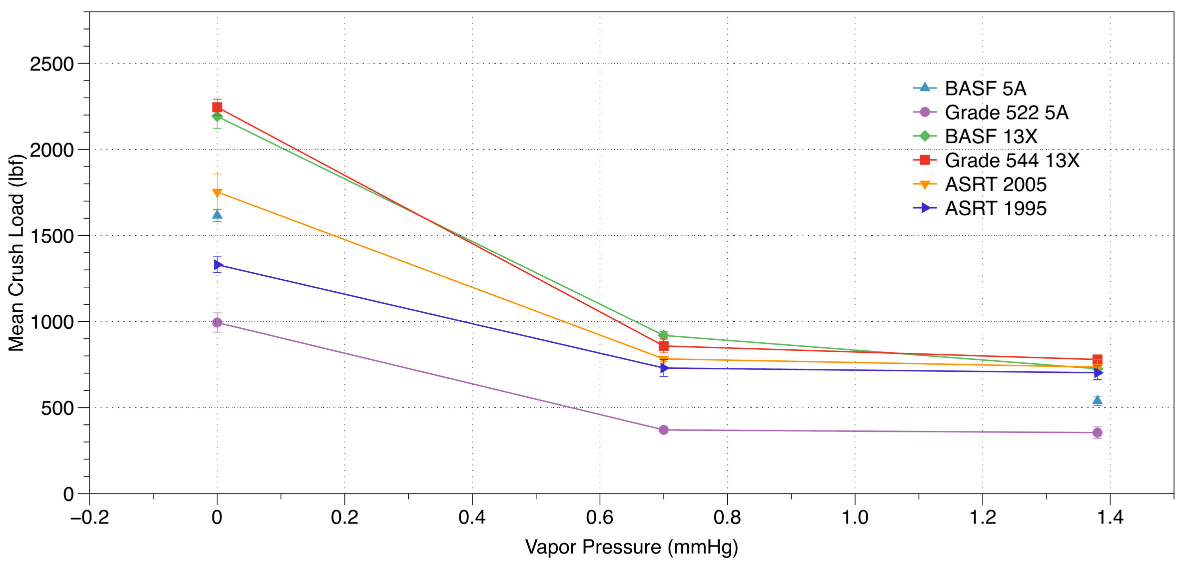
2. Results and discussion

Table 2 shows the crush force, in lbf, required to produce 1% fines for the sorbents tested at each dewpoint. Data for BASF 5A are available only for -90°C and -14°C as yet. APG-III and VSA-10 have not yet been tested. Figure 6 plots the results. The two 13X sorbents show greater crush resistance than all other sorbents when dry, and are comparable to each other. All sorbents, except for the 522, which shows the most degradation, show similar degradation when exposed to moisture.

		Grade 522 5A	Grade 544 13X	BASF 13X	BASF 5A	ASRT 2005	ASRT 1995	APG-III	VSA-10
Dewpoint	Vapor Pressure, mmHg	Crush Load, lbf							
-90C	7.25E-05	994.4	2245.3	2192.6	1616.8	1752.9	1330.2		
-21C	0.7	370.5	858.3	919.4		783.0	730.2		
-14C	1.38	354.5	779.5	725.5	538.8	735.4	702.6		

Table 2. Crush Force for 1% Fines

Figure 6. Bulk Crush Load for 1% Fines vs. Vapor Pressure



B. Single Pellet Crush Testing

1. Experimental

The Marshall Space Flight Center's MTF Instron 5569 electro-mechanical test frame was used to perform single pellet crush testing of various sorbent materials to gain information regarding the ability of a material to retain physical integrity during use. Tests were performed on pellet samples conditioned at all three dewpoints used in Bulk Crush and Attrition tests. This testing was performed in accordance with the ASTM standard D4179-11, Standard Test Method for Single Pellet Crush Strength of Formed Catalysts and Catalyst Carriers and, in modified form, D6175-03, Standard Test Method for Radial Crush Strength of Extruded Catalyst and Catalyst Carrier Particles. D6175-03 calls for reporting the crush force per unit length of an extruded sample, but for these tests, the sample length was not taken into account since in a packed sorbent bed the sizes of the extruded sorbents vary widely. It was assumed that the average crush strength measured by the testing of various sized pellets will correlate with bulk crush behavior.

