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Investigation of Desiccants and CO_2 Sorbents for Advanced Exploration Systems 2016-2017

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and

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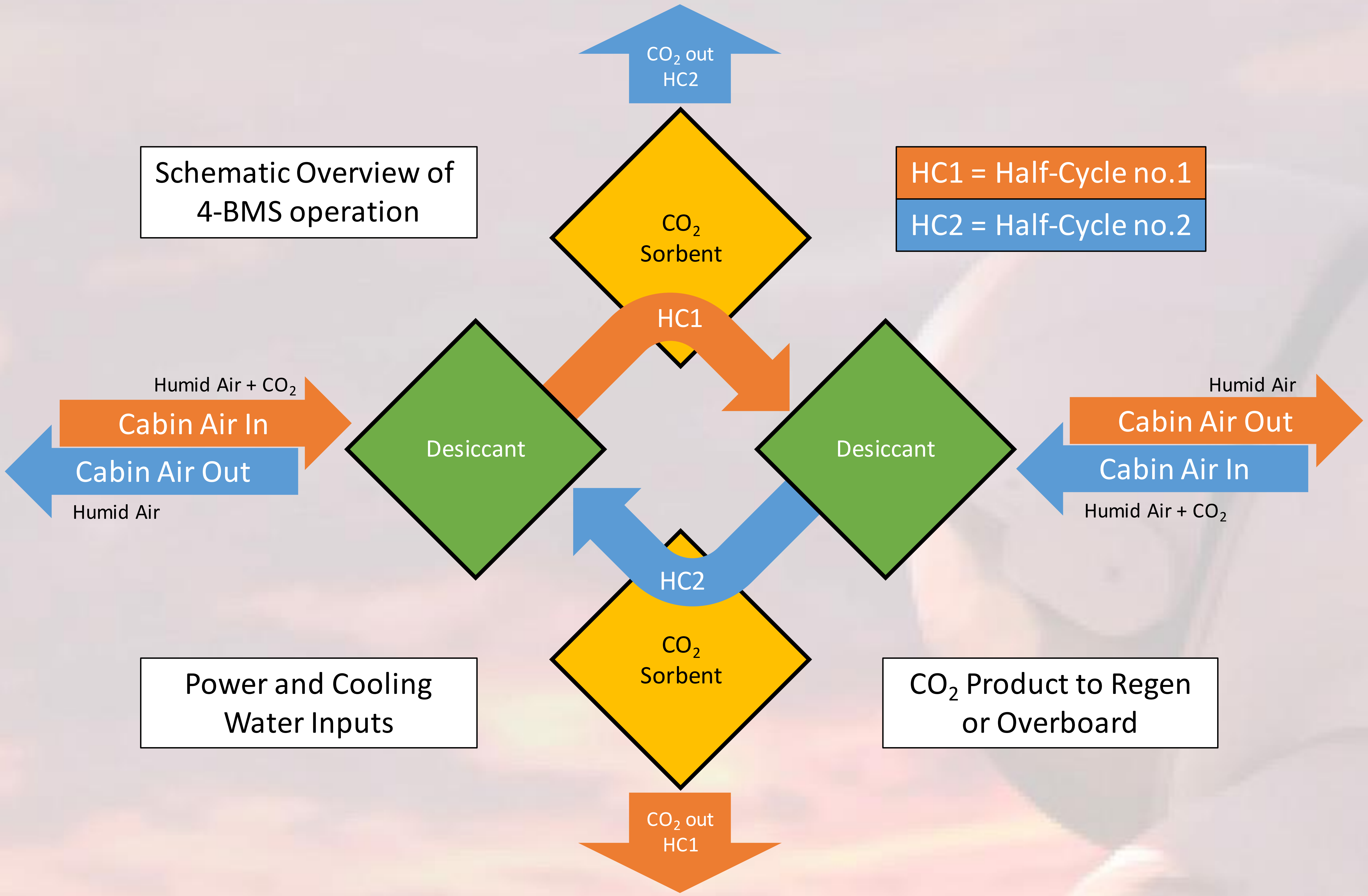
Background – 4BMS



- 4BMS = 4-Bed Molecular Sieve system
  - CDRA is the variant in use on the ISS
    - Concerns over performance and reliability
- The present CO_2 sorbent material can no longer be manufactured
- Final selection criteria:
  - Remove 4 kg CO_2/day at 2 torr
  - No shutdowns due to dust
  - Integrated “closed-loop” operation

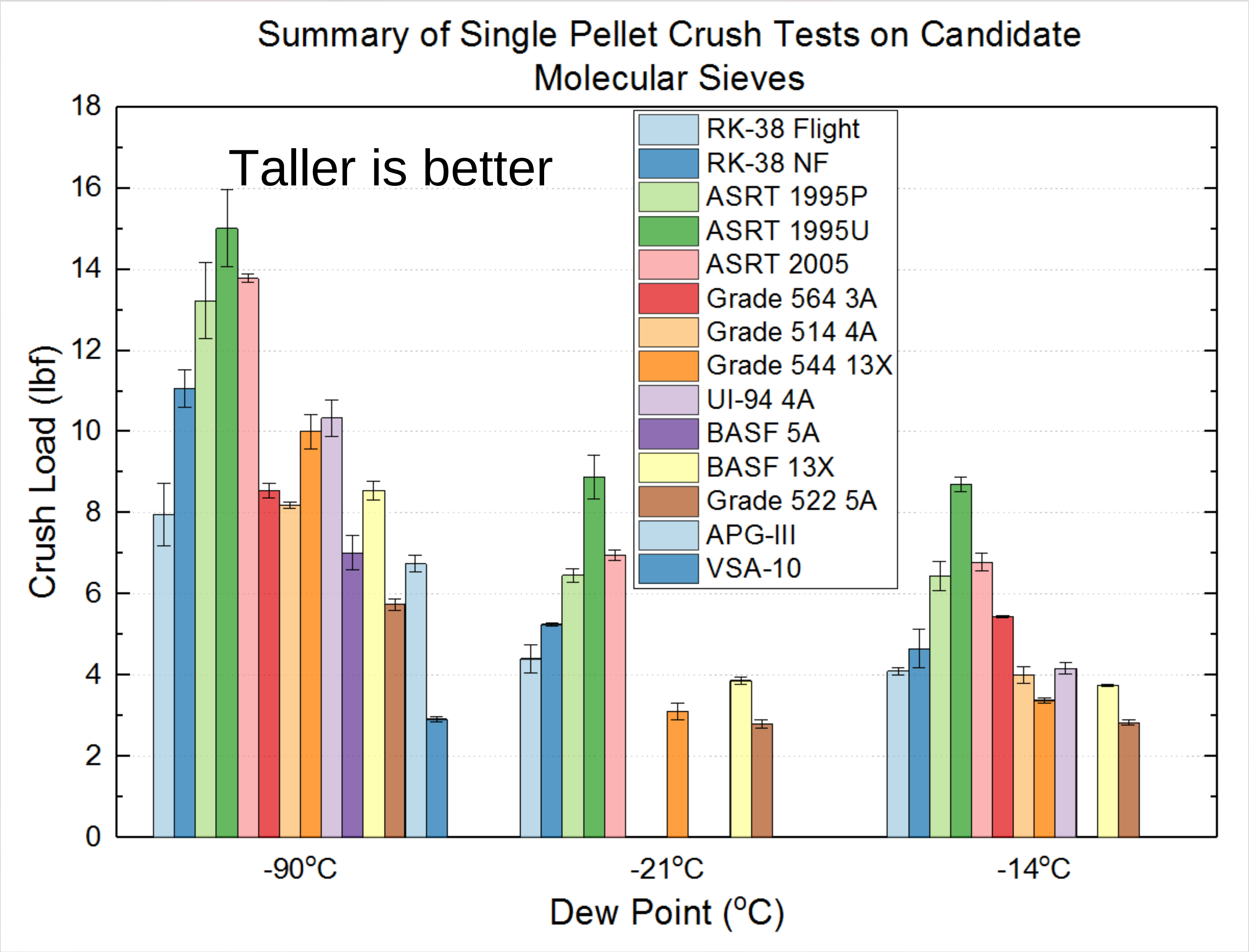
Sorbent Selection and Characterization

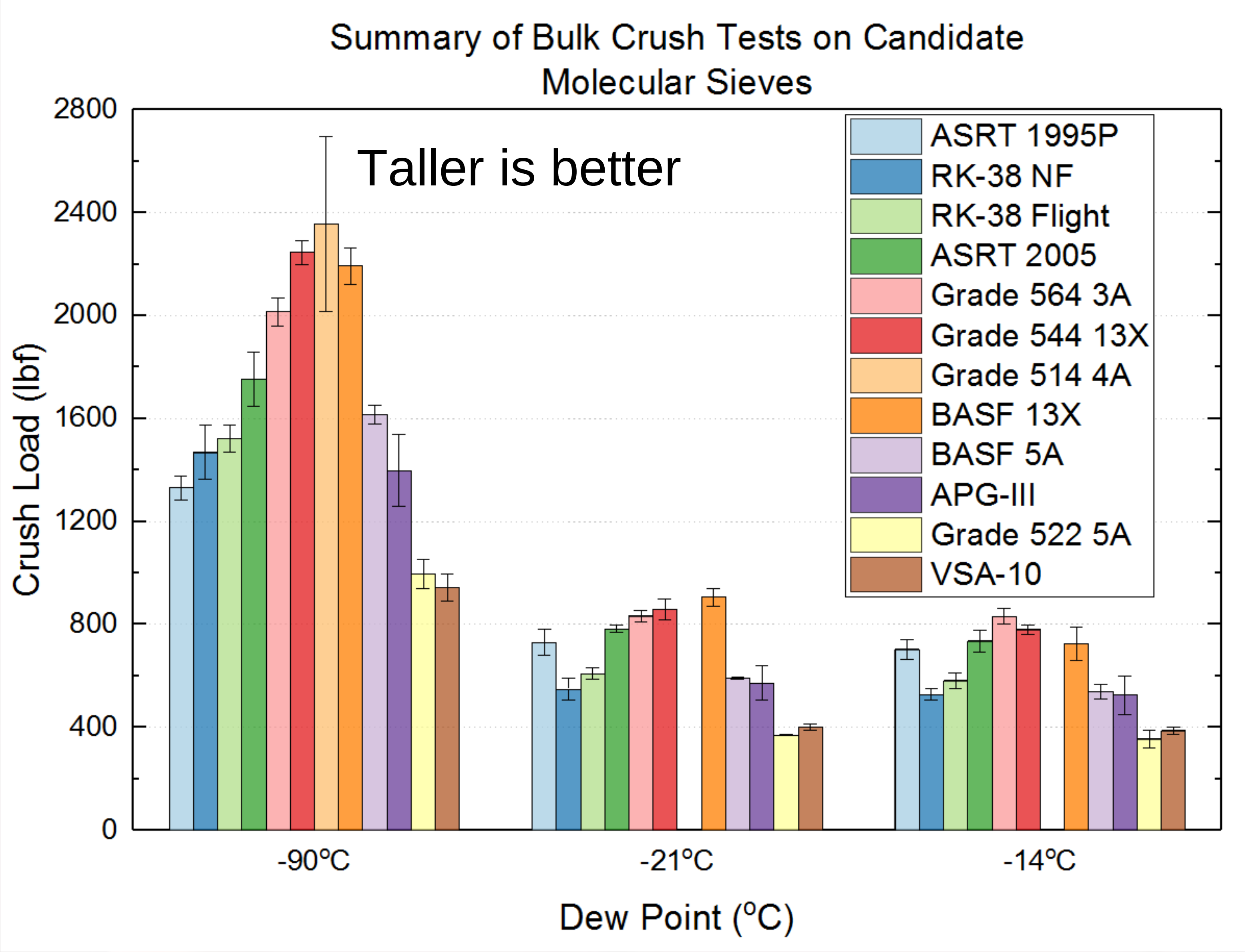
- Collaborative effort among the CO_2 removal teams at MSFC/ARC/JSC
  - Multiple aspects to study on these materials:
    - *Pellet integrity*
    - *Adsorption performance*
    - *Fault tolerance and recovery*

