

Zeolite Degradation: An Investigation of CO₂ Capacity Loss of 13x Sorbent

Roger Huang¹

KBR Wyle, NASA Ames Research Center, Moffett Field, CA 94035

Tra-My Justine Richardson²

Logyx LLC, NASA Ames Research Center, Moffett Field, CA 94035

Grace Belancik,³ Darrell Jan,⁴ and John Hogan⁵
NASA Ames Research Center, Moffett Field, CA 94035

and

James Knox⁶

NASA Marshall Space Flight Center, Huntsville, AL 35812

System testing of the Carbon Dioxide Removal and Compression System (CRCS) has revealed that sufficient CO₂ removal capability was not achieved with the designed system. Subsystem component analysis of the zeolite bed revealed that the sorbent material suffered significant degradation and CO₂ loading capacity loss. In an effort to find the root cause of this degradation, various factors were investigated to try to reproduce the observed performance loss. These factors included contamination by vacuum pump oil, o-ring vacuum grease, loading/unloading procedures, and operations. This paper details the experiments that were performed and their results. From the experimentation performed, a definitive cause of failure could not be determined, and a more detailed zeolite failure analysis will need to be conducted.

Nomenclature

AES	=	Advanced Exploration Systems
ARC	=	Ames Research Center
CDRA	=	Carbon Dioxide Removal Assembly
CRCS	=	Carbon Dioxide Removal and Compression System
CO ₂	=	Carbon Dioxide
ISS	=	International Space Station
MSFC	=	Marshall Space Flight Center
TGA	=	Thermogravimetric Analysis
TSAC	=	Temperature Swing Adsorption and Compression
PSA	=	Pressure Swing Adsorption

¹ Engineer, KBR Wyle, Bioengineering Branch, ARC, CA 94035

² Research Engineer/Scientist, Logyx LLC, Bioengineering Branch, ARC, CA 94035

³ Physical Scientist, Bioengineering Branch, ARC, CA 94035

⁴ Physical Scientist, Bioengineering Branch, ARC, CA 94035

⁵ Physical Scientist, Bioengineering Branch, ARC, CA 94035

⁶ CO₂ Removal Lead Engineer, ECLSS Development and Test Branch, MSFC, AL 35812

I. Introduction

Current CO₂ capture technologies aboard the International Space Station (ISS) consists of a 4-bed molecular sieve system in which two beds remove humidity and CO₂ in series while two opposing humidity and CO₂ removal beds regenerate.¹ The released CO₂ from the regeneration bed is then pumped via mechanical compressor into an accumulator and storage tank for usage in oxygen recovery.¹ In an effort to reduce system complexity and address the problems of mechanical compression, NASA's Advanced Exploration Systems (AES) division funded a project at NASA Ames Research Center to develop the CO₂ Removal and Compression System (CRCS). The goal of the CRCS was to replace the accumulator, compressor, and storage functions utilizing Temperature Swing Adsorption and Compression (TSAC) technology previously developed at Ames.^{2,3} The CRCS was focused on CO₂ removal and compression without the additional burden of humidity removal – as such, the architecture consisted of a 4-bed sorbent system in which two Stage 1 beds remove CO₂ from dry cabin simulated air loaded with 2600ppm CO₂ and two Stage 2 beds store concentrated CO₂ that has been captured from Stage 1.³ The sorbent used in Stage 1 was Grace Davison Grade 544 13X spherical form factor, while the sorbent in Stage 2 was UOP 5A zeolite granular form factor. For more information about the CRCS and its operation, see Richardson et al (2015).⁴ This paper will explore the issues observed during integrated system testing of the CRCS in terms of Stage 1 sorbent failure.

