A System Level Mass and Energy Calculation for a Temperature Swing Adsorption Pump used for In-Situ Resource Utilization (ISRU) on Mars

Hashmatullah Hasseeb
Anthony Iannetti
NASA Glenn Research Center

Presented By
Hashmatullah Hasseeb

Thermal & Fluids Analysis Workshop
TFAWS 2017
August 21-25, 2017
NASA Marshall Space Flight Center
Huntsville, AL

Outline

- Introduction
- Objective
- TSA Pump Overview
- TSA Pump: System Level Design and Analysis
- Results
- Conclusion

Introduction

- Mars ISRU converts atmospheric CO_2 to generate O_2 and CH_4
  - Reduces launch mass, thus mission cost
  - Increases mission duration and independence

- CO_2 acquisition system must:
  - Reliably extract CO_2 over the varying Martian environment
    - ~0.67 – 0.93 kPa pressure
    - - 125 ℃ to 40 ℃
  - Provide and compress high purity gas to chemical plants
    - Separate N_2, Ar_2, etc. from ~ 95% CO_2 atmosphere
    - Current pressure targets: 50 kPa – 500 kPa

Temperature Swing Adsorption(TSA) Pump

- Working Principle: Adsorption & Desorption of CO_2
  - Adsorption is the process of bonding CO_2 particles to the surface of a material called an adsorbent (or sorbent). Cooling the adsorbent increases its saturation limit
  - Desorption is the process of freeing CO_2 particles through the application of heat
  - Through heating in a closed volume, high pressure products can be achieved
  - Select sorbents with high CO_2 selectivity to generate high purity outputs
    - N_2, Ar_2, etc are separated out of the air stream

- Can operate reliably in the Martian environment
  - Sorbents can effectively capture CO_2 at low pressures
  - Adequate power source allows for continuous operation
  - Thermally-activated processes require minimal moving parts

Objective

- Determine how much power and sorbent mass is required to meet notional production requirements
  - Currently have 2 scenarios:
    1. Generate only O_2 on Mars : **6.10 kg/hr CO_2**
    2. Generate both CH_4 and O_2 on Mars: **1.94 kg/hr CO_2**
       - Requires input of $H_2O/H_2 \Rightarrow$ Less CO_2 required
  - Two TSA pumps will work to meet the mass flow rates
    - Rapid Cycling: 60 second adsorption/desorption cycles

- Consider the following operating conditions and targets:
  - <u>Target Output Pressures:</u> $50\ kPa \leq P \leq 500\ kPa$
  - <u>Temperatures for adsorption:</u> $-50\ ℃ \leq T \leq 40\ ℃$
    - Cooling to the ambient temperature range, except the lower limit modified to prevent CO_2 freezing
  - <u>Temperature for desorption:</u> $120\ ℃$

- Compare the following sorbents:
  - Grace 544 13X
  - BASF 13X
  - Grace 522 5A
  - VSA 10 LiX

TSA PUMP OVERVIEW

Idealized Cycle

- Idealized cycle consists of simple isobaric and isochoric processes
  - Adsorption is an exothermic process, requires heat rejection
  - Desorption is an endothermic process, requires heat input

