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

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Abstract

A major component of a Martian In-Situ Resource Utilization (ISRU) system is the CO_2 acquisition subsystem. This subsystem must be able to extract and separate CO_2 at ambient Martian pressures and then output the gas at high pressures for the chemical reactors to generate fuel and oxygen. The Temperature Swing Adsorption (TSA) Pump is a competitive design that can perform this task using heating and cooling cycles in an enclosed volume. The design of this system is explored and analyzed for an output pressure range of 50 kPa to 500 kPa and an adsorption temperature range of -50 ℃ to 40 ℃ while meeting notional requirements for two mission scenarios. Mass and energy consumption results are presented for 2-stage, 3-stage, and 4-stage systems using the following adsorbents: Grace 544 13X, BASF 13X, Grace 522 5A and VSA 10 LiX.

Introduction

The feasibility and success of future Martian missions may become dependent on In-Situ Resource Utilization (ISRU) systems. These systems are able to take resources from the environment and generate products, such as propellant and life-support consumables, to sustain missions involving return vehicles and exploration. An ISRU system, therefore, would reduce mission launch mass, increase mission performance and independence and subsequently reduce costs.

Using CO_2 from the atmosphere and water from the soil, a Mars ISRU system can generate O_2 and CH_4. The CO_2 acquisition system is, therefore, a vital component of the ISRU system and it must reliably operate in an environment characterized by pressures that range from 5 torr to 7 torr and temperatures that may vary from $-125℃$ to $40℃$. To enable proper operation of the chemical reactors that generate O_2 and CH_4, the acquisition system must also compress and provide high purity gas.

Multiple designs, such as a cryocooler[1] and an ionic liquid system[2], have been proposed to serve as this unit. The Temperature Swing Adsorption (TSA) Pump concept is another viable candidate, and it utilizes adsorption and desorption processes to complete its tasks. Adsorption is the process of bonding particles to the surface of a material called an adsorbent, while desorption is the process of freeing those particles. In a TSA pump, these processes are thermally activated as an adsorbent with high selectivity to CO_2 is cooled for extraction at low pressures and subsequently heated in a closed volume to release and compress the gas. As a result, the TSA pump concept requires a minimal amount of moving parts and can run continuously in the Martian environment using an adequate power source.

Multiple TSA pump concepts have been proposed, where Rapp et al. analyzed a system that passively extracts CO_2 during the cool Martian night and then actively outputs high pressure gas during the

warmer Martian days[3]. The Pacific Northwest National Laboratory (PNNL), on the other hand, produced and optimized a TSA concept to meet a 100 kPa target pressure for various temperature conditions using a system that is active during both the extraction and output phases[4].

In this paper, the TSA pump concept will be analyzed for various temperature and output pressure conditions with the work by Rapp et al. and PNNL serving as a basis. In preparation for future designs, preliminary mass and energy calculations will be made in this paper while considering multiple adsorbents for a fully active system that operates continuously. The results of this analysis will provide insights into the design of a TSA pump in order to meet potential requirements proposed by the National Aeronautics and Space Administration (NASA) for a future mission on Mars.

General Description of the TSA Pump

The properties of an adsorbent are dependent on both pressure and temperature, where the material's capacity to adsorb increases with increasing pressure and decreasing temperature. Conversely, the material's capacity to adsorb decreases with decreasing pressure and increasing temperature. Using these characteristics, a Mars TSA pump operates by sufficiently cooling the adsorbent until an appropriate amount of CO_2 is captured and then heating the material in a closed volume to release and compress the gas. Since adsorption is an exothermic process, additional energy must be rejected in order to lower the adsorbent's temperature. In addition, since desorption is the opposite process, an additional input of energy is required to raise the material's temperature to free the CO_2 particles.