II. Background

Upon testing of the CRCS, it was found that the Stage 1 mechanical valve seals were prone to failure due to the high operative temperature (280°C) and the nature of their design. Over the period of 8 months in FY2016, the CRCS was disassembled 3 times due to mechanical valve seal failures; each time the sorbent was removed, baked out in an external oven, and reloaded into the CRCS. Data collected with the fully integrated system showed that CO₂ breakthrough occurred much faster than expected in the Stage 1 beds. At first, it was suspected that the beds were not properly baked out during initial regeneration, so measures were taken to improve the initial bakeout and loading procedure. Custom made bakeout canisters (see Figure 1) were manufactured and sorbent was regenerated in a large oven held at 350°C with N₂ purge gas for over 20 hours. In an attempt to load the sorbent into the CRCS



Figure 1: Custom CRCS Bakeout Canisters. These canisters were designed to aid in activating the CRCS sorbent material.

units as cleanly as possible, purge N₂ gas was flowed through the empty Stage 1 canisters before and during the loading of sorbent (Figure 2). The canisters were closed and sealed as quickly as possible with the combined experiences of multiple repetitions and improvements to the take-down and reload of the CRCS canisters, and in-line integrated bakeout was performed with the regeneration heater coils. Even with the extensive loading procedure improvements, CO₂ breakthrough still occurred faster than expected. At this point, an adsorption capacity isothermal analysis was run on the Stage 1 sorbent and revealed that the sorbent was severely degraded and could only adsorb at 25% of the capacity of fresh sorbent at 2 Torr ppCO₂ (approximately 0.3 kPa ppCO₂, or 2600 ppmCO₂ at 1 atm). This degraded performance was repeatable between four samples drawn from different locations inside the Stage 1 bed. The degradation seemed to be pervasive throughout the Stage 1 beds.

Other potential causes of degradation were then theorized. Contamination sources such as vacuum pump oil, vacuum grease, process flow source air, and even the physical process of unloading and loading the sorbent were considered. In order to perform the Airsave function in the CRCS, an oil-based vacuum roughing pump was used, and it was suspected that during initial functional testing of valves and plumbing, oil may have been allowed to come into contact with the Stage 1 sorbent material. During the first unloading of a tested bed, minor staining was observed on the high-definition mesh screen under the vacuum port, suggesting liquid contamination. Also, two different types of vacuum grease were used to seal the o-rings between the Stage 1 and Stage 2 chambers, as well as the o-rings in the dynamic Stage 1 valves. It was suspected that the heating during regeneration may have caused vacuum grease vapors to contaminate the sorbent, because the Stage 1 bed is exposed to vacuum during Airsave.



Figure 2. CRCS sorbent loading process. Bakeout canisters hoisted up by crane and manually tilted to pour sorbent. N₂ gas purge flow through bottom of CRCS and bakeout canister.

Another candidate for contamination was the lab air source that was augmented with k-bottle CO₂ to provide the Stage 1 input flow. This air source was provided by a high output compressor that went through various oil filters, including a Pressure Swing Adsorption (PSA) system, see Figure 3. It was thought that perhaps hydrocarbons had made it through the filtration and contaminated the Stage 1 sorbent. Another potential cause of degradation explored was the CRCS unloading and loading procedure. In order to unload the Stage 1 canisters, sorbent was vacuumed out and captured in a large flask, shown in Figure 4. During this vacuum unloading, it was

observed that the zeolite expelled copious amounts of dust, and it was hypothesized that perhaps the mechanical shock of the unloading procedure somehow could affect the sorbent capacity. It was also a consideration that perhaps the CRCS in-line bakeout was ramped too fast and possibly degraded the sorbent structure. A series of experiments were devised to determine the cause of sorbent failure.