A → B : <u>Isochoric Compression</u>

- Sorbent is heated until the target pressure is reached

B → C : <u>Isobaric Desorption</u>

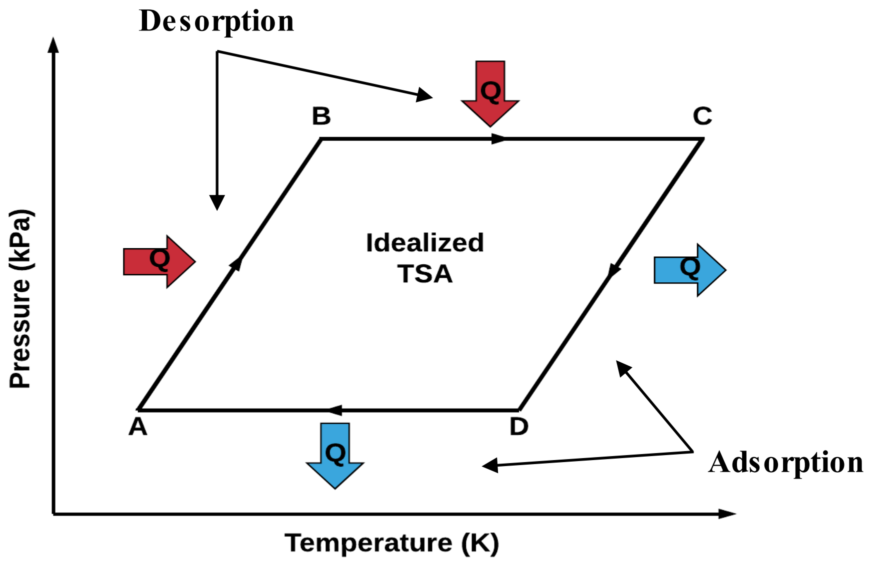
- Sorbent is heated to maintain a constant pressure throughput until the temperature at state C is reached. **This temperature is the <u>desorption temperature.</u>**

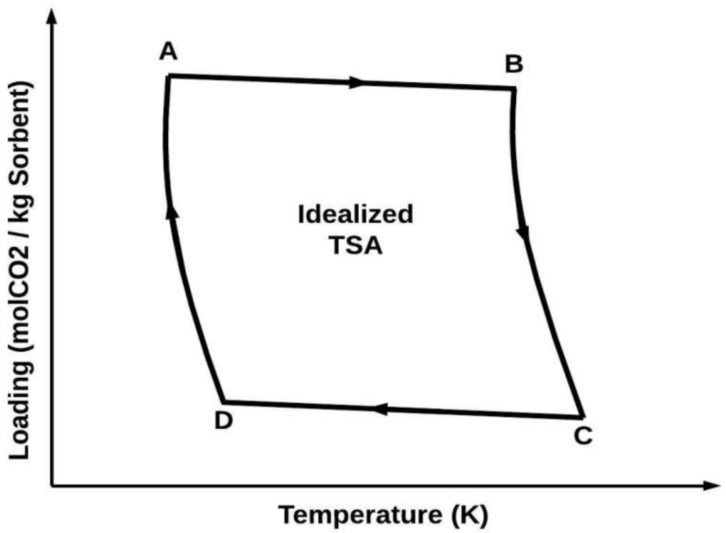
C → D : <u>Isochoric Cooling</u>

- Sorbent is cooled to readsorb remaining CO_2 and prepare for adsorption with the atmosphere

D → A : <u>Isobaric Adsorption</u>

- Sorbent is cooled until the target saturation is reached. **The temperature at state A is the <u>adsorption temperature.</u>**





Adsorbent Modeling

- Toth model used to characterize sorbent properties as functions of pressure and temperature
  - Validated for:
    - $0.001\ kPa \leq P \leq 101.325\ kPa$
    - $0\ ℃ \leq T \leq 200\ ℃$
  - Extended to encapsulate operating ranges in this analysis for extrapolation
  - Provided by James Knox et al. (NASA MSFC)