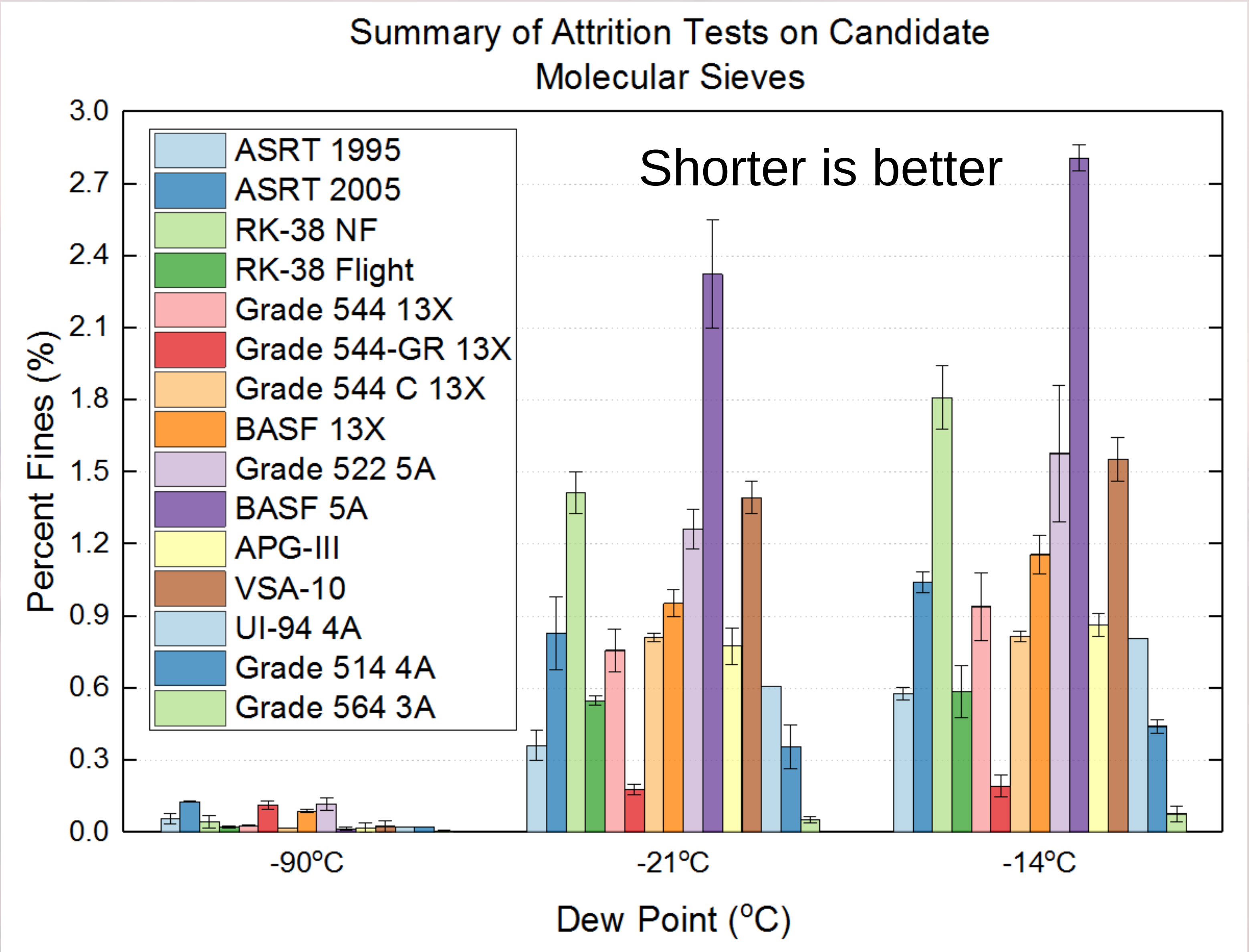
- This is a summary of recent results as well as previously presented work:
  - Single Pellet Crush, Bulk Crush, Attrition, and Hydrothermal Stability tests
  - Pure Component CO_2 Isotherms and Water Vapor Isotherms at 0 to 200°C
  - CO_2 Isotherms on Water Preloaded Samples at 25 to 100°C
  - CO_2 Breakthrough Measurements
  - Thermal Profiles for Adsorption Performance Recovery
  - Cyclic CO_2 Adsorption Performance
  - Layered Desiccant Breakthrough Comparison

Sorbent Structural Reliability

Sorbent Structural Tests

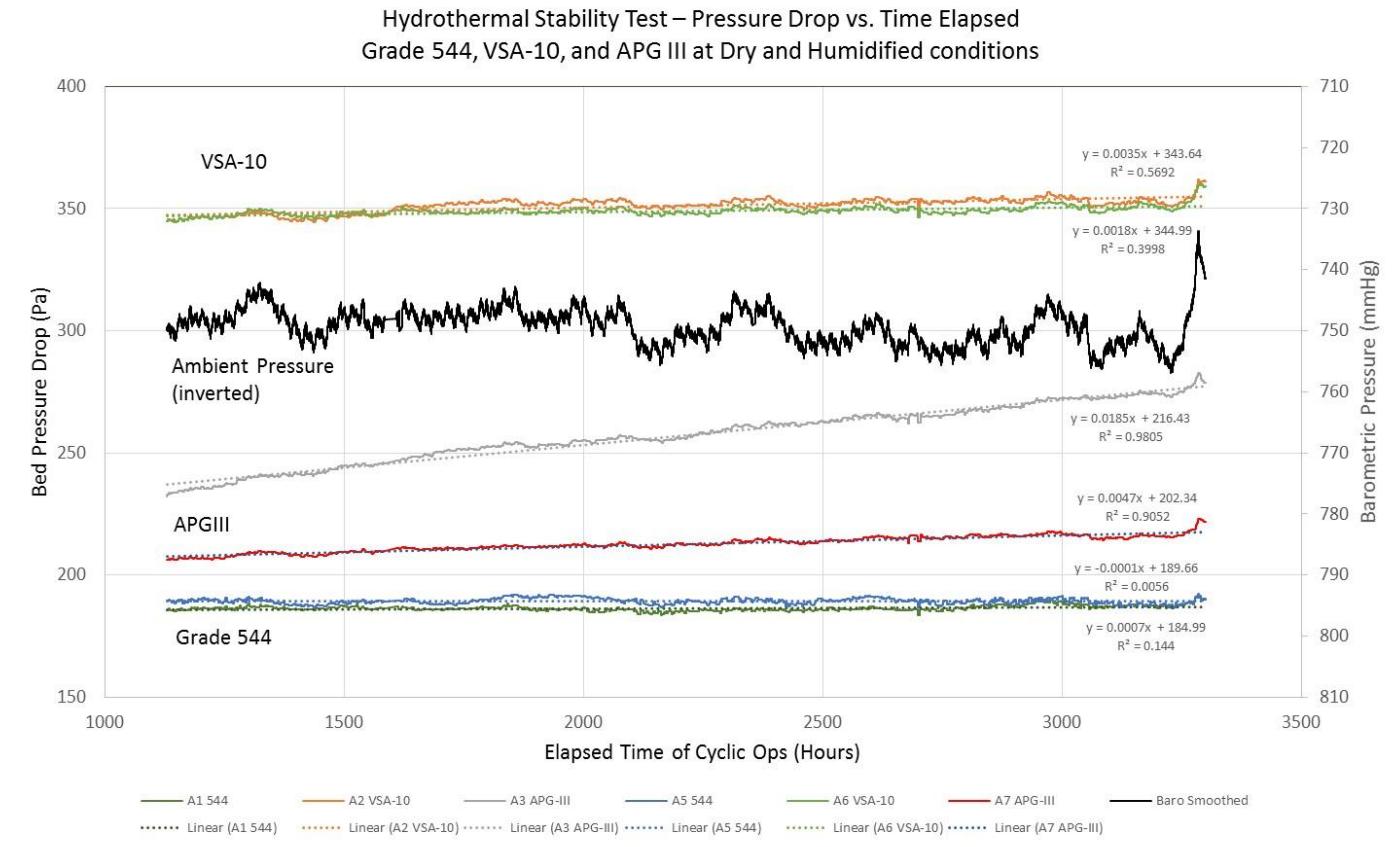


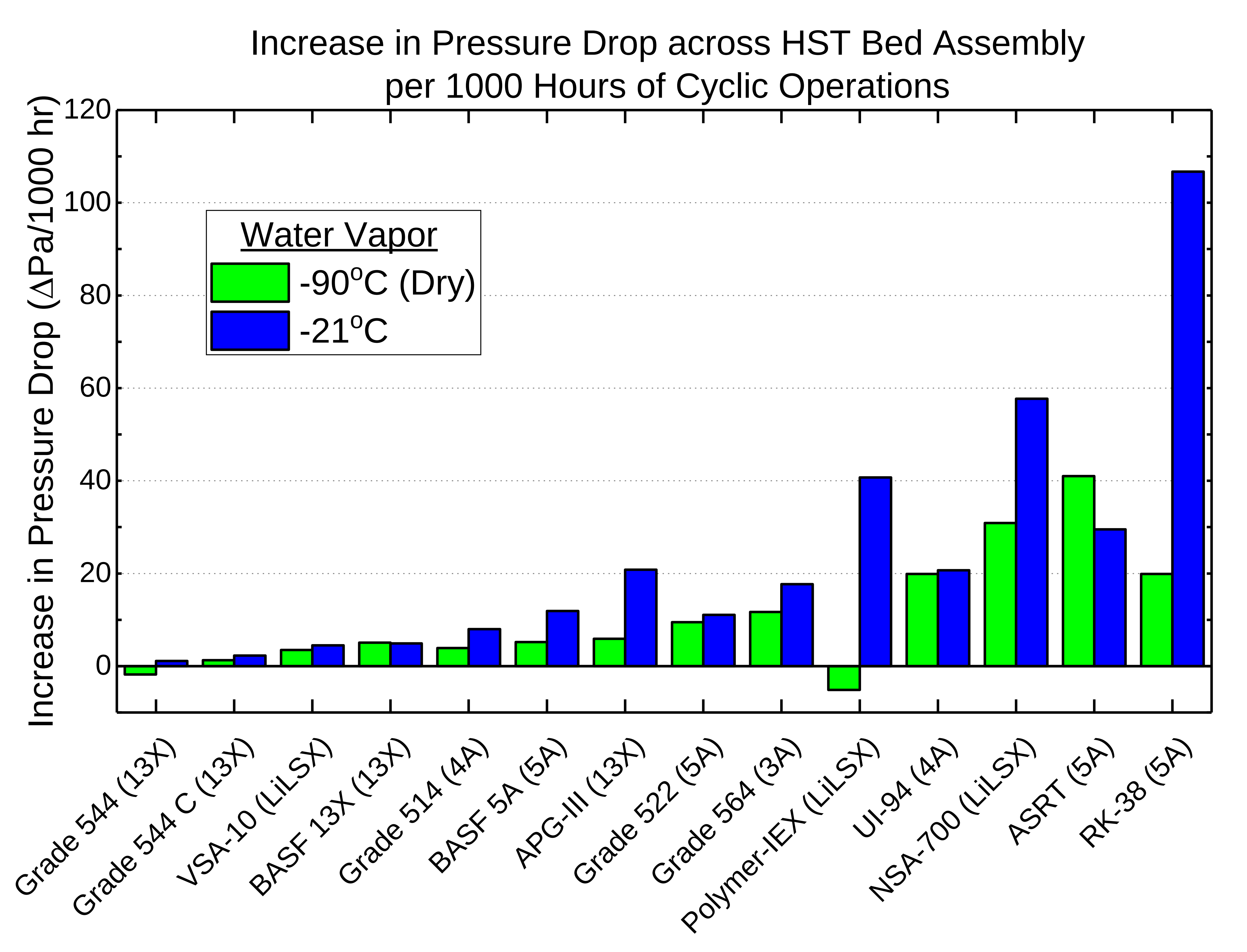




- Criteria: Match or exceed ASRT in structural performance metrics
  - No material was as robust in Single Pellet Crush as ASRT
  - Several exceeded ASRT in Bulk Crush and Attrition testing
- Two prime candidates are Grade 544 13X and BASF 13X
  - Other sorbent options that passed the 2016 downselect: VSA-10 LiLSX, APGIII 13X, Grade 522 5A