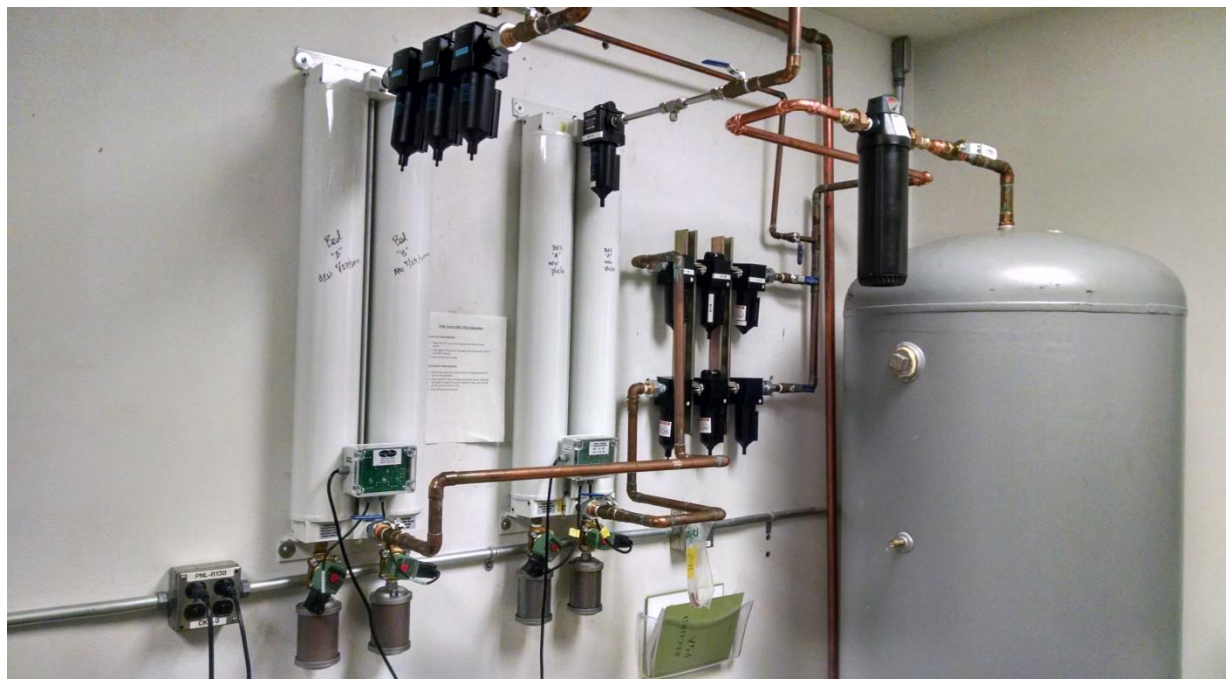


Figure 3: Pressure Swing Adsorption Beds. Twin Towers® pressure swing bed air filtration system provides compressed air to the laboratory.