Equilibrium Adsorption Capacity

$$x = \frac{aP}{\left(1 + (bP)^t\right)^{\frac{1}{t}}}$$

$\uparrow P \Rightarrow \uparrow x$
$\uparrow T \Rightarrow \downarrow x$

Isosteric Enthalpy of Adsorption

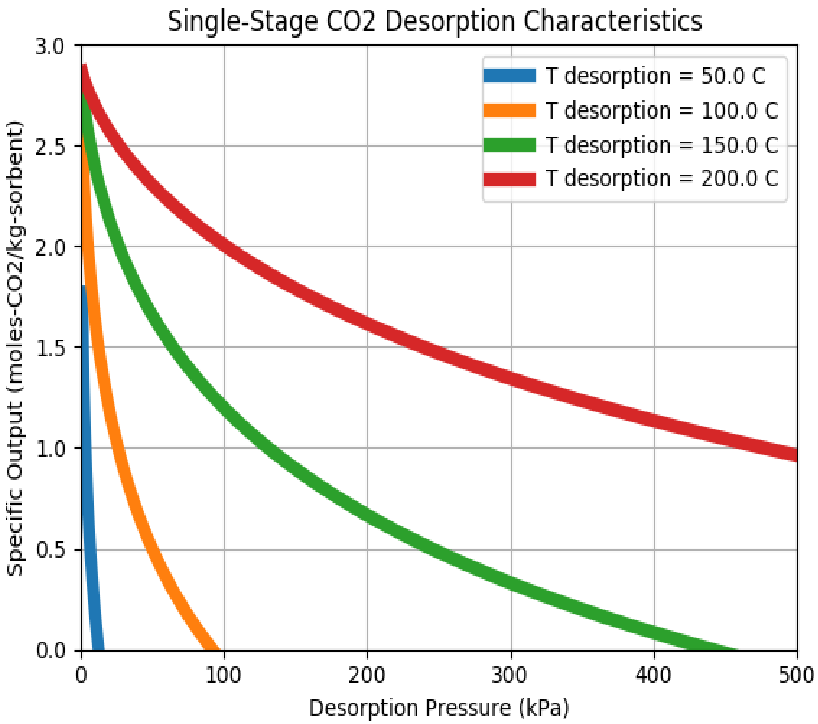
$$q_{st} = -\frac{R}{1000}\left(\frac{T^2}{P}\right)\left(\frac{\frac{dx}{dT}}{\frac{dx}{dP}}\right)$$

$\uparrow P \Rightarrow \downarrow q_{st}$
$\uparrow T \Rightarrow \uparrow q_{st}$

P = Pressure
T = Temperature
R = Universal Gas Constant
a, b, t are functions of temperature

Meeting the Target Pressures: Stages

- $Amount\ desorbed\ (n) = x_A - x_C$
  - Therefore, a TSA system has a pressure limit (n = 0)



Determined for the Grace 544 13X sorbent for an adsorption temperature of 0 C

- Single-stage systems cannot meet the high target pressures without:
  - Increasing the desorption temperature
    - $\downarrow x_C$
  - Decreasing the adsorption temperature
    - $\uparrow x_A$
  - Using a large amount of adsorbent

- Multi-stage systems successively compress a gas to the desired target pressure
  - Cause x_C to decrease and x_A to increase
  - Require smaller desorption temperatures
  - Are more complex and require inter-stage pressures to be chosen judiciously

TSA PUMP DESIGN

Stage Optimization: Inter-stage Pressures

- Improperly chosen pressures will decrease system efficiency
  - Pressures must be chosen such that each stage desorbs the same amount.
- Determine the inter-stages pressures for each target pressure and adsorption temperature combination:

$$minimize\ J = \sum_{i=1}^{k} -n_i^2$$

$$subject\ to\ n_i = n_{i+1}$$

$$and\ P^{Mars} < P_i < P^{Output}$$

$$\boxed{m_{sorbent} = \frac{m_{required}}{n\ \epsilon}}$$

$\boldsymbol{J}$ = Objective Function

$\boldsymbol{n_i}$ = Specific Amount of CO_2 desorbed by the ith stage

$$n_i = x_{A_i} - x_{C_i}$$

$\boldsymbol{P_i}$ = Output Pressure of the ith Stage

$\boldsymbol{P^{Output}}$ = Target Pressure of the TSA pump

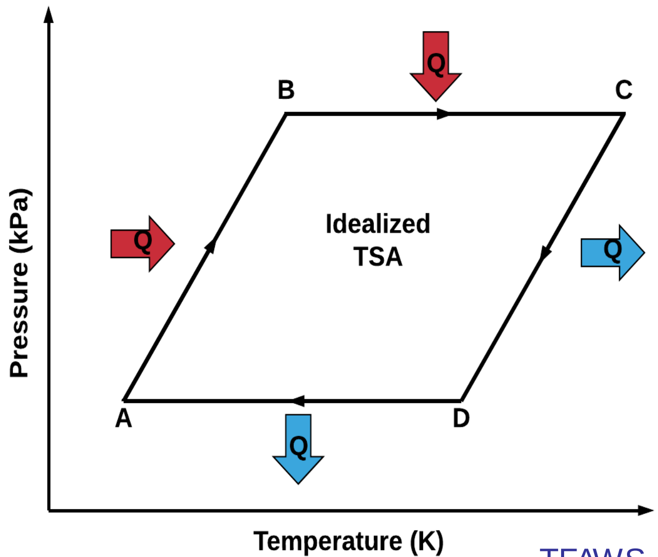
$\boldsymbol{P^{Mars}}$ = Mars Atmospheric Pressure

$\boldsymbol{m_{required}}$ = Required CO_2 output per cycle

$\boldsymbol{\epsilon}$ = CO_2 transfer efficiency (set to 95 % here)

Energy Analysis

- Assumptions
  - Negligible Kinetic and Potential differences. Neglect adsorbent and pump component thermodynamics
  - CO_2 behaves as an ideal gas and does no work
  - CO_2 sensible change in state is negligible in BC, and DA.
  - Same adsorption temperature for all stages of a system
  - Plenum between each stage for continuous operation



- Process A-B: Isochoric Compression

$$Q_{in} = (U_B - U_A) + Q_{desorption}$$

- Process B-C: Isobaric Desorption

$$Q_{in} = Q_{desorption}$$

- Process C-D: Isochoric Cooling

$$Q_{out} = (U_C - U_D) + Q_{adsorption}$$

- Process D-A: Isobaric Adsorption

$$Q_{out} = Q_{adsorption}$$

- Cooling of the Output Gas

$$Q_{out} = \overline{\Delta h}\, n\, m_{stage} \epsilon$$

$$\overline{\Delta h} = \frac{1}{T_C - T_B} \int_{T_B}^{T_C} (h - h_A)\, dT$$

State Determination

- Known States
  - P_A, P_B, P_C, P_D
    - These are fixed by the isobaric assumptions and set by the determination of inter-stage pressures
    - $50\ kPa \leq P_{target} \leq 500\ kPa$
  - T_A, T_C
    - $-50\ ℃ \leq T_A \leq 40\ ℃$
    - $T_C = 120\ ℃$

- Unknown States
  - T_B
    - Select a temperature to reach the appropriate output pressure
  - T_D
    - Select a temperature that allows the TSA pump to recover all transferred CO_2

Determination of T_B

- First determine the volume of each stage and then iterate the ideal gas law to get T_B