Hydrothermal Stability Testing

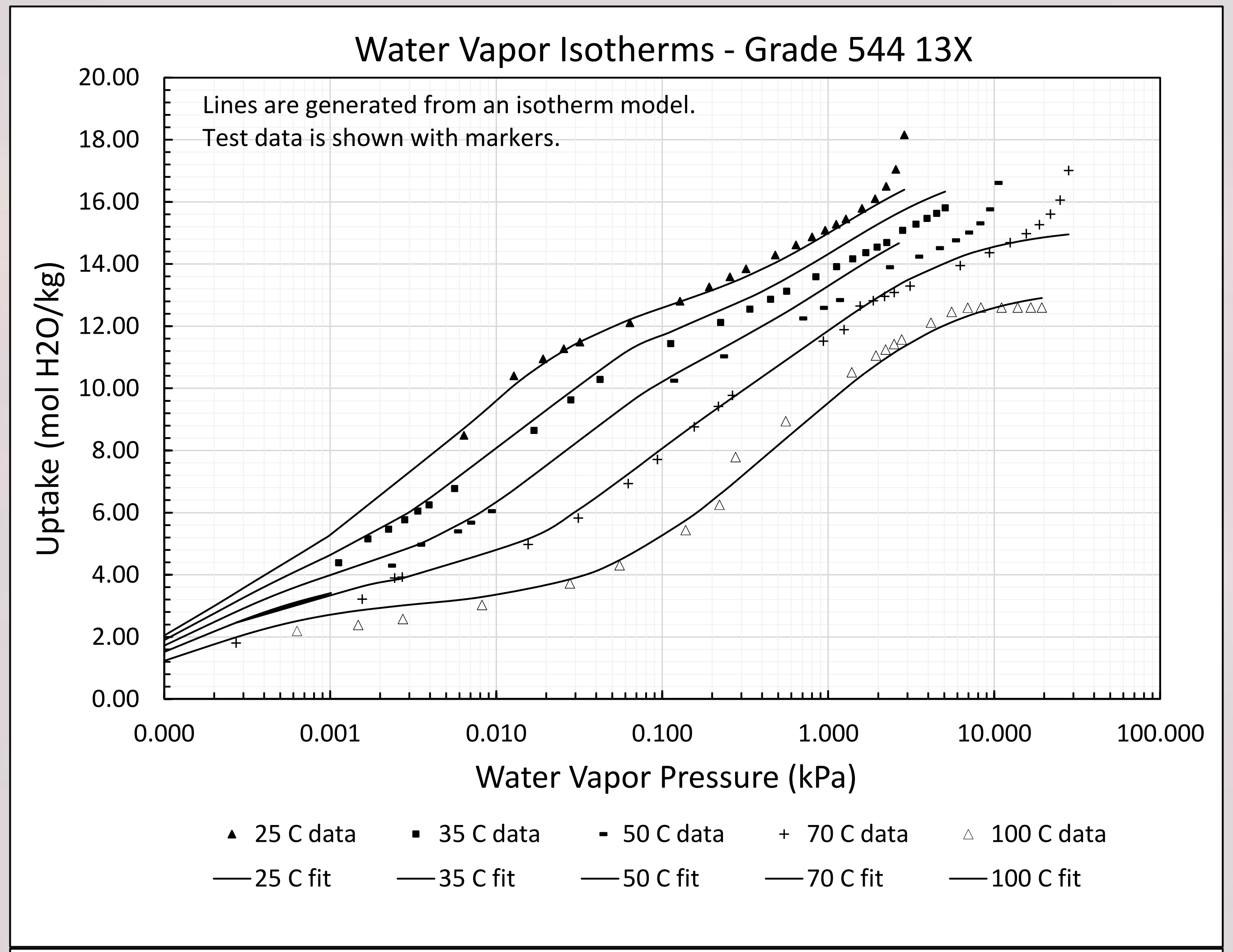


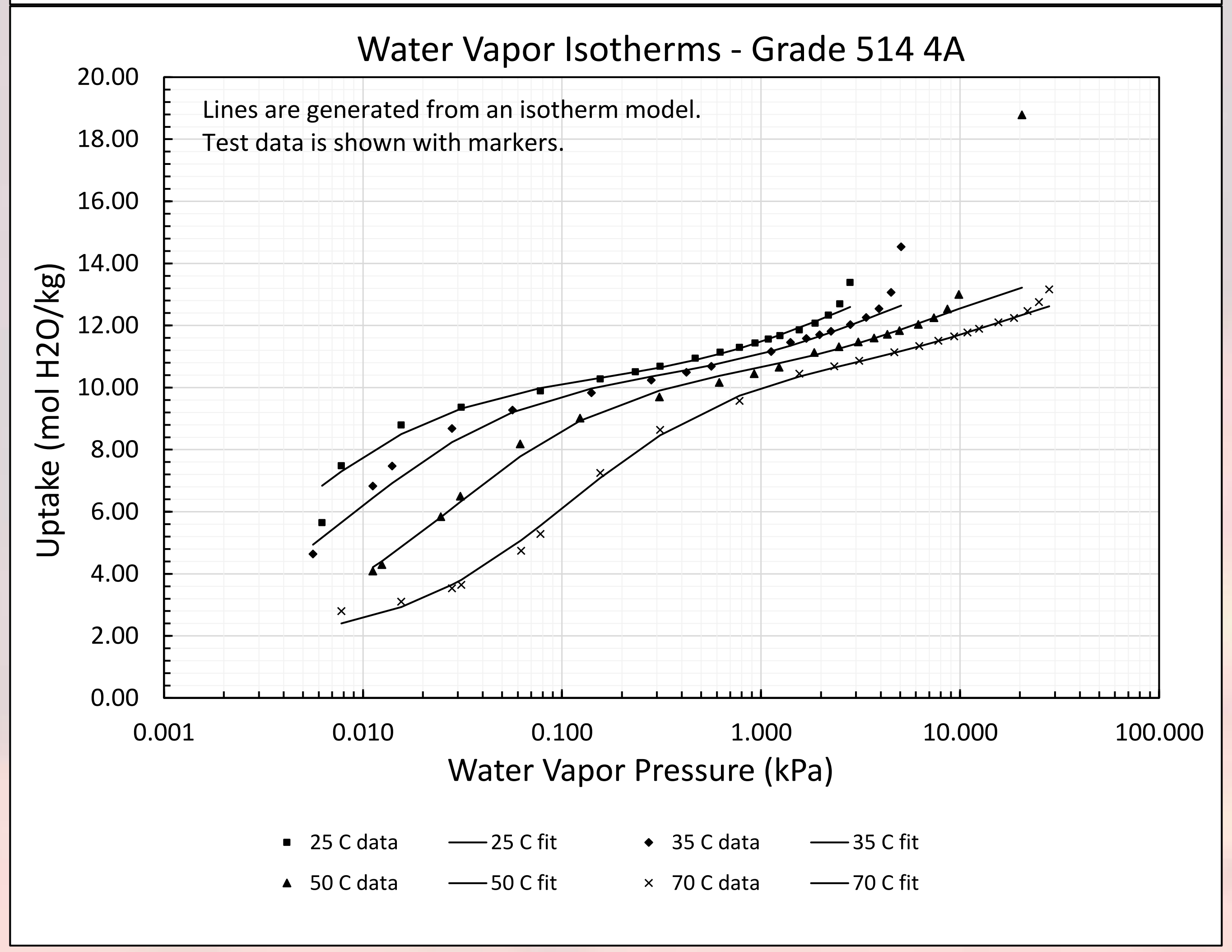


- The testing with the HST system has correlated very strongly with flight data on sorbent degradation.
  - ASRT is presently operating for over 2 years without incident while RK-38 failed within 6 months.
  - Numerous options to outperform ASRT and RK-38