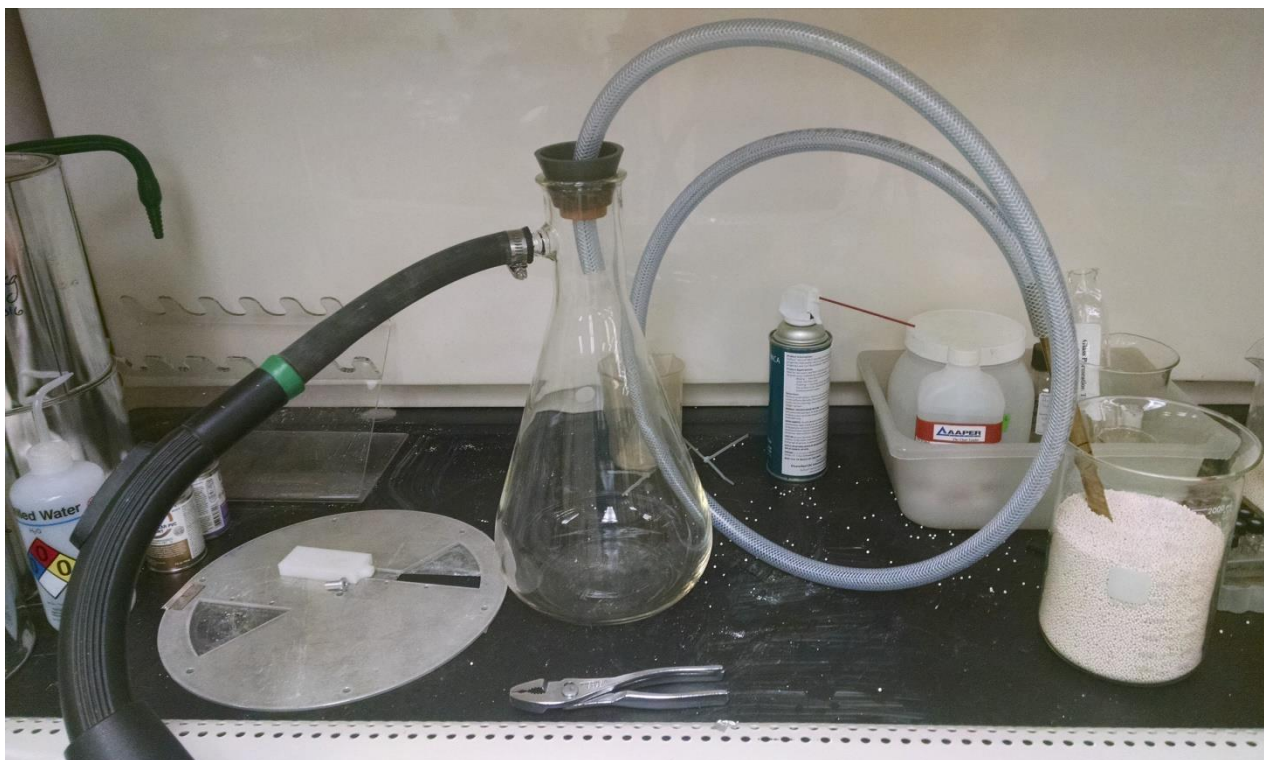


Figure 4: CRCS sorbent unloading system. This flask was used to unload the CRCS Stage 1 and Stage 2 sorbents. The vacuum hose attaches to the flask via the black hose on the left and the hose attached to the top of the flask is used to suck the sorbent out of the CRCS.

III. Experimental Method

In order to quantify the sorbent capacities of the various sorbents used in the CRCS, isotherm adsorption analysis was performed using a Micromeritics ASAP 2020 instrument. The ASAP 2020 operates on a volumetric analysis principle by which the sorbent is inserted into a sample tube which is then placed in an insulated temperature controlled bath for the duration of the analysis. CO₂ is metered into the sample tube to allow adsorption and high accuracy pressure transducers are used to calculate the volume adsorbed at points on a user-defined analysis pressure table. Isotherm curves are generated to show sorbent loading capacity over the prescribed pressure range. The ASAP 2020 has a customizable sorbent activation procedure with heaters that can be set to ramp and hold at desired temperature values. For the purposes of finding the cause of CRCS Stage 1 sorbent failure, 25°C isotherms were generated for all experimental and control cases.

A. Chemical Sorbent Degradation

To test the theories of external contaminants such as vacuum oil and vacuum grease, samples of fresh 13X zeolite were exposed directly to the contaminants in a manner thought to be more severe than would have occurred in the actual CRCS. This exaggeration was meant to amplify the effects of contamination, since it was not known whether or not degradation occurred acutely or over the period of testing (months). In order to apply vacuum oil to the sample, a ½" SS tube sample cell was filled with sorbent and Edwards Ultra Grade 19



Figure 5: Chemical contamination cells. These cells are filled with Stage 1 sorbent and suspected contaminants – Krytox LVP, 240AC, and Edwards Ultra Grade 19 vacuum pump oil.

vacuum pump oil was dripped into it on top of the sorbent. To apply the two vacuum greases, Krytox LVP and 240AC, a cotton swab was used to apply a generous coating of grease to the inside of empty ½” SS tube sample cells and then sorbent was poured in. See Figure 5. To test the theory of PSA hydrocarbon contamination, a ½” SS tube sample cell was filled with sorbent and placed in a constant flow of PSA air for approximately 120 hours. All experimental samples (and control) were then placed in an oven and baked out a 300°C for 12 hours to simulate the in-line bakeout procedure of the CRCS.

B. Physical Sorbent Degradation

In order to test the theory of physical shock affecting the sorbent capacity, approximately 1.5 liters of sorbent was vacuumed into a flask similar to the way the CRCS was unloaded. The sorbent was then poured back into the original beaker and this vacuuming procedure was repeated 10 times, with small samples of sorbent removed for isotherm analysis each time. To test the theory of binder degradation due to heating the sorbent too fast after it has been allowed to adsorb water from the lab, the sorbent was allowed to sit in the lab overnight and then placed into a pre-heated oven to quickly bring it to 300°C (faster than the MSFC recommended heating ramp rate of 3°C/min). This heated sorbent was then vacuumed and allowed to sit in the lab again, with samples removed between heat-vacuum cycles. A test matrix of the samples taken is as follows:

Samples were removed from the large beaker on the “x’s.” The sorbent was first baked out once after allowing lab humidity adsorption and vacuumed and poured back into the beaker 10 times in succession. Then the remaining sorbent was baked out and vacuumed 4 more times. The green highlighted cases denote the samples that were analyzed on the ASAP 2020, and they will be referred to as Vac x1/Bakeout x1, Vac x10/Bakeout x1, and Vac x14/Bakeout x5.