$$minimize\, J = \left(P^{check} - P_i\right)^2$$

$$subject\ to$$

$$V_i \geq 0.001\ m^3$$

$$T^{adsorptoin} < T_{B_i} < T^{desorption}$$

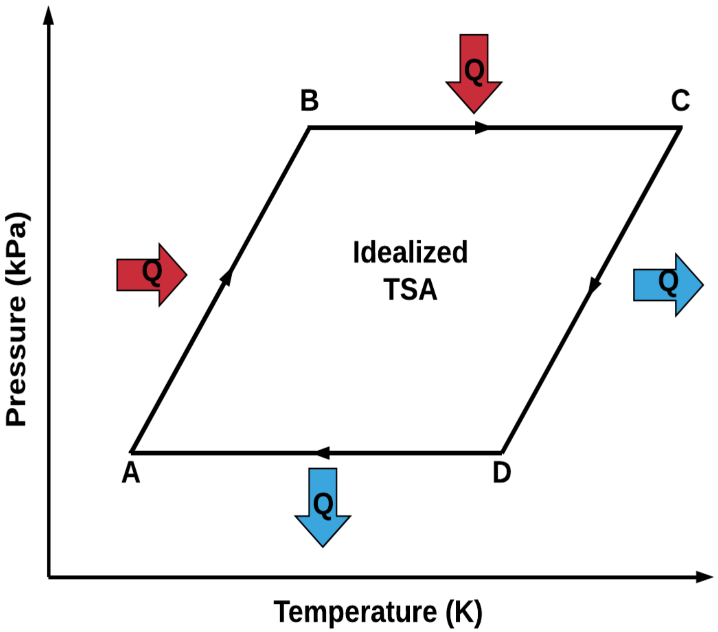
$$where\ P^{check} = \frac{N_i R T_{B_i}}{V_i}$$

$$N_i = n_i m_{stage,i}^{worst}$$

Determination of T_D

- Solve for the capacity at state D to iteratively determine T_D from the Toth model

$$x_A - x_D = (x_A - x_C)(\epsilon)$$



RESULTS

Minimum Number of Required Stages

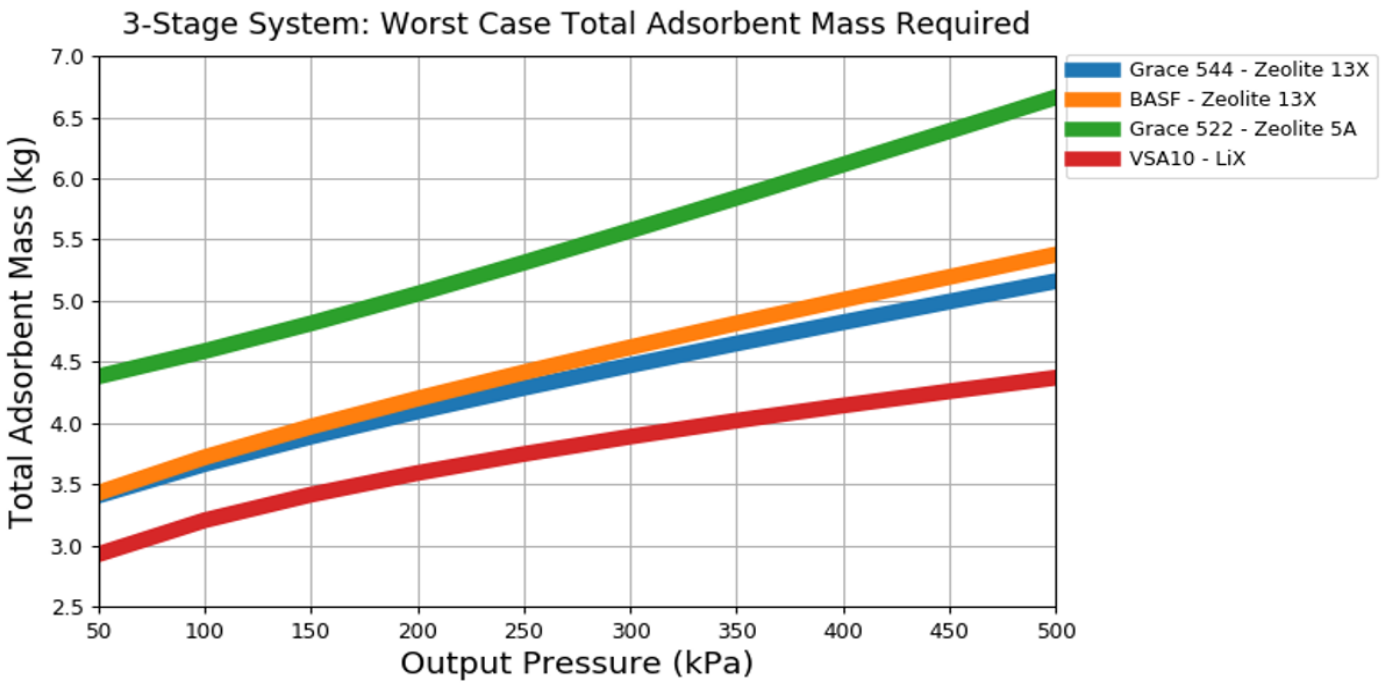
- Since the TSA pump will operate in a varying environment, the amount of sorbent it requires corresponds to its hottest adsorption temperature: 40 ℃