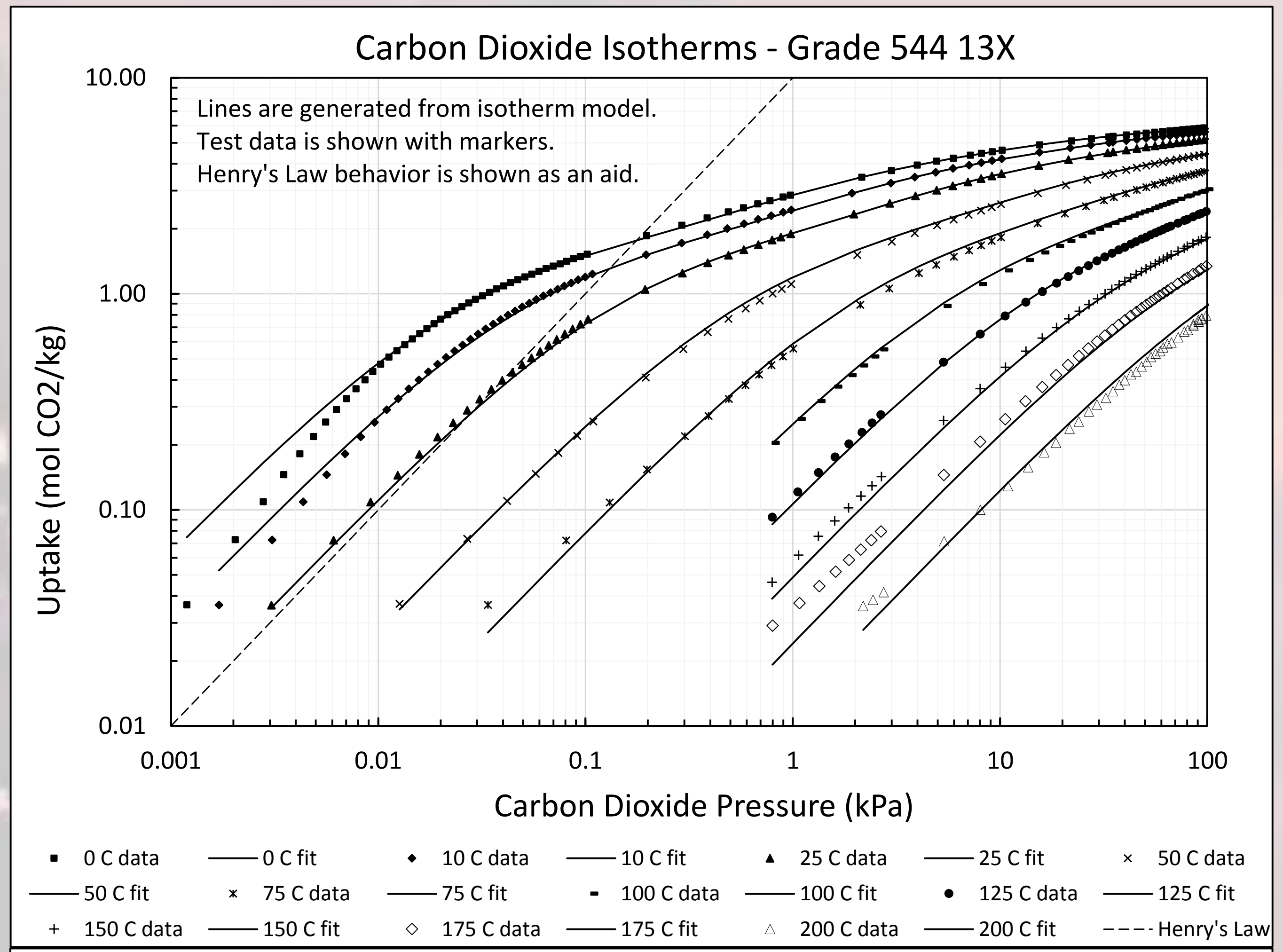
Adsorption Performance

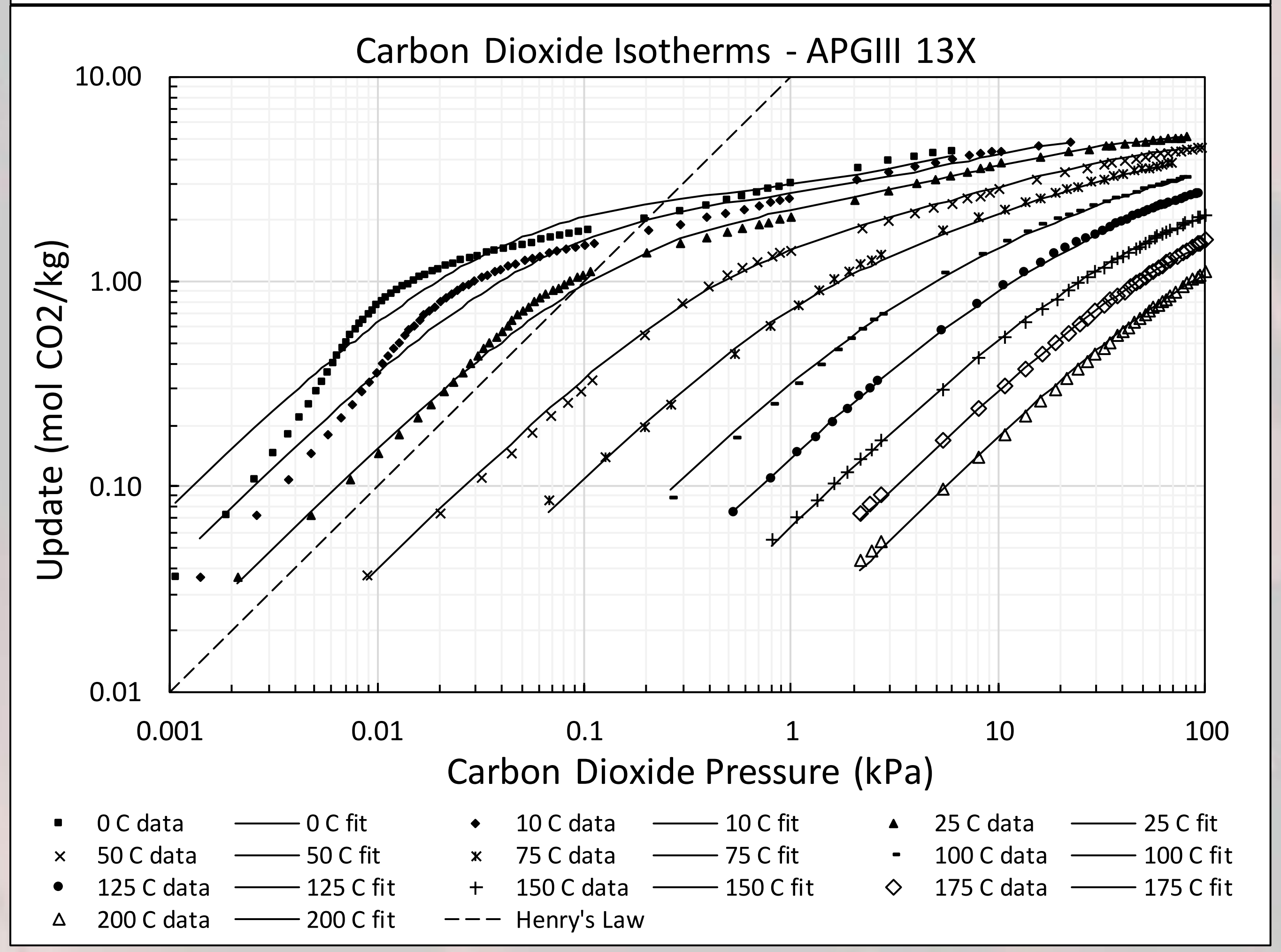
Pure Isotherm Measurement





- Collaboration with Ames Research Center
  - Pure Component CO_2 and Water Vapor Isotherms
  - Measured data encompasses all conditions found in 4BMS operation
- Data fit to a 3-site Langmuir model
  - High precision for interpolation in computer simulations



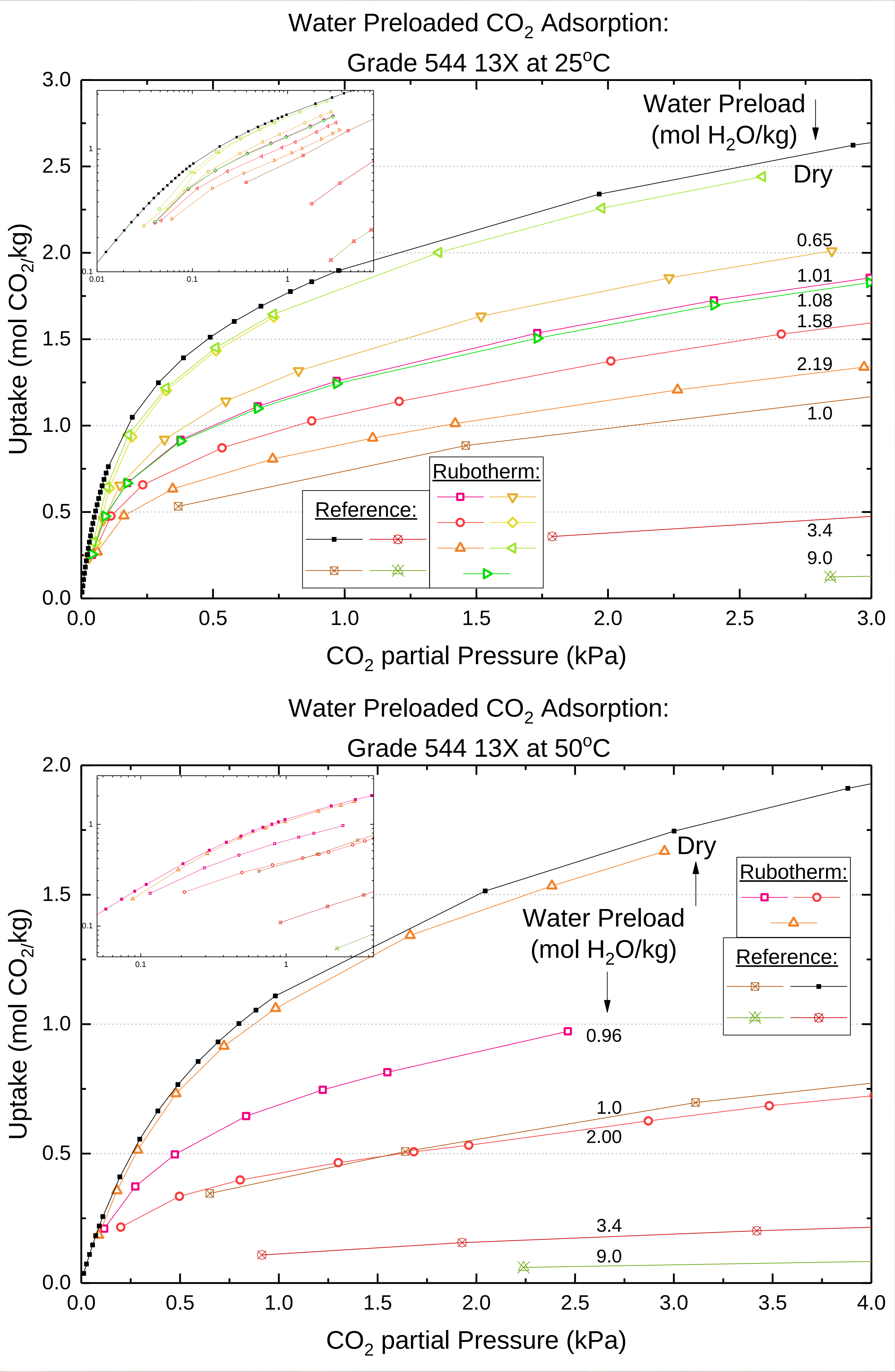


Huang, R., Belancik, G., Jan, D., Cmarik, G., Ebner, A. D., Ritter, J., and Knox, J. C. "CO2 Capacity Sorbent Analysis using Volumetric Measurement Approach," 47th International Conference on Environmental Systems. Charleston, 2017.

Mixture Isotherm Measurement

- A custom instrument built by Rubotherm was used to obtain CO_2/H_2O mixture isotherms
  - Samples are loaded with water vapor during a timed, continuous operation
    - Preloading is not intended to reach equilibrium
    - Preloading is determined by the change in mass observed with a microbalance
  - CO_2/He mixtures are prepared in a mixing loop and measured with a GC
  - The prepared mixture is circulated across the sample
  - The composition of the gas phase is sampled again after circulation
    - No water is observed to desorb at temperatures of 25, 50, 75, and 100°C
    - Measurements at 175°C show small, measurable quantities of desorbed water

- Comparisons made to reference data show:
  - Good agreement to dry isotherms
  - Disagreement to the preloaded isotherms. This is attributed to the activation temperature achievable in that work