Figure 1 describes this operation as an idealized cycle consisting of isobaric and isochoric processes. Starting at state A, the adsorbent is fully saturated with CO_2 and all system valves are shut to create a closed volume for compression. The adsorbent is then heated at a constant volume until the desired output pressure of the CO_2 acquisition system is reached at state B. Afterwards, the system valves open to downstream systems and the pressurized CO_2 is allowed to flow out. To maintain a constant pressure output, the adsorbent is continually heated until the maximum temperature for desorption (known here as the desorption temperature) has been reached at state C.
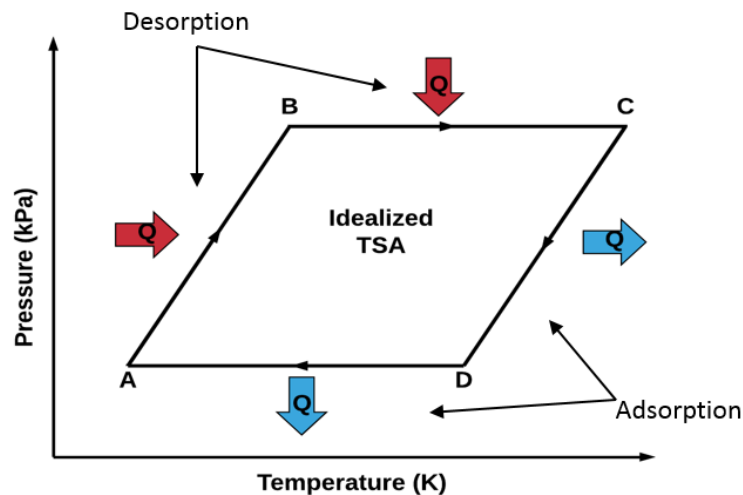

Figure 1: Idealized TSA pump processes represented on a Pressure-Temperature diagram.

Afterwards, the regeneration process begins with the system valves closing and the adsorbent cooling at a constant volume in preparation for adsorption with the atmosphere. Any free gas remaining by the end of state C is readsorbed and any heat released by the adsorption process must be rejected by the heat exchanger. Once state D has been reached, the system valves open once again to the atmosphere and the adsorbent adsorbs until it is fully saturated; thereby closing the cycle. In this paper, the temperature of the adsorbent at state A will be known as the adsorption temperature of the cycle.

The loading profile of an adsorbent is generically represented in *Figure 2*, where it is shown that a majority of desorption generally occurs in process BC and the majority of adsorption occurs in process DA. Depending on the operating conditions and the system design, Process AB can become the main desorption step.
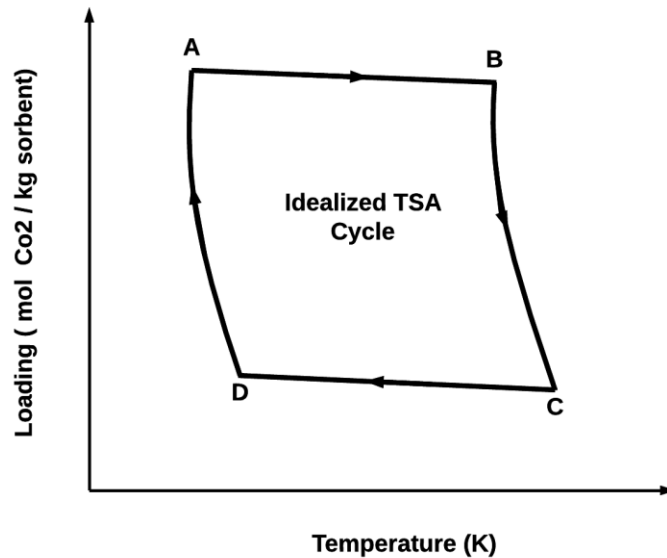

Figure 2: Loading profile of a generic TSA pump.

Mission Requirements and the Range of Operation

There are two scenarios currently proposed by the mission requirements for the ISRU system: 1) generate O_2 only and 2) generate O_2 and CH_4. In the first case, CH_4 is brought from Earth and the chemical plants generate only O_2 using processes like solid oxide electrolysis. In the second case, a hydrogen source is required to generate O_2 and CH_4 using processes like the Sabatier reaction. For the first case, a total mass flow rate of 6.10 kg/hr of CO_2 is required while the second case requires 1.94 kg/hr[5]. The disparity in requirements is reconciled by the fact that the second case requires a hydrogen source in order to generate methane. This hydrogen source can be supplied by water, which can be electrolyzed to generate H_2 and O_2. Since additional amounts of O_2 are being generated, less CO_2 is needed to in order to generate the necessary amounts of O_2 and CH_4.