The test apparatus and procedure is described in greater detail in Ref. 2 and shown schematically in Figure 7. One enhancement to the system is the addition of a small environmental control system that allows the sorbents to be stored in a humidity-controlled container before and during crush testing. The system consists of a dry nitrogen source that flows nitrogen directly through the container to maintain dryness of the sorbents, or through a dewpoint generator set to control the container dewpoint to the same as the conditioned sorbent. This insures that the sorbents remain at the proper conditioning, providing more accurate results. The design of the system is shown in Figure 8. In addition, in order to reduce variability due to additional adsorbed moisture, the following steps are taken at the MTF for testing of all samples:

1) Exposure of a pellet to the room air is limited to a maximum of one minute.
2) The platen is heated to 165 °F during testing.
3) A dry (Missile Grade) air purge is directed across the platen and pellet during testing.

Individual pellets from a representative sample of fifty pellets are crushed one at a time between two flat platens. Video capture was used to establish a dusting load criteria and a catastrophic event criteria for each sorbent. A load/displacement curve was generated for each test and the dusting load and the maximum load of the test was recorded. All dusting loads and maximum loads for the sample were averaged. To insure that the maximum loads being recorded were at catastrophic failure and not at points of limited fracturing, video confirmation was obtained for several test samples.

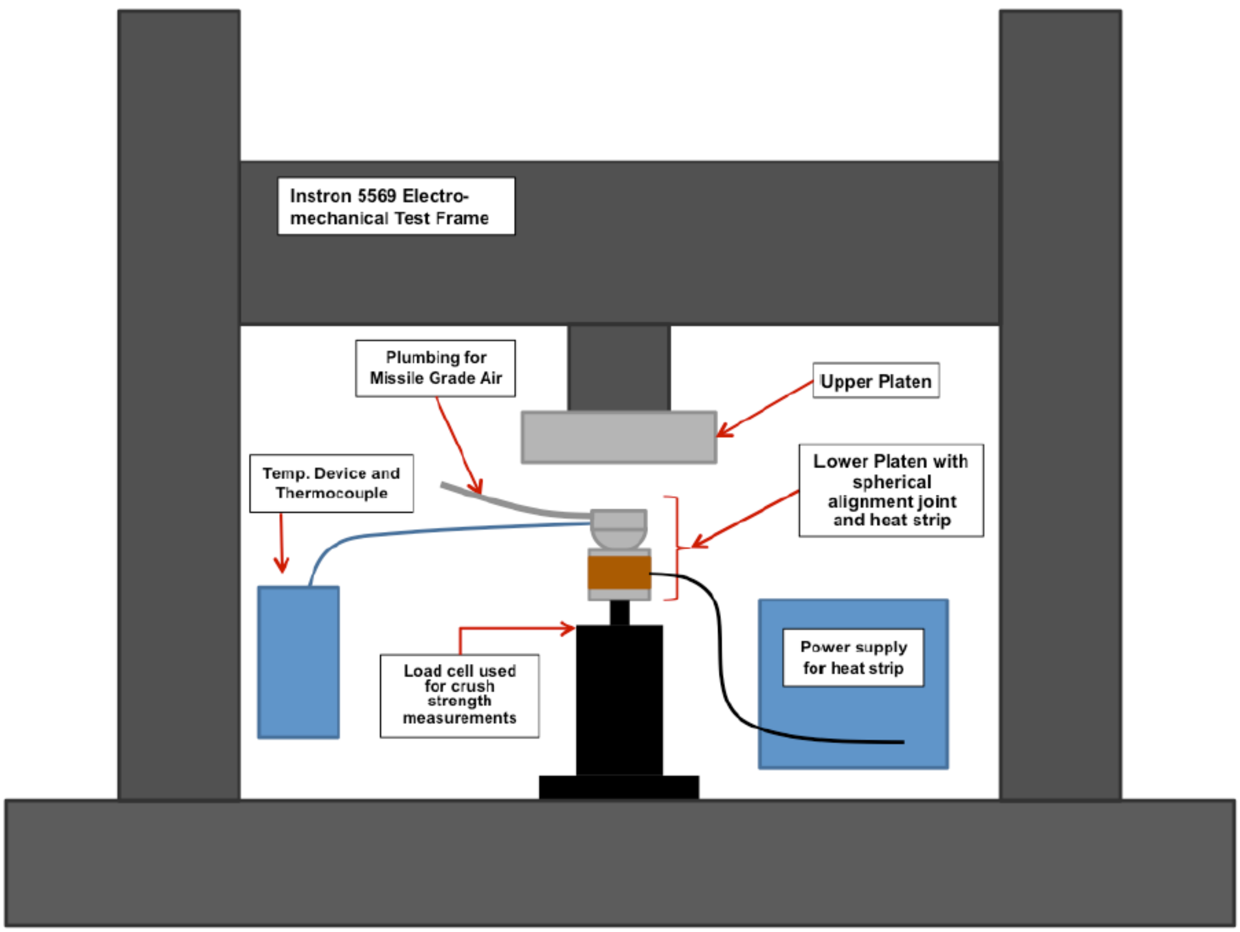


Figure 7. Apparatus for Pellet Crush Strength Testing

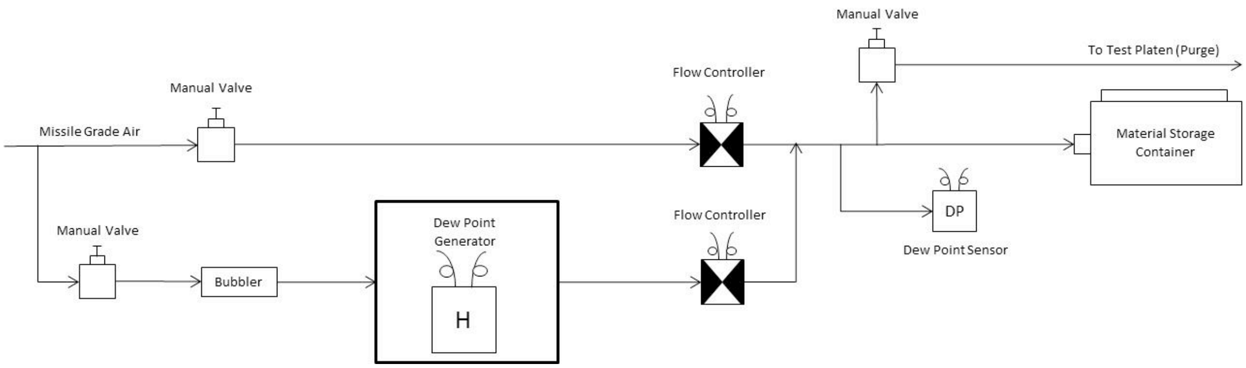


Figure 8. Schematic of MTF test stand to maintain sorbent material conditioning for humid single pellet crush testing.

Table 3 lists the average pellet crush data for sorbents tested to date. Figure 9 plots the results.

Table 3. Pellet Crush Results

	Mean Catastrophic Load			Coefficient of Variation			Mean Dust Load			% Sample Dusted		
Humidity Level, C	-90	-21	-14	-90	-21	-14	-90	-21	-14	-90	-21	-14
Vapor Pressure, mmHg	7.25E-05	0.70	1.38	7.25E-05	0.70	1.38	7.25E-05	0.70	1.38	7.25E-05	0.70	1.38
ASRT 2005	10.2	5.16	5.04	37.73	34.32	32.37	5.94	3.18	3.39	27.33	38.00	38.67
ASRT 1995	13.23	6.46	6.45	37.29	31.74	40.51	-	3.42	3.15	-	49.33	45.33
Grade 544 13X	9.76			15.88								
Grade 522 5A	5.75	2.80	2.84	17.70	19.51	19.24	3.64	1.62	1.96	24	24.67	36
BASF 13X	8.44			18.47								
BASF 5A	7.4			19.51								
APG-III	6.54			19.38			4.95			5.33		
VSA-10	2.92			23.01			2			8.67		