		Vacuums													
		1	2	3	4	5	6	7	8	9	10	11	12	13	14
Bakeouts	1	x	x	x	x	x	x	x	x	x	x				
	2											x			
	3												x		
	4													x	
	5														x

IV. Results and Discussion

C. Chemical Sorbent Degradation

After the LVP, 240AC, and vacuum pump oil contamination cells were baked out at 300°C for 12 hours to simulate the CRCS in-line bakeout process, the pump oil sample showed a visible difference from rest of the samples (Figure 6). The pump oil sample seemed to be much greyer overall, with a few beads showing significant discoloration. The LVP and 240AC exposed samples did not show more discoloration than the control sample. The PSA exposed sample also did not show any visible differences from the Control sample. Upon vacuum activation on the ASAP 2020 at 350°C, the samples showed very interesting developments. Typically the ASAP activated 13X samples develop some light speckling, but the LVP and 240AC contaminated samples showed very pronounced dark speckling (Figure 7). In fact, the sample contaminated with pump oil seemed to show the least change from its pre-activated visible state. All samples followed the same activation procedure: exposure to <10mTorr (1.3 Pa) vacuum, ramp at 3°C/min to 110°C, hold for 5 hours, ramp at 5°C/min to 350°C, hold for 6 hours.

All CO₂ isotherm analysis tests were performed on the ASAP 2020 using the same method and pressure table. Isotherm results are shown in Figure 8. As expected, the chemically contaminated samples (pump oil, LVP, and 240AC) all showed lower adsorption capacity compared to the Control sample. The PSA exposed sample was nearly identical in CO₂ capacity as the Control.

At the 0.3 kPa ppCO₂ loading level, the LVP, 240AC, and pump oil contaminated samples showed about 18%-20% less capacity than the PSA and Control samples. It was also noted that the < 0.1 kPa ranges varied slightly between the three different contaminated samples. This type of fanning was observed in samples that had not been properly activated on the ASAP 2020, and seem to indicate minor pre-loading in the Henry’s Law region of pressure for 13X. In comparison, the PSA and Control isotherms show very agreeable measurements and follow the Henry’s Law slope very closely. Even though the experimentally contaminated samples showed some decreased loading capacity compared to the Control, the level of degradation was not nearly as severe as was observed in the CRCS Stage 1 sample that was taken at the time of loading the CRCS for the final time. The experimentally contaminated

samples showed about ~20% less adsorption capacity at 0.3 kPa, while the CRCS Stage 1 August 2016 load showed ~75% less adsorption capacity. All isotherm analyses were performed three times.



Figure 6: Chemical contamination samples after 12h 300°C bakeout. The pump oil sample shows visible greying, with some of the beads turning very dark in comparison with the LVP and 240AC samples, which did not show significant visible changes from prior to bakeout.