To meet these mass flow rate requirements, three modules must be designed such that two modules can meet the requirements in the event of a failure. As a result, each module must be designed to produce 3.05 kg/hr, and 0.97 kg/hr for the O_2 only and O_2/CH_4 cases, respectively. Therefore, keeping in mind that two modules are running at the same time, the analysis conducted in this paper will be for

a single module. These requirements are notional and may change in the future depending on upstream and downstream components of the ISRU system.

Since the pressure requirements for the downstream chemical plants have not been fully defined yet, a range of output pressures from 50 kPa (0.50 bar) to 500 kPa (5.00 bar) will be considered. In following the Mars 2020 ERD conditions for worst-case analyses of hardware operation conditions, the TSA pump may be subjected to temperatures varying between -125 °C (148.15 K) and 40°C (313.15 K). It will be assumed that the adsorbents will be cooled to this ambient temperature range; however, the lower end of this range will surely cause the gaseous CO_2 to solidify for the considered target pressure range[6]. Therefore, for the sake of simplicity, an adsorption temperature range of -50 °C (223.15 K) to 40°C (313.15 K) will be considered in this paper; otherwise, more complex design choices will have to be considered. Based on previous analysis on adsorbents, a desorption temperature of 120 °C (393.15 K) will be used for all analyses in this paper. Lastly, an average cycle time of 60 seconds will be used in order to understand the design considerations of a rapid cycle acquisition system.

Adsorbent Mass Calculation

The adsorbents considered in this paper are the following: Grace 544 13X, BASF 13X, Grace 522 5A, and VSA 10 LiX. The Grace and BASF materials are zeolite-based adsorbents while VSA 10 LiX is lithium-based. In order to initially size the TSA system, an appropriate adsorbent model that will predict both an adsorbent's CO_2 capacity and the amount of energy released upon adsorption is required. One popular model used in industry is the Toth model, which is a curve-fit technique that describes an adsorbent's properties as functions of pressure and temperature[7]:

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

(1)

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

(2)

where, x is the equilibrium adsorbent capacity, q_{st} is the isosteric enthalpy of adsorption, a, b and t are curve-fit parameters that are functions of temperature, P is pressure while T is the adsorbent's temperature. The fit parameters used in this paper were provided by James Knox (NASA MSFC) and his group for various adsorbents. The parameters have been validated for pressures ranging from 0.001 kPa to 101.325 kPa and temperatures ranging from 0 °C (273.15 K) to 200 °C (473.15 K). The Toth curve-fits are extended to encapsulate the pressure and temperature ranges considered in this paper for extrapolation.*

Using equation (1), the amount of CO_2 desorbed in moving from state A to state C is given by the following equation:

$$n = x_A - x_C$$

(3)

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*In the early stages of this analysis, 2-site and 3-site Langmuir models were used; however, these models displayed unrealistic isosteric enthalpies of adsorption for high pressures outside of the validated range. Gregory Cmarik (NASA MSFC) compared the behaviors of the Toth and Langmuir models and recommended the Toth model for use in extrapolation.

This equation can also be used to describe the output of a single-stage TSA pump which, as shown in *Figure 3*, has an upper-limit on the output gas pressure. The pressure limit can be shifted upward if the desorption temperature increases; thereby reducing x_c and allowing for more CO_2 to desorb. However, the amount of energy consumed by the system also increases.