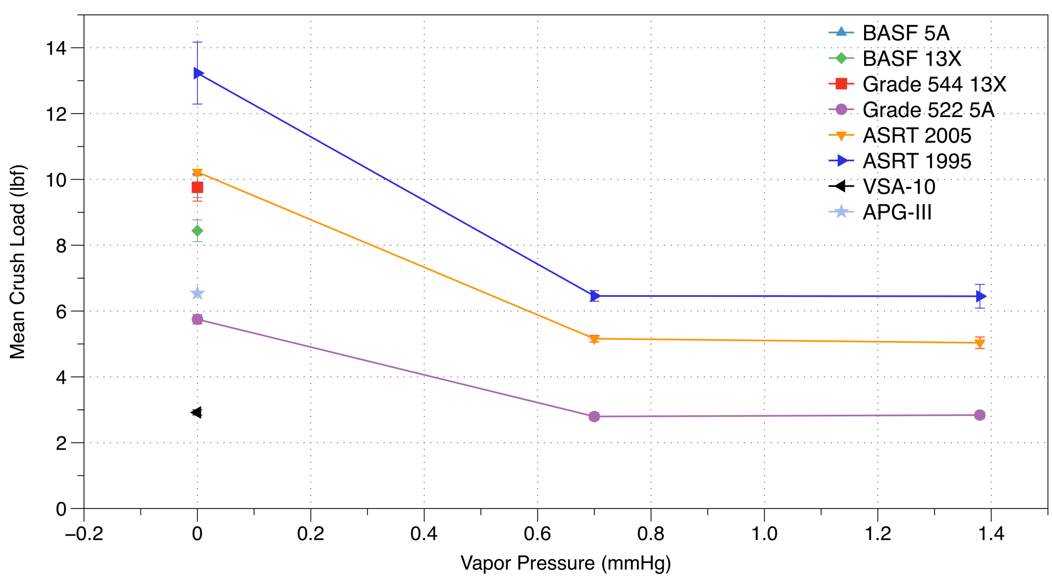


Figure 9. Single Pellet Crush Loads vs. Vapor Pressure

2. Results and discussion

Figure 9 shows the results of single pellet crush tests on the candidate sorbents. ASRT 1995, 2005 and Grade 522 5A are the only sorbents fully tested as yet. ASRT 1995 performed better at all conditions than all sorbents tested. The others have only been partially tested dry as yet, and no conditioned tests have yet been done. These incomplete tests show the two 13X sorbents and the BASF 5A falling close to ASRT 2005. Grade 522, VSA-10 and APG-III show less resistance to crushing. There is a larger variation in crush loads for the ASRTs, certainly due to the fact of it's cylindrical shape, compared to the spherical shape of the other sorbents. The ASRTs also had a higher dusting characteristic than the others. The Mean Dust Load reported is the crush force at which dusting is first seen; there is no quantitate way to measure the actual amount of dust produced.

C. Attrition Testing

Attrition testing provides valuable information about a sorbent's propensity to produce dust which provide additional criteria to consider in sorbent selection for long-term missions. The attrition test method is based on ASTM D4058–96, Standard Test Method for Attrition and Abrasion of Catalysts and Catalyst Carriers.