	Worst-Case Total Required Sorbent Mass(kg) for Grace 544 13X								
Output Pressures	$100\ kPa$			$350\ kPa$			$500\ kPa$		
Number of Stages	2 Stage	3 Stage	4 Stage	2 Stage	3 Stage	4 stage	2 stage	3 stage	4 stage
$\boldsymbol{O_2}$ **Only**	4.22	3.67	4.27	16.03	4.65	4.66	137.13	5.16	4.86
$\boldsymbol{O_2}$ **/** $\boldsymbol{CH_4}$	1.34	1.17	1.36	5.10	1.48	1.48	43.61	1.64	1.55

- TSA pump requires a minimum of 3 stages for the high pressure targets
  - 2 stages can be used for below 100 kPa targets using the above sorbent
  - Can reduce the number of stages by increasing the desorption temperature
    - Greatly affects heat exchanger design and increases energy consumption

Sorbent Comparison: Mass

- O_2 only mission, 3-stage configuration results:
  - Grace 522 5A requires the most mass
  - Grace 544 13X and BASF 13X had comparable results
  - VSA 10 LiX requires the least, 0.5 kg – 1.0 kg difference between the 13X sorbents
- Is VSA 10 LiX the most competitive?



Sorbent Comparison: Power Input

	Average Power Required (kW per module) 2-Stage System, $P^{Output} = 350\ kPa$					
Adsorption Temperature	$253.15\ K\ (-20\ ℃)$		$273.15\ K (0\ ℃)$		$293.15\ K\ (20℃)$	
Mission	O_2 / CH_4	O_2 Only	O_2 / CH_4	O_2 Only	O_2 / CH_4	O_2 Only
Grace 544 Zeolite 13X	0.89	2.80	0.97	3.06	1.04	3.26
BASF Zeolite 13X	0.90	2.84	0.98	3.07	1.04	3.25
Grace 522 Zeolite 5A	1.11	3.47	1.08	3.39	1.09	3.43
VSA10 LiX	0.98	3.08	1.07	3.35	1.14	3.57

	Average Power Required (kW per module) 3-Stage System, $P^{Output} = 350\ kPa$					
Adsorption Temperature	$253.15\ K\ (-20\ ℃)$		$273.15\ K (0\ ℃)$		$293.15\ K\ (20℃)$	
Mission	O_2 / CH_4	O_2 Only	O_2 / CH_4	O_2 Only	O_2 / CH_4	O_2 Only
Grace 544 Zeolite 13X	1.33	4.19	1.45	4.56	1.55	4.87
BASF Zeolite 13X	1.36	4.25	1.46	4.58	1.54	4.85
Grace 522 Zeolite 5A	1.68	5.24	1.65	5.18	1.63	5.12
VSA10 LiX	1.47	4.62	1.60	5.01	1.70	5.35

Sorbent Comparison: Worst Mass and Power

- Grace 522 5A performs the worst
  - Requires the most mass and consumes the most energy