Another way to increase the pressure upper-limit is to introduce multiple stages that successively compress the gas to the target pressure. As a result, the difference in pressure between states A and state C are effectively reduced in each stage such that the differences in temperature allow for more effective desorption. Consequently, the minimum desorption temperature to initiate desorption also goes down; thereby reducing the energy cost of a single stage.
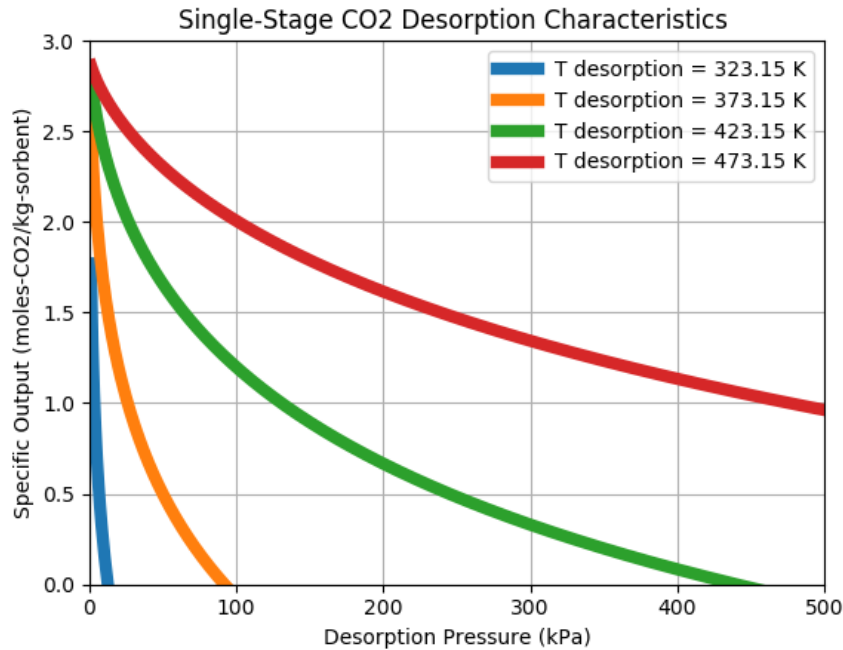

Figure 3: Single-stage desorption characteristics for the Grace 544 Zeolite 13X adsorbent. The adsorption temperature is $0\,°C$.

In adding more stages, the complexity of the system additionally increases as the designer must now choose appropriate inter-stage pressures. If these pressures are not judiciously chosen, then the efficiency of the system plummets as one stage adsorbs more or less than another. The PNNL has shown that the optimal inter-stage pressures are chosen such that the specific output of each stage is the same, which results in each stage having the same amount of adsorbent. The search for optimal inter-stage pressures can be posed as a constraint minimization problem for select adsorption and desorption temperatures, as shown in equation (4). This problem was solved using OpenMDAO's optimization solvers:

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

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

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

(4)

where, n_i represents the amount of CO_2 desorbed in moving from state A to C in the ith stage, and P_i represents the output pressure of the ith stage. A negative sign is added to the objective function so that the maximum specific output is found in order to minimize the required amount of adsorbent. The amount of adsorbent required per stage can now be determined using the required mass flow rates, a transfer efficiency, and a cycle time. For the various operating conditions, the total amount of adsorbent required to meet the O_2 only requirement is plotted in **Figure 4** using the Grace 544 13X adsorbent, the 60 second cycle time, and a transfer efficiency of 95%. A maximum adsorption temperature of 30°C (303.15 K) was chosen for this plot in order to provide a better representation of the TSA pump's output while using a 2-stage, 3-stage and a 4-stage configuration.
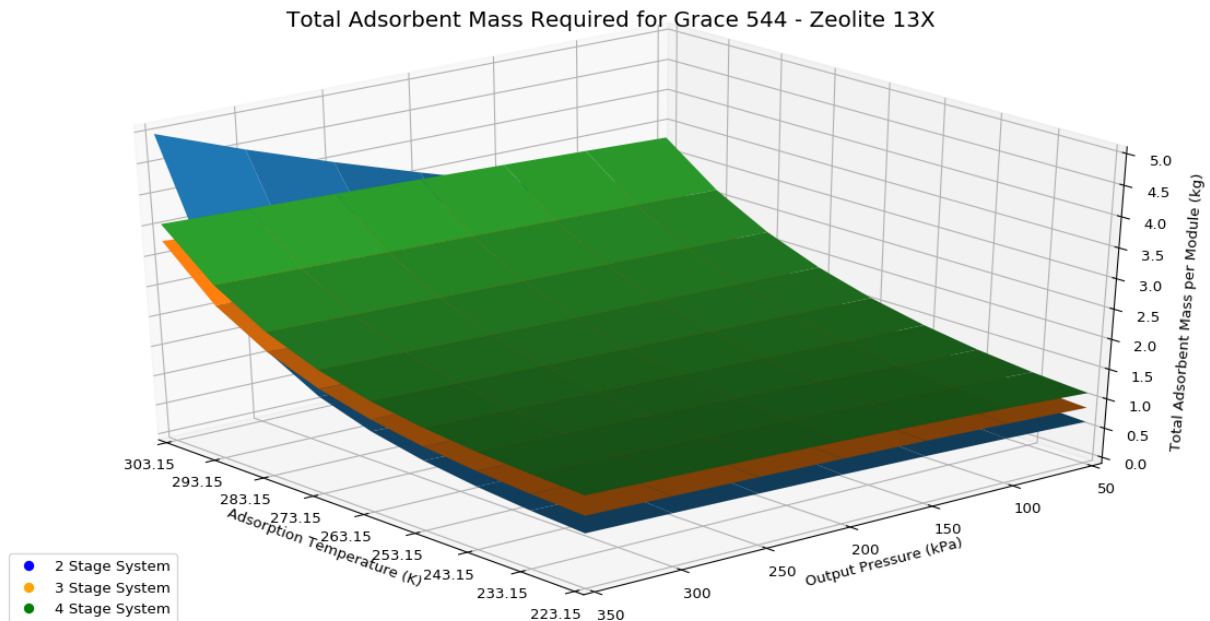