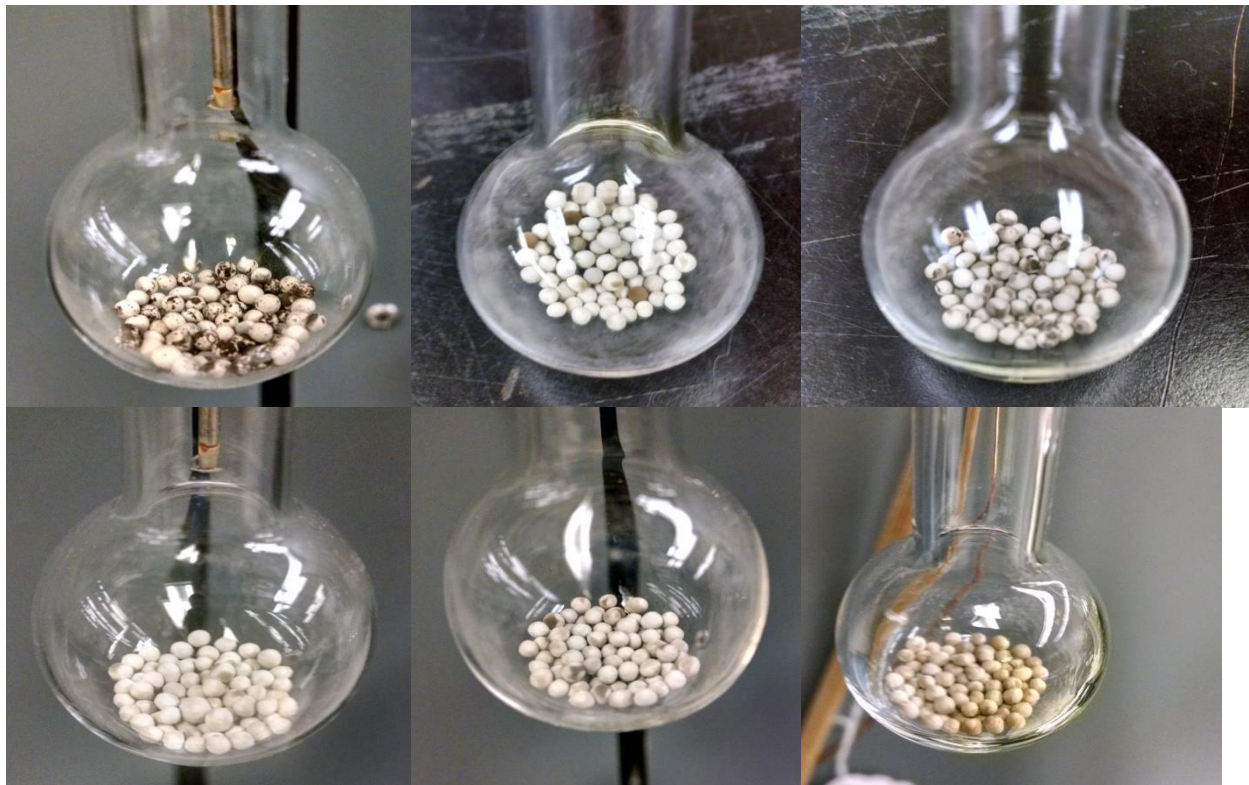
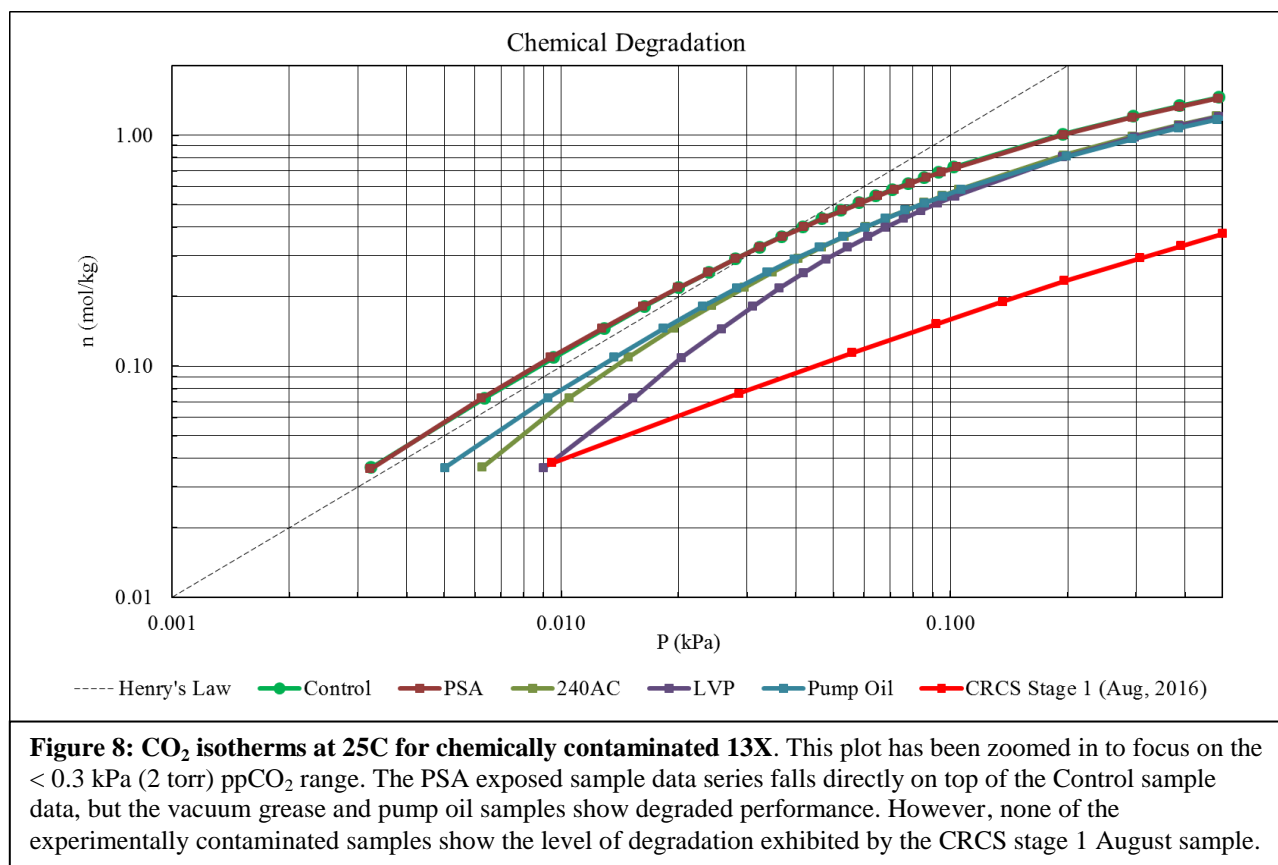