1. Experimental

As with Bulk and Pellet Crush tests, a sample of sorbent was activated according to ES62-TCP-SORB-14-001, Test and Checkout Procedure for Sorbent Activation, and a measured amount of activated sorbent, approximately 100 grams, was gently poured into a Materials Technology RoTab-AS abrasion test device, shown in Figure 10. The device was set to rotate 1800 cycles at one cycle per second. The resulting pellets and dust were separated through sieving and the dust re-activated in the Quantachrome MasterPrep vacuum degasser and weighed. If a humidity conditioned test was to be performed, the sorbent was conditioned on the Humidity Conditioning Test stand (HCT) before loading in the attrition device. In all tests, the attrition device drum and the activated/conditioned sorbent were placed in a dry glovebox for sorbent loading.

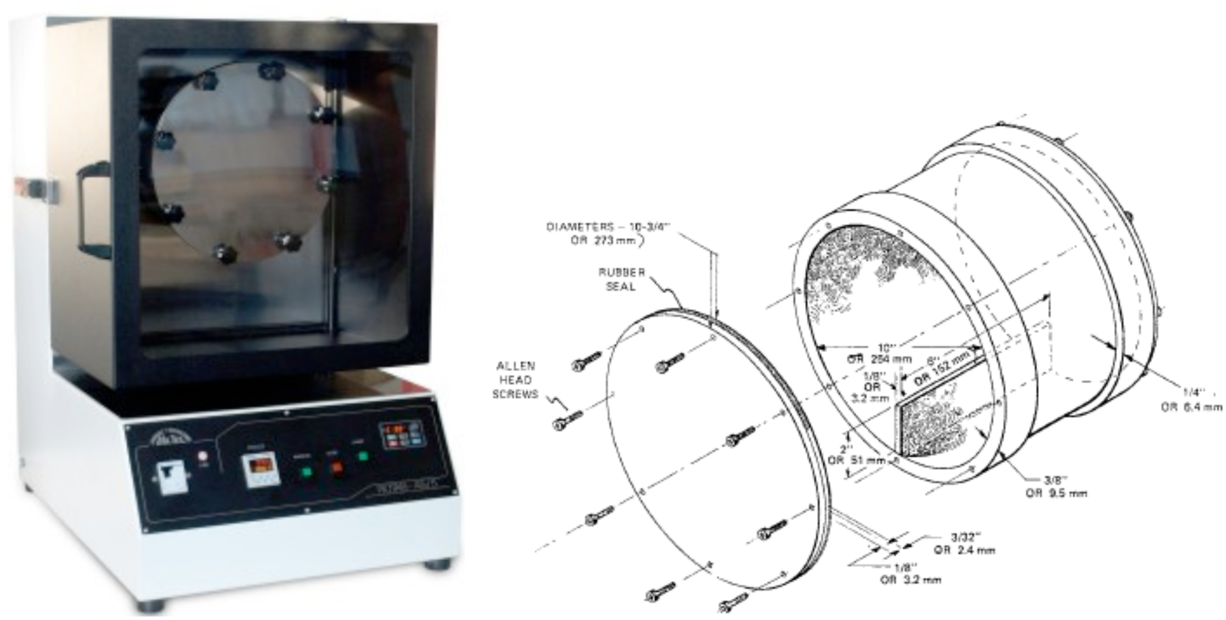


Figure 10. Material Technology Ro-Tab-AS Apparatus

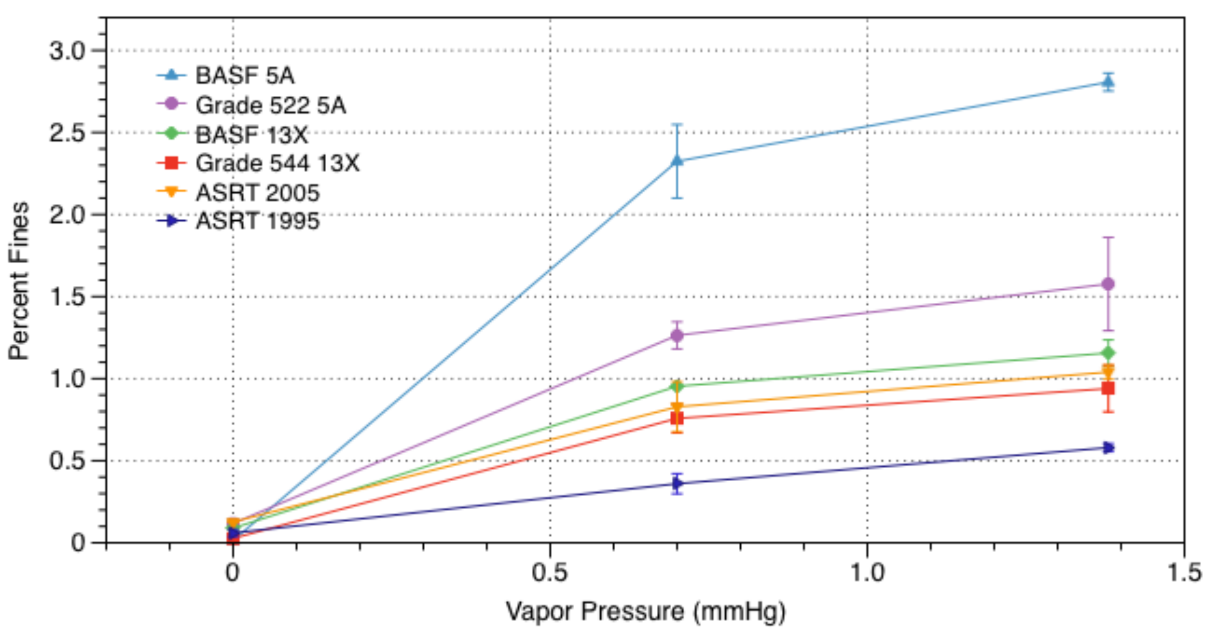
2. Results and discussion

Table 4 tabulates the percent fines produced by the attrition tests. It can be seen that ASRT 1995 produced the fewest fines, thus showing the greatest resistance to attrition, at all dewpoints, followed by Grade 544 13X, ASRT 2005, BASF 13X and Grade 522 5A, with BASF 5A producing the most fines. Figure 11 plots the results.

Table 4. Attrition Test Percent Fines

	% Fines			Mean % Fines		
Humidity Level, C Vapor Pressure, mmHg	-90C 7.25E-05	-21C 0.7	-14C 1.38	-90C 7.25E-05	-21C 0.7	-14C 1.38