Sorbent Comparison for a 3-stage System Meeting the O_2 only Requirement						
Output Pressure	**300 kPa**		**400 kPa**		**500 kPa**	
Comparative Parameters	Worst-Case Total Mass (kg)	Average Power Required (kW)	Worst-Case Total Mass (kg)	Average Power Required (kW)	Worst-Case Total Mass (kg)	Average Power Required (kW)
Grace 544 13X	4.47	5.12	4.82	5.10	5.16	5.08
BASF 13X	4.62	5.07	5.01	5.05	5.38	5.06
Grace 522 5A	5.57	5.09	6.11	5.10	6.66	5.11
VSA10 LiX	3.89	5.64	4.14	5.62	4.37	5.61

- BASF 13X vs VSA 10 LiX
  - Requires 11% less power than VSA 10 LiX, on average
  - Requires 21 % more sorbent than VSA 10 LiX, on average
  - VSA 10 LiX appears to be the “best”
- Large power input: ~5 – 5.5 kW per module

Summary

- 2 Stage system is optimal for low pressure targets
  - Minimum of 3 stages required for $P \geq 350\ kPa$
- Grace 522 5A performed the worst out of the four
  - Required the most mass and power
- 13X sorbents vs VSA 10 LiX
  - 13X sorbents require the least amount of power
  - VSA 10 LiX requires the least amount of mass (~4.3 kg for 500 kPa target)
  - Appears VSA 10 LiX is the most competitive, further analysis required
- Must reduce power input
  - Meeting 350 kPa for the O_2 only case:
    - 2-stage: ~ 2.8 – 3.8 kW
    - 3-stage: ~ 4.0 – 5.3 kW
  - Meeting 500 kPa: ~ 5-5.6 kW per module using a 3-stage system

Conclusion

- Develop/ select better sorbents with:
  - Lower enthalpies of adsorption to reduce power input
  - Higher outputs of CO_2 to reduce the number of stages required to meet the high pressure targets. This also reduces the amount of mass
    - Higher capacities at lower pressures
    - Higher desorption at higher pressures

- Consider recuperation strategies
  - Potential savings in power
    - Locally: Between stages and modules
    - System-Wide: Chemical Plants

References

1. Muscatello, A., Santiago-Maldonado, E., "Mars In Situ Resource Utilization Technology Evaluation", National Aeronautics and Space Administration (NASA), 2012.

2. Muscatello, A., Hintze, P., Meier, A., Bayliss, J., Karr, L., Paley, S., Marone, M., Gibson, T., Surma, J., Mansell, M., Lunn, G., Devor, R., Berggren, M., "Mars Atmospheric In Situ Resource Utilization Projects at the Kennedy Space Center", In Earth and Space 2016 Conference, 2016.

3. Rapp, D., Karlmann, P.B., Clark, D.L., Carr, C.M. "Adsorption Compressor for Acquisition and Compression of Atmospheric CO2 on Mars", 33rd Joint Propulsion Conference and Exhibit, American Institute of Aeronautics and Astronautics (AIAA), 1997.

4. Brooks, Kp., Rassat, SD., TeGrotenhuis, WE., " Devleopment of a Microchannel In Situ Propellant Production System", Pacific Northwest National Laboratory, 2005.

5. "Requirements for ISRU Technology Project Version 0", National Aeronautics and Space Administration (NASA), 2017.

6. "Carbon Dioxide: Temperature – Pressure Diagram", ChemicalLogic Corporation, 1999.

7. Knox, J. , Ebner, A., LeVan, M.D., Coker, R. F., Ritter, J. A., "Limitations of Breakthrough Curve Analysis in Fixed-Bed Adsorption", Industrial & Engineering Chemistry Research, 2016.

8. Incropera, F. P., DeWitt, D. P., Bergman, T. L., Lavine, A. S. "Fundamentals of Heat and Mass Transfer 7E", John Wiley & Sons Inc., 2011. Pg. 929

9. Sanders, G. B., "In-Situ Resource Utilization: Integration, Design, Operation, Development", Presentation to the University of Houston, National Aeronautics and Space Administration (NASA), 2017

Back up

Results: Average Power Required