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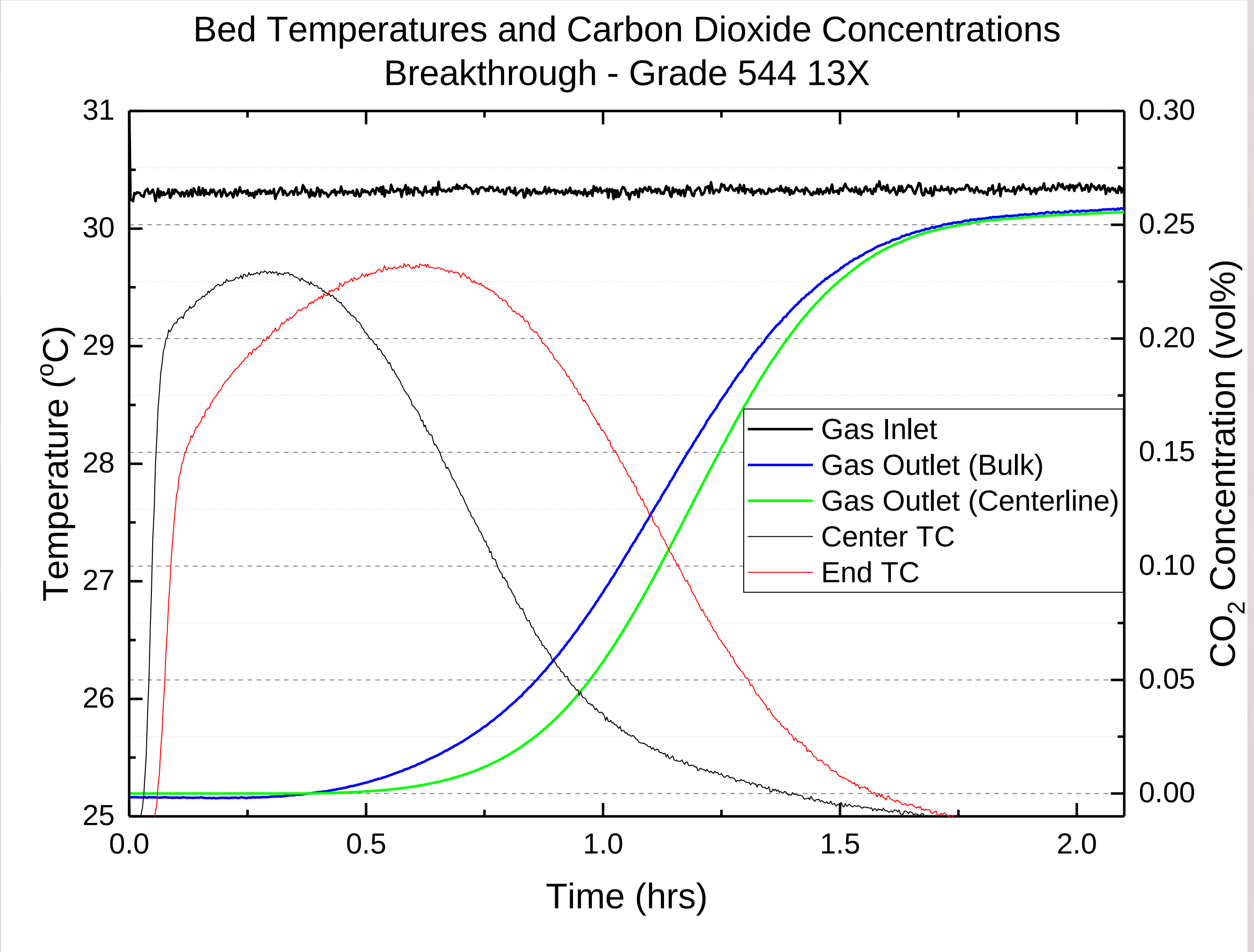
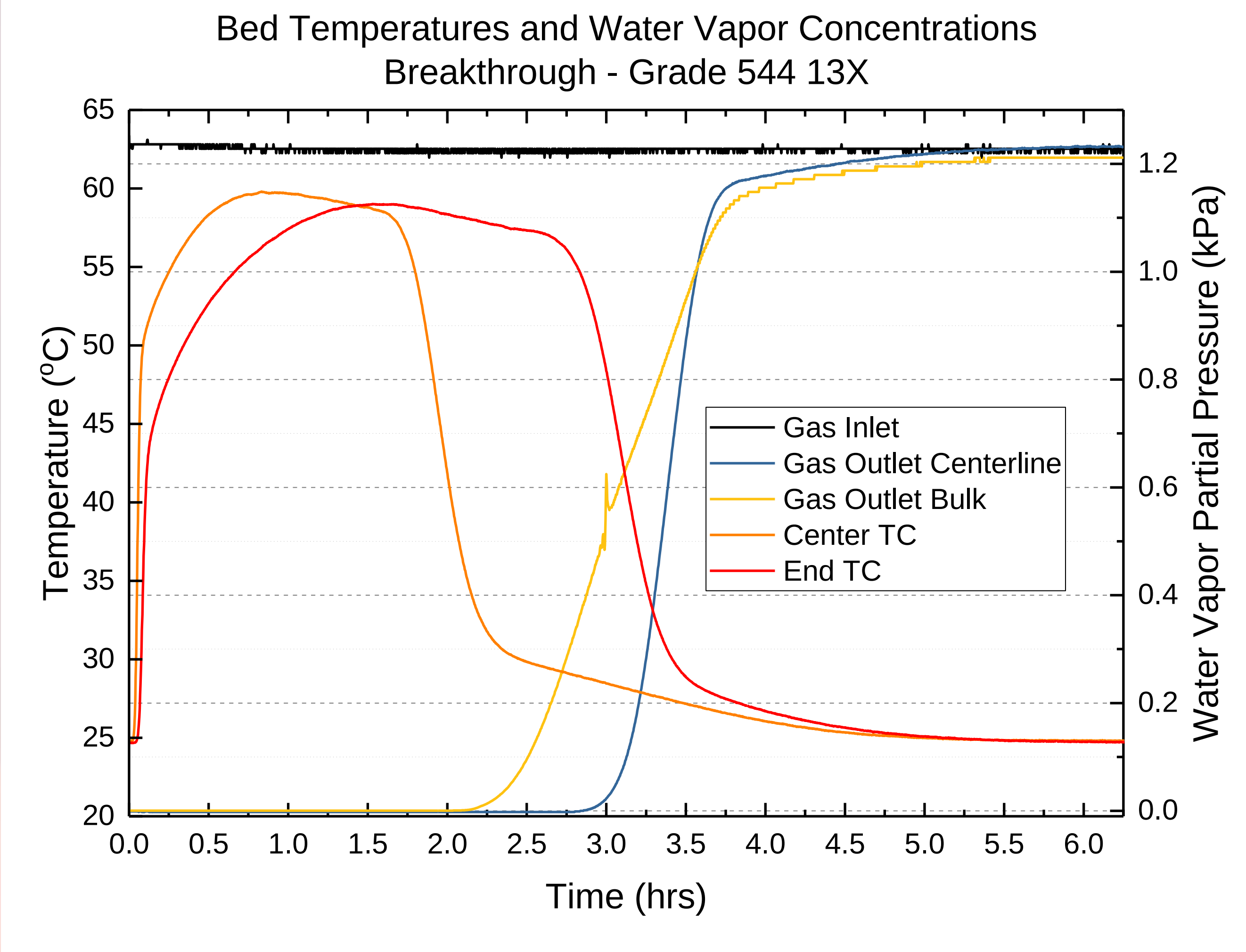
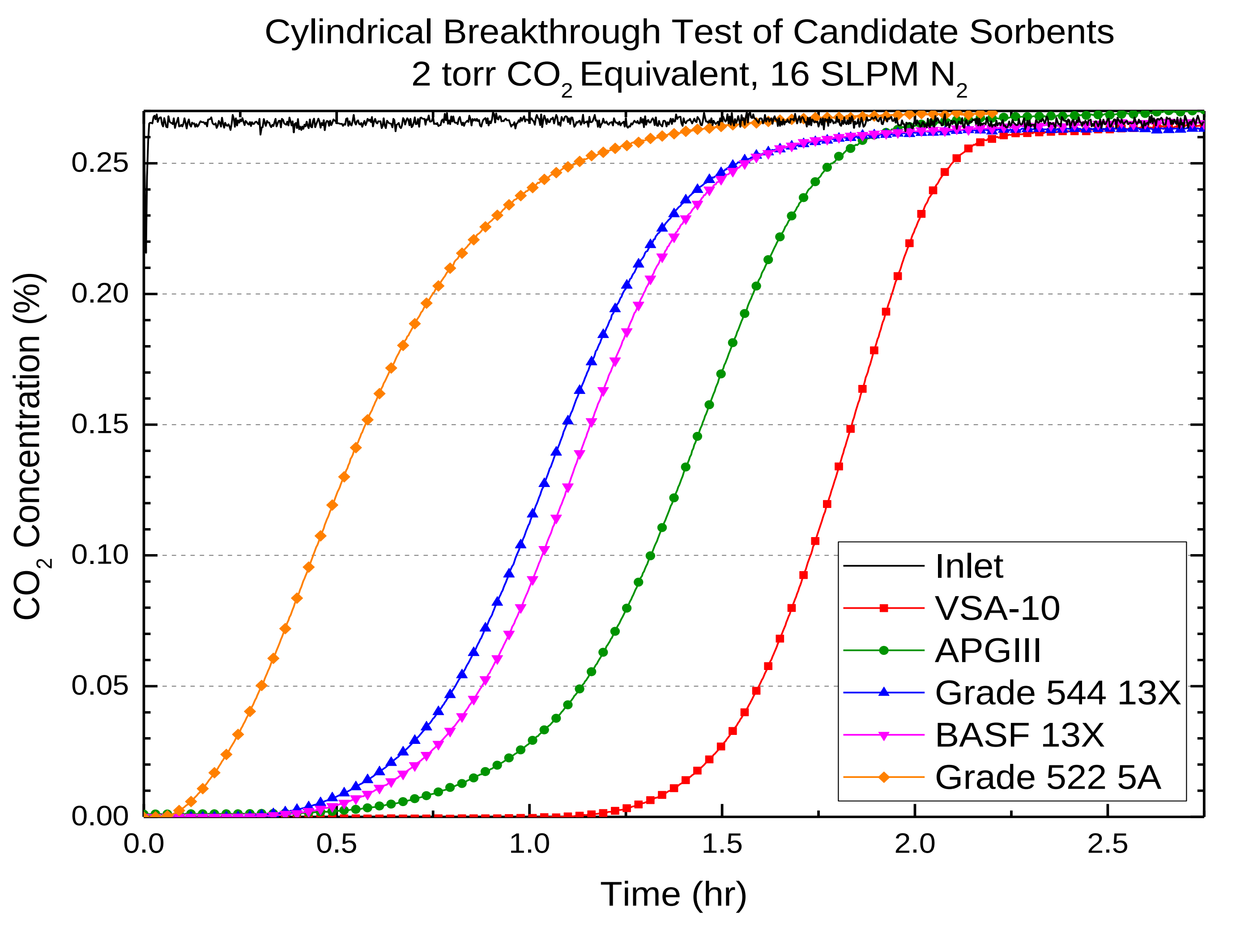
Wang, Y., and LeVan, M. D. "Adsorption Equilibrium of Binary Mixtures of Carbon Dioxide and Water Vapor on Zeolites 5A and 13X," *Journal of Chemical & Engineering Data* Vol. 55, No. 9, 2010, pp. 3189-3195.

Breakthrough Measurement





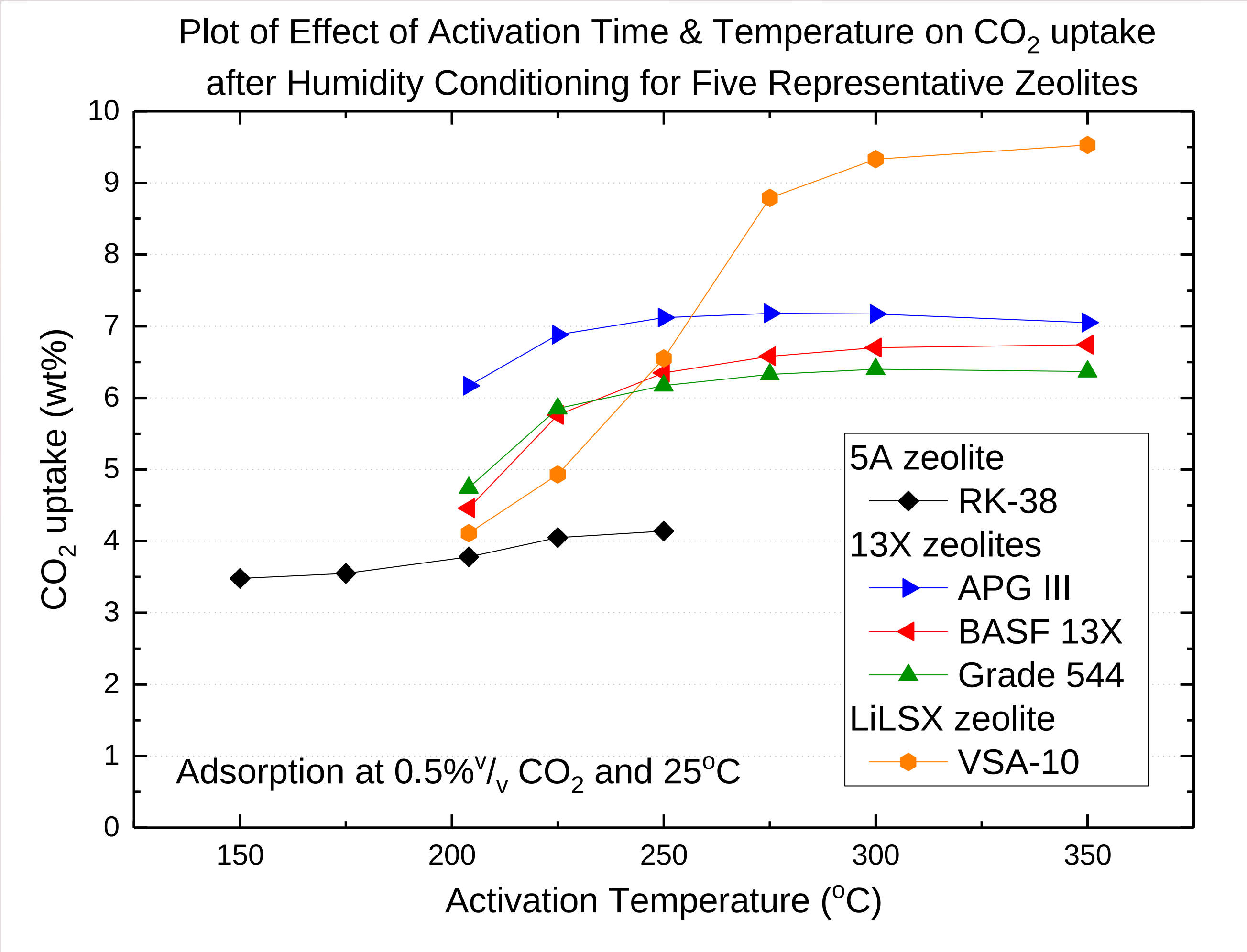
- CO_2 and Water Vapor tests with the Cylindrical Breakthrough Test stand
  - The CBT is a lab-scale system (roughly 14 pellet diameters across)
    - This means 'wall channeling' is a significant contributor to early breakthrough and model-data mismatch