Grade 522 5A	0.144 0.121 0.088	1.187 1.352 1.252	1.857 1.289 1.584	0.118	1.264	1.577
Grade 544 13X	0.024 0.027 0.029	0.860 0.683 0.730	0.843 1.126 0.85	0.027	0.758	0.94
BASF 13X	0.093 0.092 0.083	0.968 0.889 1.004	1.060 1.22 1.188	0.089	0.954	1.156
BASF 5A	0.010 0.010 0.024	2.152 2.600 2.220	2.874 2.782 2.765	0.015	2.324	2.807
ASRT 2005	0.125 0.126 0.130	0.894 0.643 0.948	1.002 1.089 1.028	0.13	0.83	1.04
ASRT 1995	0.059 0.034 0.077	0.365 0.423 0.3	0.583 0.599 0.548	0.057	0.362	0.577
APG-III						
VSA-10						

Figure 11. Average Attrition Percent Fines vs. Vapor Pressure



IV. Conclusion

The need for atmosphere revitalization systems to employ sorbents that perform satisfactorily even if exposed to some level of water vapor has been demonstrated by the issue of moisture exposure to the ISS CDRA. This paper described tests performed or to be performed on sorbents ASRT 2005 and 1995, Grace Davison Grades 522 5A and Grade 544 13X, BASF 5A and 13X, and UOP APG-III and VSA-10, each conditioned at three humidity levels (-90°C, -21°C, and -14°C), and their performance compared. These tests, along with adsorption capacity tests[8], contamination sensitivity, process characterization testing and simulation development[9], will be used as input to provide critical data to support sorbent selection for use in optimized carbon dioxide removal systems for atmosphere revitalization systems used in future exploration vehicles.