Figure 4: Total required adsorbent required for a Grace 544-Zeolite 13X TSA pump to meet the O_2 *only* requirements.

From **Figure 4** it is apparent that as both the target output pressure and the adsorption temperature increase, more adsorbent is required to meet the mission requirements. In fact, the required amount of adsorbent increases strongly with increasing adsorption temperature because the material adsorbs less (x_A gets smaller) as it gets hotter. As a result, the TSA pump's output pressure limit is further lowered and additional stages must be added in order to meet the target. However, each additional stage brings with it additional hardware mass and thus increases the total system mass; therefore, it is highly desirable to use the least amount of stages to meet the mission requirements.

For each target pressure, therefore, the worst operating condition corresponds to the hottest ambient temperature on Mars, which is 40 °C (313.15 K). Since it is assumed that the adsorbent is cooled to ambient temperature in this analysis, the worst operating condition also sizes the TSA pump. The required total amount of adsorbent corresponding to this temperature condition is tabulated in **Table 1** for select pressures using the Grace 544 13X adsorbent.

Table 1: Worst-Case Total Adsorbent Mass of Grace 544 Zeolite 13X Required for Various Pressures

Output Pressures	Worst-Case: Total Required Adsorbent Mass(kg/module)								
	$100\ kPa$			$350\ kPa$			$500\ kPa$		
Number of Stages	2 Stage	3 Stage	4 Stage	2 Stage	3 Stage	4 stage	2 stage	3 stage	4 stage
O_2 Only	4.22	3.67	4.27	16.03	4.65	4.66	137.13	5.16	4.86
O_2 / CH_4	1.34	1.17	1.36	5.10	1.48	1.48	43.61	1.64	1.55

Table 1 shows that for pressures around 100 kPa, the 2-stage system requires a comparable amount of adsorbent to the 3-stage and 4-stage systems; therefore, a minimum of 2 stages should be used here for the TSA pump. However, in increasing the pressure target, the 2-stage configuration requires so much more mass than the other systems that it makes better sense to use a minimum of 3 stages to feasibly meet the higher target pressures.