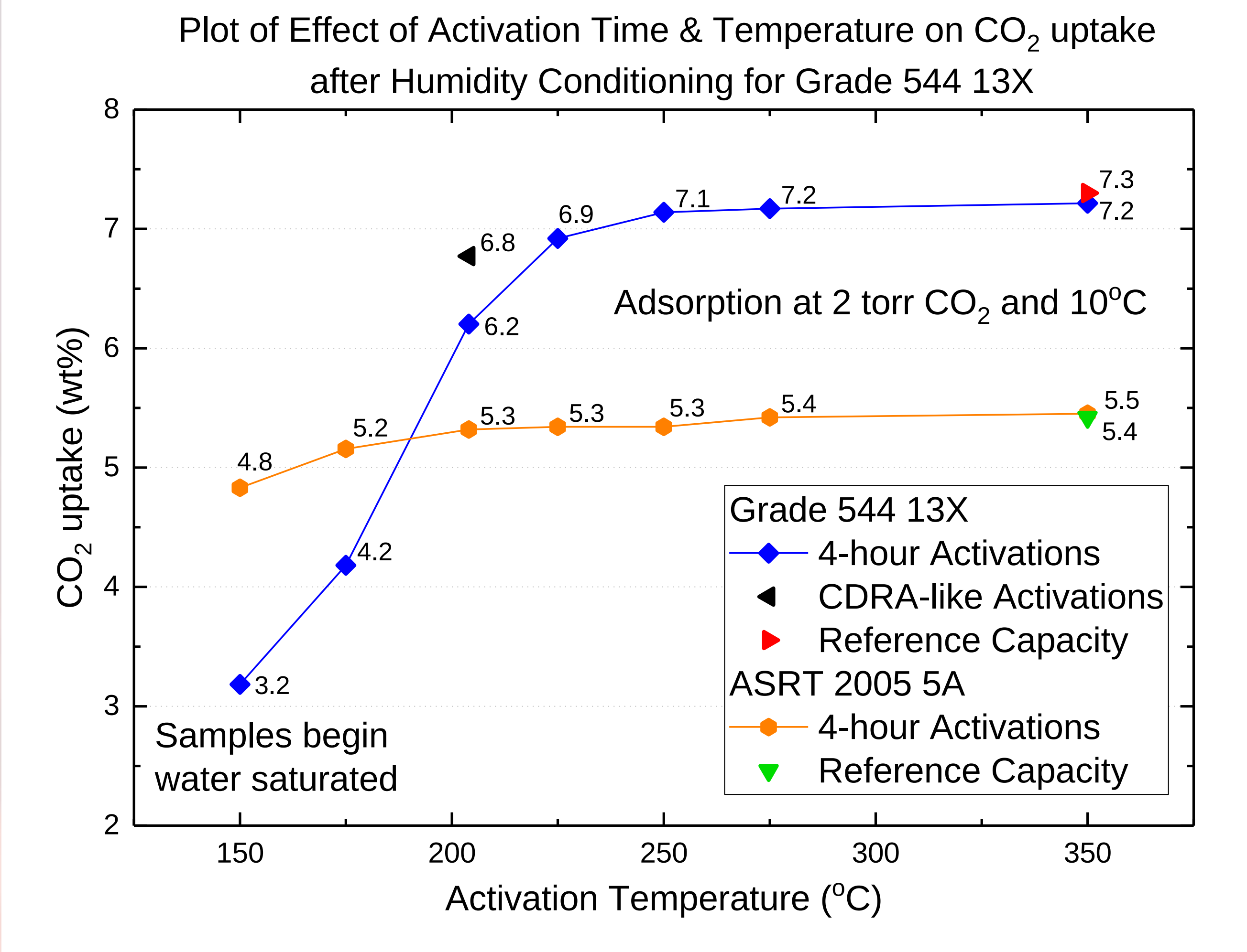


- Centerline sampling capabilities were added to the existing CBT
  - Centerline concentration measurements provide experimental data for fitting of kinetic parameters such as an LDF constant
  - Measurements made with both a GC and an optical sensor (when available)

Performance reliability

Thermal Recovery Profiles





- Purpose: Determine the required temperature to recover performance after an off-nominal event (i.e. water saturation during a maintenance operation)

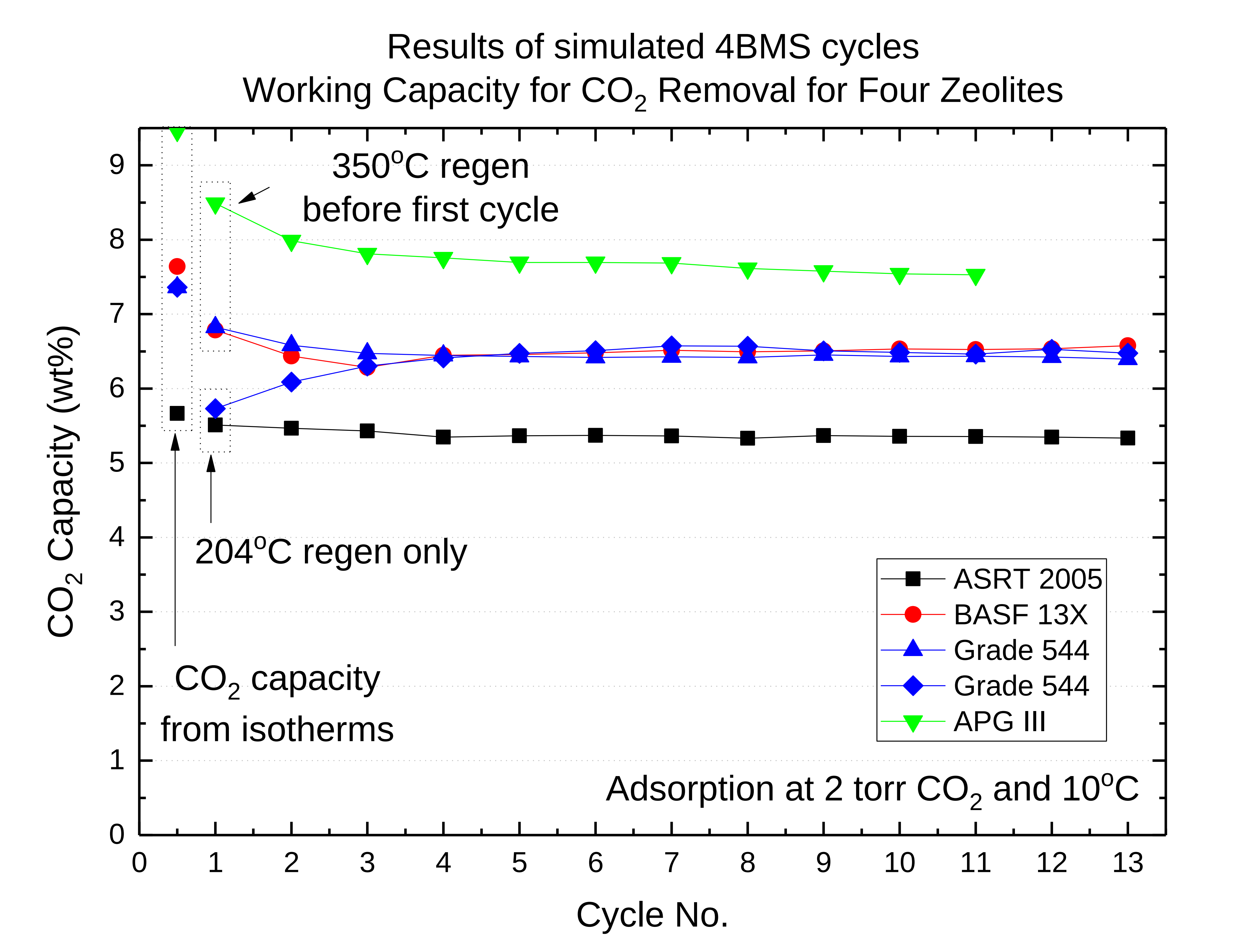
- Tests performed:
  - Recovery with a 4 hour ‘bakeout’ with a N_2 purge at sequentially higher temperatures. This is not identical to conditions in a 4BMS but is a fair approximation.
  - Recovery after a series of simulated CDRA operating cycles.

- Results indicate that 204°C will recover a 13X material to ~95% of peak performance and that a 13X will always outperform a 5A as long as 204°C is achieved.

Simulated 4BMS Cyclic Performance

- Upgrades to the TGA system enabled testing of the equilibrium conditions found a 4BMS cycle
  - Imperfections may have allowed trace water vapor onto the samples between cycles

- Results support the previous data and indicate that all three 13X materials can reliably outperform the benchmark 5A
  - Regardless of initial state or off-nominal events, operations with the current temperature of 204°C will enable better performance than with ASRT



Sorbent Selection

Sorbent Selection

- After the 2016 report, the field of CO_2 sorbents was downselected to five:
  - Grade 522 5A, Grade 544 13X, BASF 13X, APGIII 13X, and VSA-10 LiLSX
- New, Overarching Requirement is "No System Downtime Due to Dust"
  - Two materials are standout performers: Grade 544 13X and BASF 13X
    - Grade 544 13X is selected due to familiarity (successful usage history in desiccant beds)
- Performance Reliability/Recovery Concerns for 13X are Eliminated
  - No major system changes are needed as the present system will be fault tolerant
- Residual Desiccant Selection is Final Outstanding Selection Point

Desiccant Comparison (preliminary)

Desiccant Comparison (preliminary)

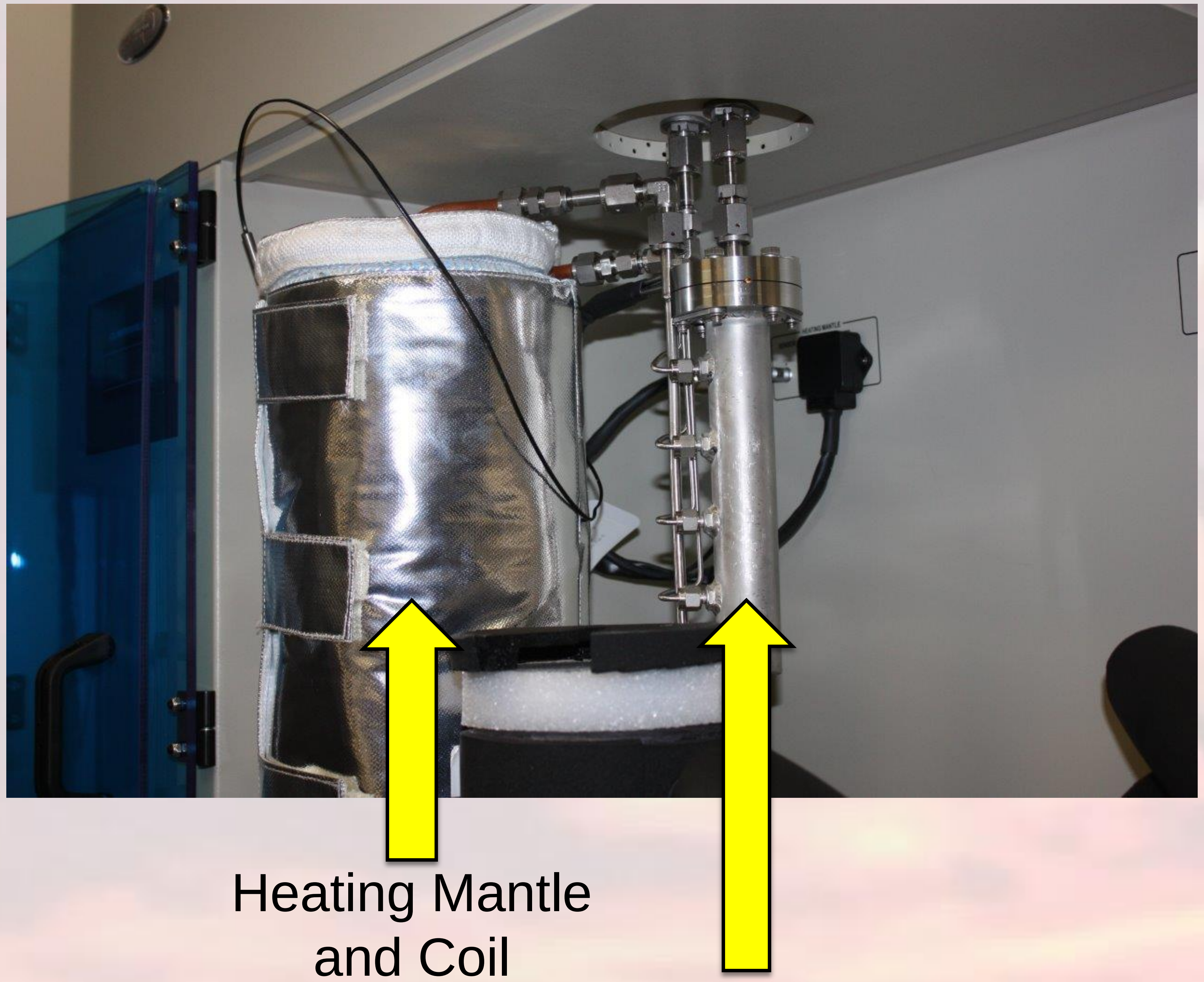
- System simulation team uncovered large CO_2 removal efficiency hits when the residual layer of 13X is oversized
    - Predictions confirmed via full-scale 4BMS-X test data