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V. Appendix

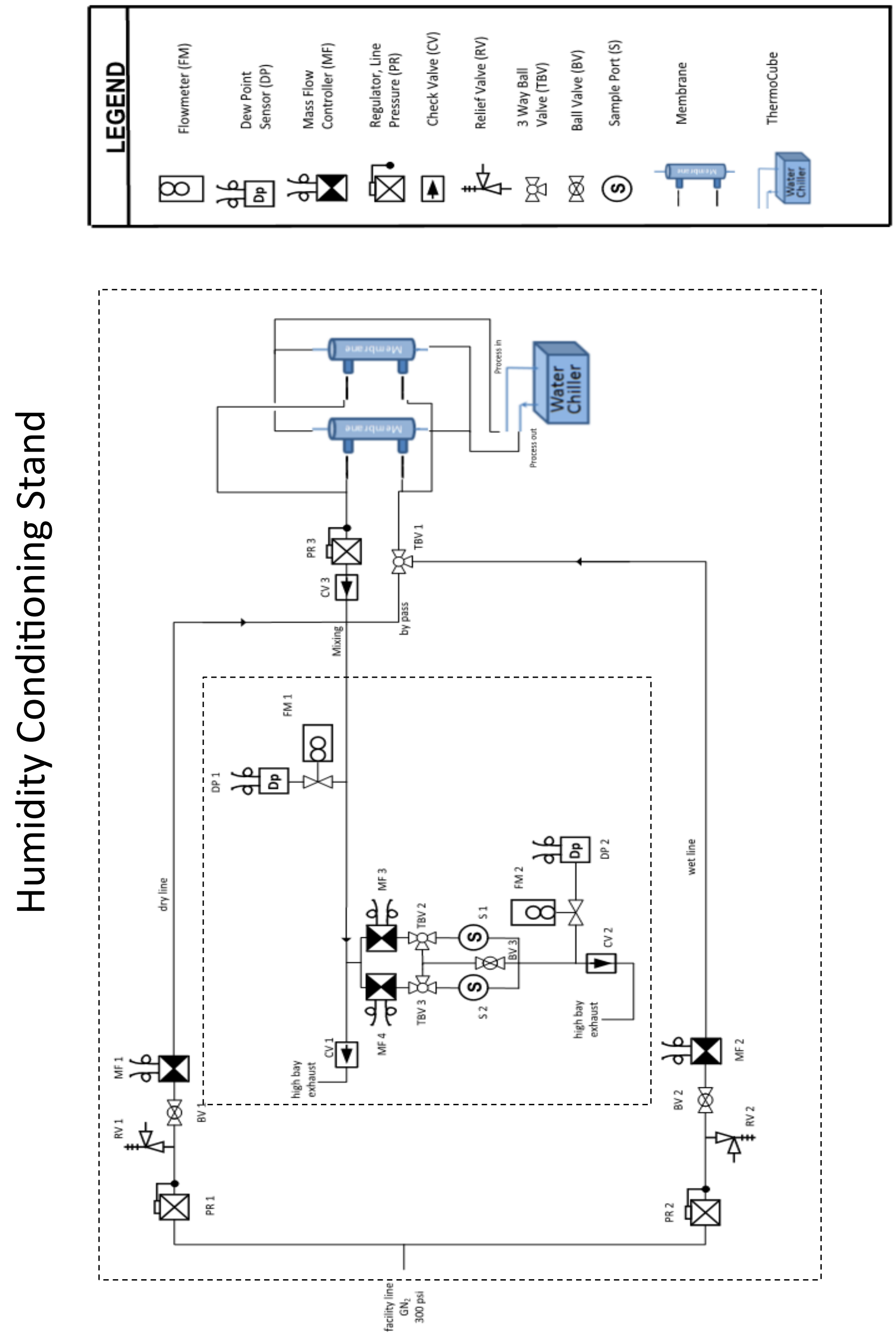

Figure A1. Humidity Conditioning Stand