Figure 7: ASAP-activated, chemically contaminated samples. The 240AC and LVP samples developed very dark speckling compared to the Control sample. The PSA sample and the CRCS Stage 1 sample that was loaded in August show very similar speckling that is typical of 13X materials after ASAP activation at 350°C.



D. Physical Sorbent Degradation

Figure 9 shows the results from the vacuum/bakeout test matrix. The three experimental cases all show slightly lower capacity in comparison with the Control sample, but again, not enough to warrant a definitive conclusion that explains why the CRCS Stage 1 sorbent exhibited such severe degradation. The mechanically degraded samples were prepared on the ASAP 202 in the same way as the chemically degraded samples and the Control sample, and all analyses were repeated three times.

E. Overall Results Discussion

In all of the experimental cases studied, none of them produced the clear cause of failure for the CRCS Stage 1 sorbent. The chemical contaminants were initially thought to be the most likely candidates for degraded CO₂ adsorption capacity, but the visual cues and isotherm results show that none of these contaminants were the cause of sorbent degradation. In all three of these experimental cases, the contaminant exposure was simulated at a much more severe case than would have been seen in the CRCS during operation – evidenced by the facts that the pump oil contaminated sample was clearly greyed and some beads were very darkly discolored, while the LVP and 240AC contaminated samples displayed much heavier speckling than did the CRCS Stage 1 sorbent after activation on the ASAP 2020. The PSA-exposed sample isotherm clearly



Figure 10. Physical Sorbent Degradation Experiments. The left image was taken during the vacuuming of sorbent from a large beaker into the flask. The zeolite dust coats the inside of the flask, hose, and vacuum line. The right image is a sample removed from the larger volume of sorbent after it has been poured back into a large beaker. Visible chips of sorbent created by the violent nature of the vacuuming process are shown.

showed no degraded performance. The vacuum/bakeout experiment also revealed no conclusive cause of failure. Over the vacuum and bakeout cycles the sorbent dusted and chipped (see Figure 10), but still performed reasonably well in an isotherm analysis.