- Candidate desiccants must maintain an extremely low dew point for substantial time
  - Cyclic operation is the ultimate test required to compare these materials, but requires dedicated lab capability

- 4 materials for comparison
  - Simple Breakthrough testing on: Zeolites 13X, 4A, and 3A and an Alumina
    - The 3A adsorbs no CO_2 but adsorbs water too slowly which allows rapid breakthrough
    - The Alumina does not have enough capacity

  - 13X and 4A are possible candidates
    - 13X is presently used, but it has been shown to cause CO_2 hold-up which reduces system efficiency
    - Further study is needed to make this decision

Desiccant Comparison (preliminary)



Heating Mantle and Coil

Sample Column

- Simulate a 4BMS desiccant bed adsorption and desorption cycles
  - Augment a commercial instrument
  - Adsorb at conditions similar to 4BMS tests for various lengths of time
  - Achieve desorption cycle by pre-heating a copper coil with the system's heating mantle
  - Run sequence of cycles of this via software

Acknowledgements

- Co-Authors: David Watson, Timothy Giesy, and Lee Miller
- Collaborators at Ames Research Center and in the Materials Test Lab at MSFC who measured many of the properties reported here.
- Incredible dedication and attention to detail in the work done by NASA and affiliates.

Backup Slides

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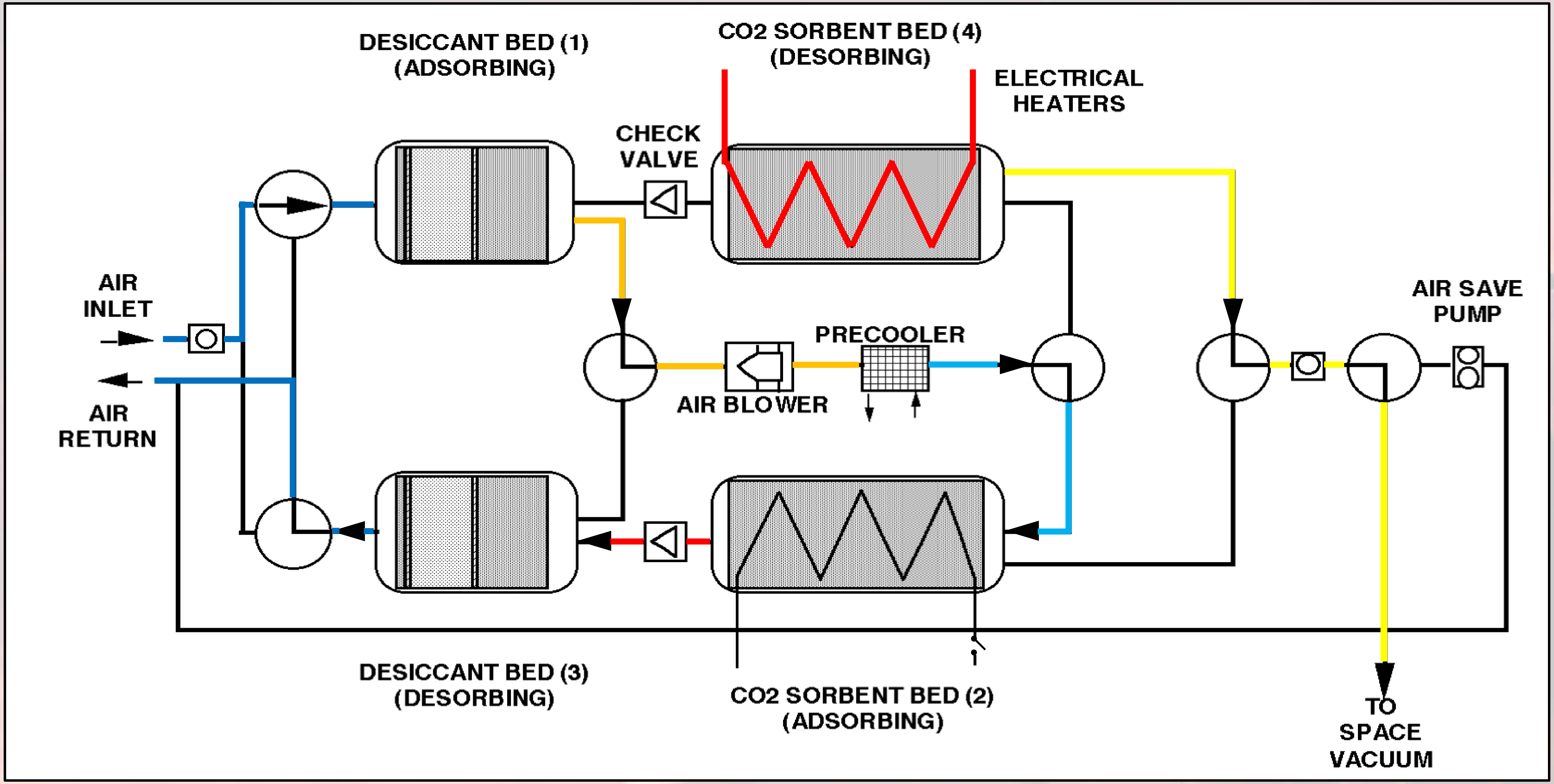

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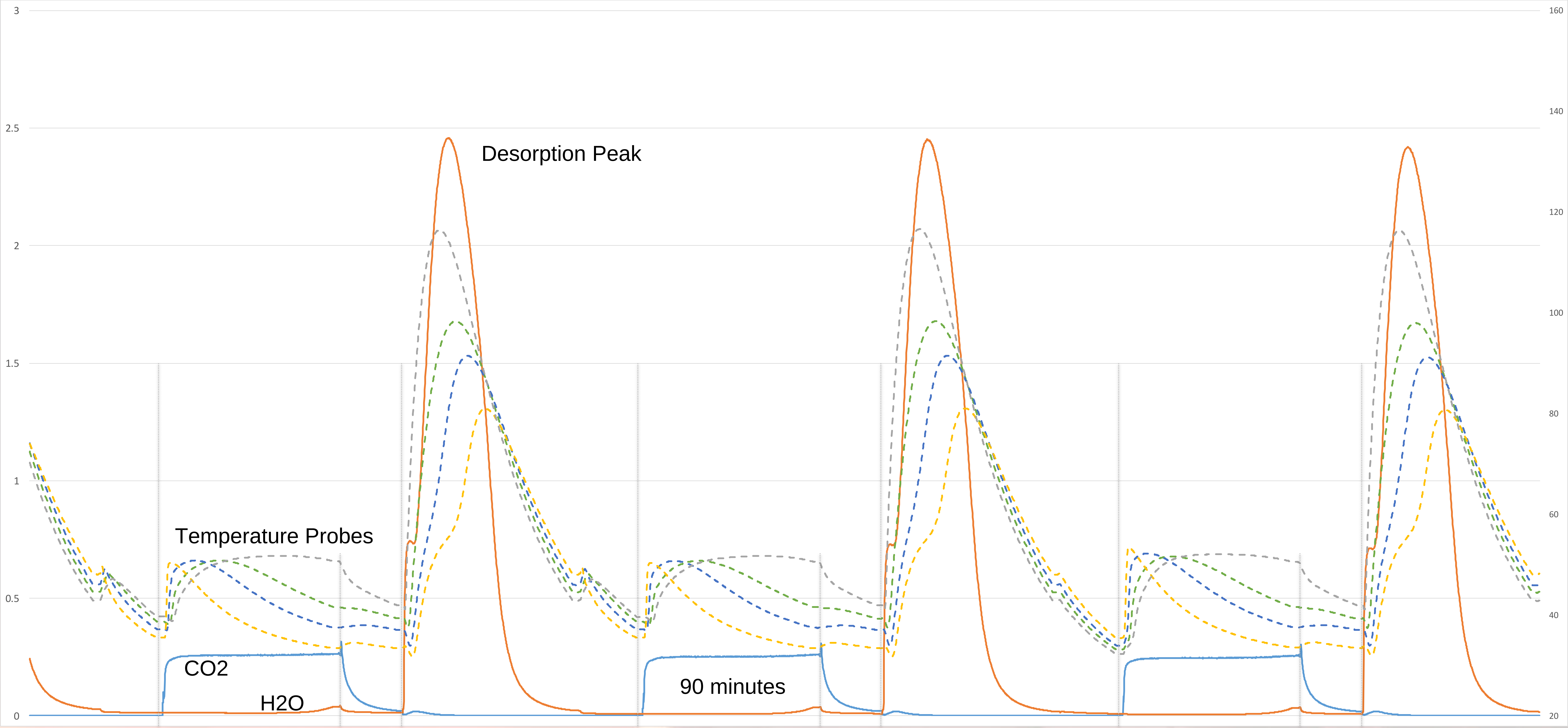