To reduce the minimum number of stages, the desorption temperature must either increase or an adsorbent must be selected such that it desorbs more at these operating conditions. Such an adsorbent, therefore, will need to have larger CO_2 capacities at Martian ambient conditions and lower capacities at higher pressures while using lower desorption temperatures. As a result, the adsorbent will extract more CO_2 during adsorption and retain less during desorption; thereby, increasing the amount of gas generated, reducing the size of the system and decreasing the system's energy cost.
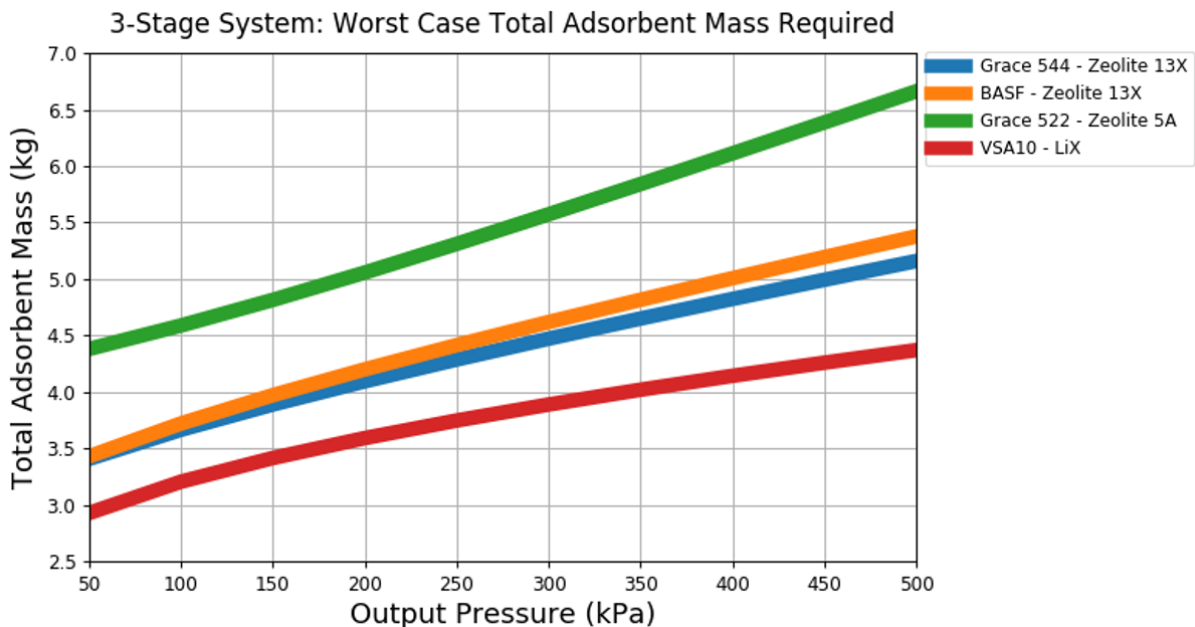

Figure 5: Worst-case adsorbent mass comparison for a 3-stage system to meet the $O_2\ only$ requirement.

The four adsorbents are now compared in *Figure 5* using a 3-stage system, where the total amount of adsorbent required for worst-case operation (per module) is plotted against the target pressure range. According to this plot, the Grace 522 5A adsorbent requires the most mass, which indicates relatively poor adsorption characteristics for the mission. Since the Grace 544 13X and BASF 13X adsorbents are

both Zeolite 13X materials, they show comparable results to each other. The final adsorbent, VSA 10 LiX, requires the least amount of mass and it differs by about 0.5 kg to 1.0 kg with the 13X adsorbents.

Energy Evaluation

With the mass of the adsorbents now known, the amount of energy required to run a TSA cycle can be predicted. In each process shown in *Figure 1*, the energy required is primarily due to the adsorption and desorption of CO_2. Desorption, which takes place in processes AB and BC, is an endothermic reaction that requires an input of energy in order to free adsorbed CO_2 particles. Adsorption, on the other hand, is an exothermic reaction and it occurs during processes DA and AD to bond CO_2 particles to the adsorbent.

In predicting the amount of energy consumed by the TSA pump, it is assumed that the CO_2 gas does no work and that all potential and kinetic differences are negligible for all processes. To simplify the predictions, the thermodynamics of the adsorbent and the casing material are not considered. In addition, it will be assumed that CO_2 behaves like an ideal gas and that adsorption and desorption can be simply treated as energy sources or sinks and that each stage is working simultaneously. Furthermore, it is assumed that the adsorption temperature for all stages of a system is the same. As a result, the gas coming out of each stage will be cooled to the temperature corresponding to state A.