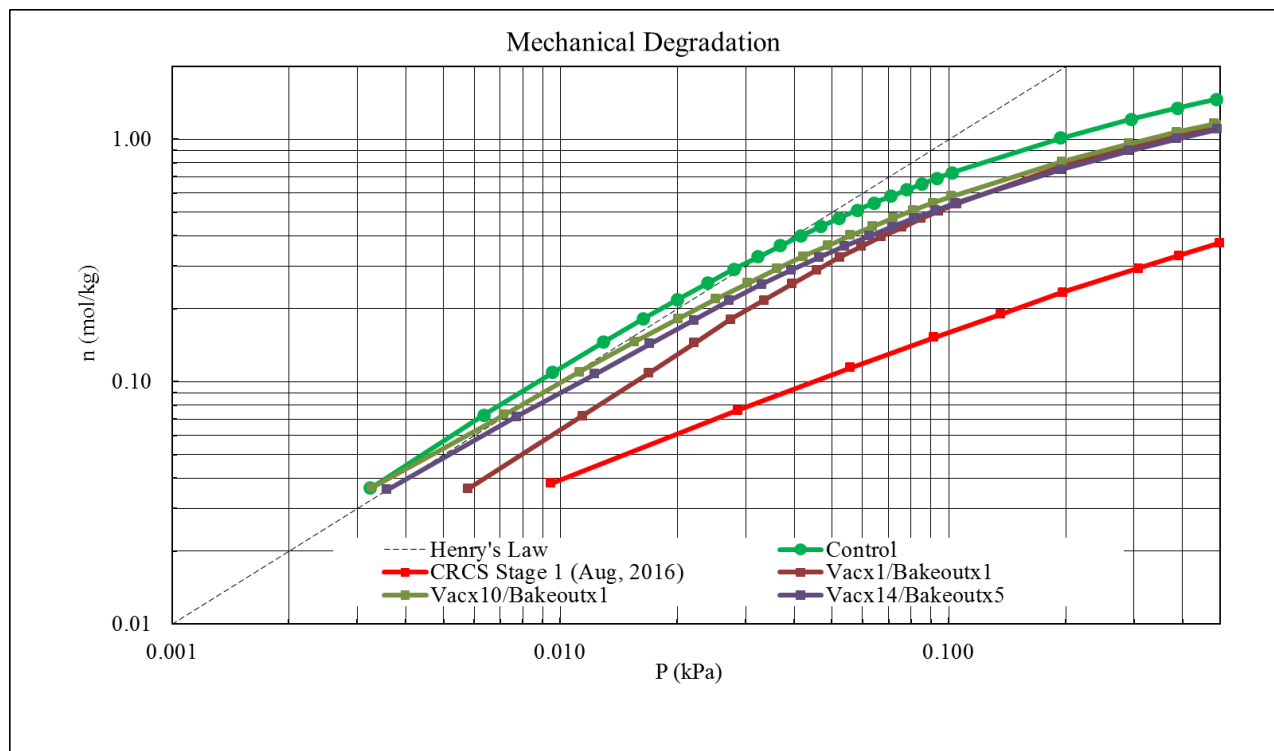


Figure 9: CO₂ isotherms at 25C for Mechanically Degraded 13X. This plot has been zoomed in to focus on the < 0.3 kPa (2 torr) ppCO₂ range. As before, the samples that underwent vacuum and bakeout cycles showed slightly degraded performance compared to the control. However, none of the experimentally degraded samples show the level of capacity loss exhibited by the CRCS stage 1 August sample.

V. Conclusion

Among the various issues that led to the failure of the CRCS Stage 1 to properly capture and deliver CO₂, the breakthrough time for CO₂ at 2600 ppm was one of the most pressing problems. Upon further investigation, it was found that the CO₂ capacity of the sorbent was severely degraded, and the sorbent was performing at 25% of full capacity. Various causes of failure were considered and explored. Chemical contaminants such as vacuum pump oil and vacuum greases were exposed to the sorbent, and the process PSA source air was also evaluated. The PSA exposed sample showed no degradation, and even though the pump oil and vacuum grease contaminated samples showed slightly degraded performance, they were not severe enough to be the cause of failure in the CRCS. The CRCS loading and unloading process was considered as possible sources of sorbent failure due to the high amounts of dusting and sorbent chipping observed. Samples were evaluated at various cycles of vacuum sucking and uncontrolled ramp bake out, but again revealed no conclusive findings. From the tests conducted, it appeared that none of the test cases showed indicative failure at the level that was observed in the CRCS sorbent. A more detailed failure analysis is necessary to find the root cause of the CRCS sorbent degradation. Future analysis will include investigative studies into the sorbent base structure, suspecting that exposing the structure to high amounts of water vapor while at an elevated temperature may be destroying the micropore structure itself.

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