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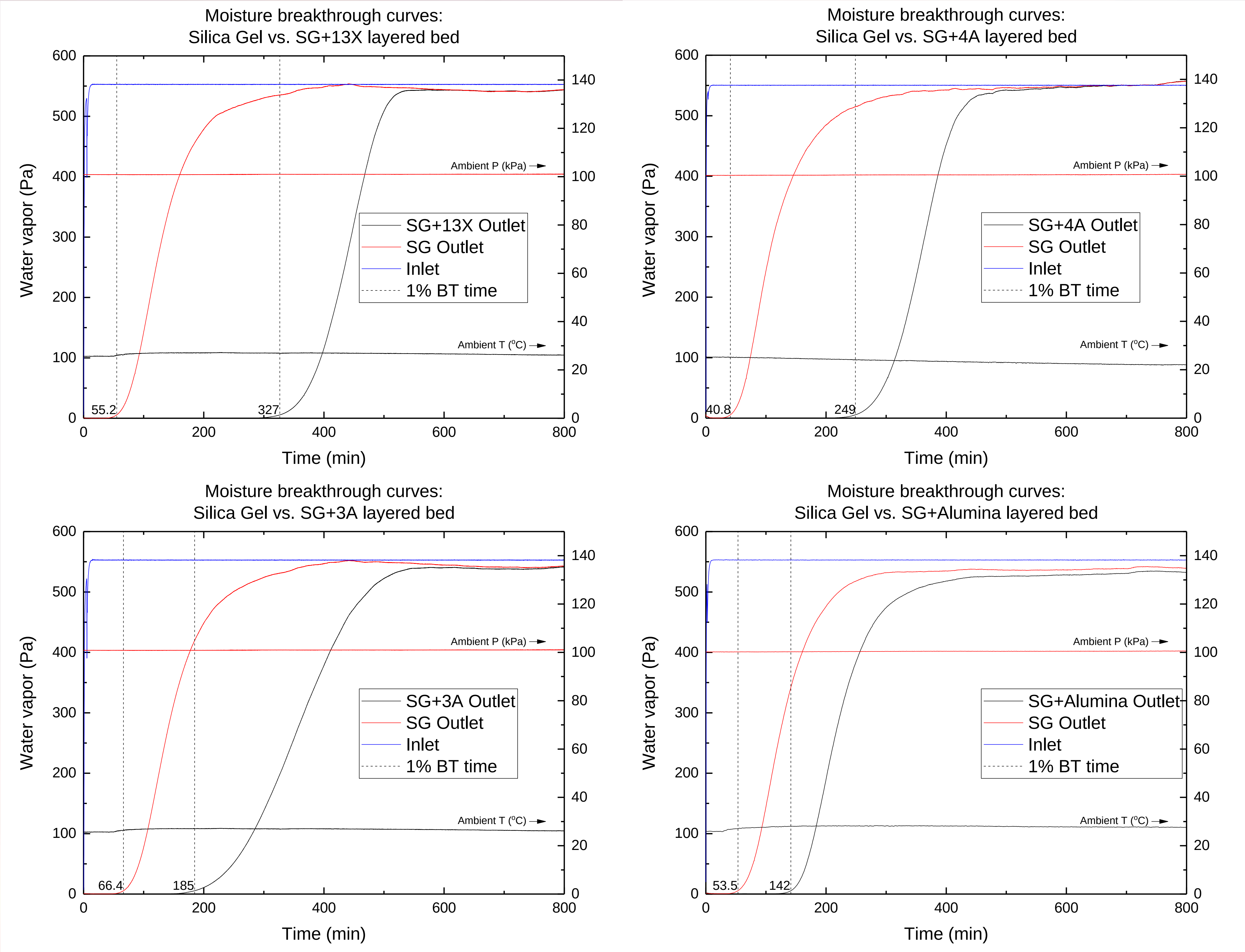

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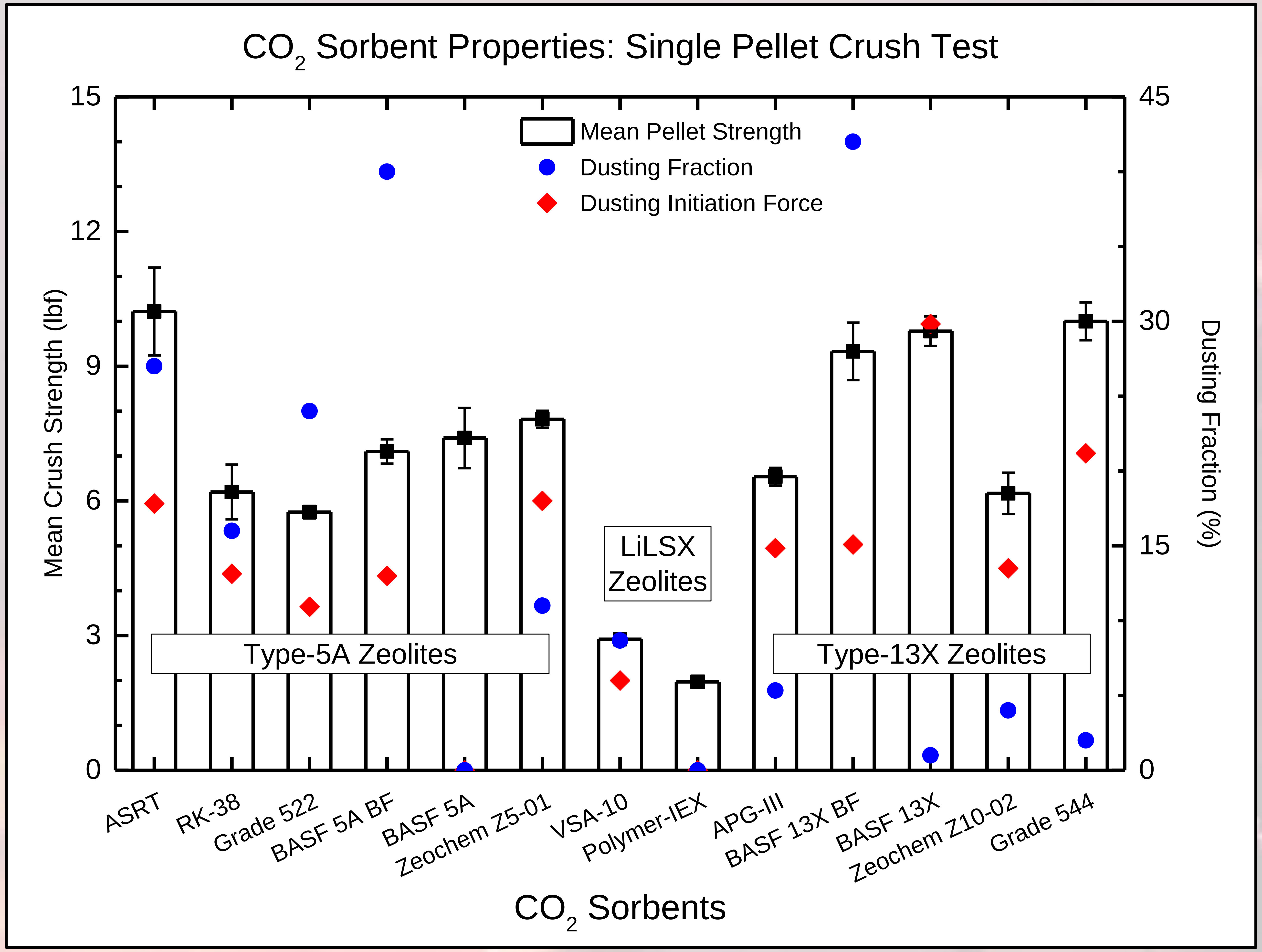

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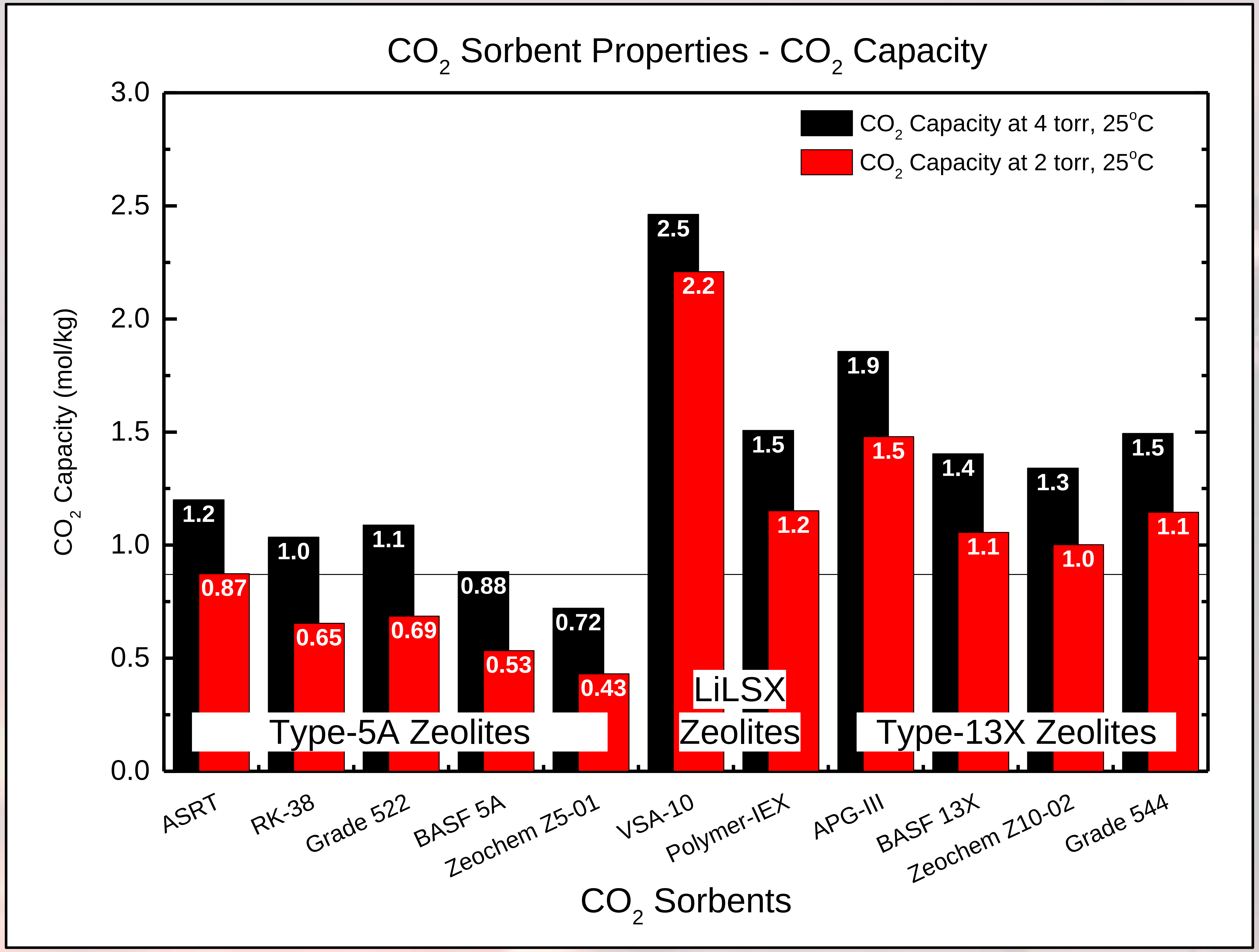

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Material Type	Sorbent Name	Use/Potential Use	Form Factor	Pore size	Notes
Silica Gel	Grace Grade 40	Bulk Desiccant	Granular	Microporous	used in CDRA
Silica Gel	Grace SG B125	Bulk Desiccant	Beads	Microporous	used in CDRA
Silica Gel	BASF Sorbead H	Bulk Desiccant	Beads	Microporous	
Silica Gel	BASF Sorbead R	Bulk Desiccant	Beads	Microporous	
Alumino-Silica Gel	BASF Sorbead WS	Guard Layer	Beads	Microporous	Misting Stable, used in CDRA
Activated Alumina	BASF F200	Bulk Desiccant	Beads	Mesoporous	Misting Stable
Molecular Sieve	UOP ASRT 1995 and ASRT 2005	CO_2 sorbent	Pellets	5Å	CaA Zeolite, used in CDRA
Molecular Sieve	UOP RK-38	CO_2 sorbent	Beads	5Å	CaA Zeolite, used in CDRA
Molecular Sieve	Grace MS 564	Residual Desiccant	Beads	3Å	KA Zeolite
Molecular Sieve	Grace MS 514	Residual Desiccant	Beads	4Å	NaA Zeolite
Molecular Sieve	UOP UI-94	Residual Desiccant	Pellets	4Å	NaA Zeolite
Molecular Sieve	Grace MS 522	CO_2 sorbent	Beads	5Å	CaA Zeolite
Molecular Sieve	Grace MS 544	CO_2 sorbent, Residual Desiccant	Beads	10Å	NaX Zeolite, used in CDRA
Molecular Sieve	BASF 5A	CO_2 sorbent	Beads	5Å	CaA Zeolite
Molecular Sieve	BASF 5A BF	CO_2 sorbent	Binder-free Beads	5Å	CaA Zeolite
Molecular Sieve	BASF 13X	CO_2 sorbent, Residual Desiccant	Beads	10Å	NaX Zeolite
Molecular Sieve	BASF 13X BF	CO_2 sorbent	Binder-free Beads	10Å	NaX Zeolite
Molecular Sieve	UOP APGIII	CO_2 sorbent	Beads	10Å	NaX Zeolite
Molecular Sieve	UOP VSA-10	CO_2 sorbent	Beads	10Å	LiLSX Zeolite
Molecular Sieve	Tosoh NSA-700	CO_2 sorbent	Pellets	10Å	LiLSX Zeolite

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