Using **Figure 1** as a guide, the first law of thermodynamics can now be applied to evaluate the amount of energy required for the adsorption and desorption of CO_2:

Process A-B: Isochoric Compression phase

For the compression phase, it will further be assumed that the sensible change in the gas's state can be represented by the simple compression of a gas in a closed volume. As a result, the amount of energy inputted to the system is given by:

$$Q_{in} = (U_B - U_A) + Q_{desorption} \tag{5}$$

Process B-C: Isobaric Desorption

In this phase of the cycle, it will be assumed that the energy pertaining to the sensible change in the state of CO_2 is negligible compared to the energy required for desorption:

$$Q_{in} = Q_{desorption} \tag{6}$$

Process C-D: Isochoric Cooling

Using the same assumption for process A-B, the amount of energy to remove in the preliminary cooling step is given by equation (7). In process C-D, any gas that is readsorbed releases heat that must be rejected by the heat exchanger.

$$Q_{out} = (U_C - U_D) + Q_{adsorption} \tag{7}$$

Process D-A: Isobaric Adsorption

Using the same assumption for process B-C, the amount of energy to remove in this process is given by the following equation:

$$Q_{out} = Q_{adsorption} \tag{8}$$

Cooling of the Output Gas

As mentioned above, the gas at the inlet of each stage is assumed to have the same temperature; therefore, the relatively hot gas outputted from process BC must be cooled down. Since the gas is flowing and it desorbs as the adsorbent is heated, an average enthalpy term $(\overline{\Delta h})$ is used to determine the amount of energy the system must remove:

$$Q_{out} = \overline{\Delta h} \, n \, m_{stage} \epsilon \tag{9}$$

where m_{stage} is the mass of adsorbent per stage and ϵ is the 95% transfer efficiency. The average enthalpy term is represented by the following equation:

$$\overline{\Delta h} = \frac{1}{T_C - T_B} \int_{T_B}^{T_C} (h - h_A) \, dT \tag{10}$$

Where h is the enthalpy of CO_2 as it varies from states B to C, h_A is the enthalpy associated with state A, and T_B and T_C are the temperatures at states B and C, respectively. Equation (10) was solved numerically using Simpson's rule and the enthalpies were taken from ideal gas properties table for CO_2 gas[8].

State Determination

Equations (5) – (10) can be readily applied once the temperatures and pressures at each state are known. Equation (4) and the mission requirements fix the state pressures for each stage, while the adsorption and desorption temperatures (states A and C, respectively) are set by the heat exchanger. As a result, only the temperatures at states B and D need to be determined in order to evaluate the energy usage of this idealized system. Furthermore, the worst-case adsorbent mass will be used to evaluate the performance of the TSA pump. As a result, the optimal inter-stages pressures determined using equation (4) must be reevaluated and new desorption temperatures must be determined for each stage. The new desorption temperatures will be less than or equal to the maximum temperature offered by the heat exchanger, which is 120 °C (393.15 K) in this paper.

Determination of the New Optimal Pressures and Desorption Temperature

Similar to equation (4), the minimization problem in equation (11) is now posed to meet a target CO_2 output with an added temperature constraint. The target CO_2 output is determined by the worst-case stage mass (m_{stage}^{worst}) and the efficiency of CO_2 transfer (ϵ) to the next stage or tank:

$$minimize\ J = \sum_{i=1}^{k}(n_i - n^{target})^2$$

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

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

$$T_i^{desorption} \leq T_{\max}^{desorption}$$

$$n^{target} = \frac{m_{co2}^{required}}{M_{CO_2}\ m_{stage}^{worst}\ \epsilon}$$

(11)

Determination of the Temperature at State B

In moving from state A to state B, CO_2 gas is desorbed into a closed volume. The pressure of the gas can be related to its temperature through the ideal gas law; however, the volume of the enclosure is unknown and there is not enough information to bound the problem. As a result, both the temperature and volume must be iterated upon and a minimum volume of 0.001 m^3 is set as a constraint for the purposes of this analysis. Future research and design will aid the determination of a proper minimum volume. As a result, the determination of the temperature at state B can also be posed as a minimization problem for the multi-stage system:

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

$$subject\ to$$

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

$$T^{adsorption} < T_{B_i} < T^{desorption}$$
$$where\ P^{check} = \frac{N_i R T_{B_i}}{V_i}$$
$$N_i = n_i m_{stage,i}^{worst}$$

(12)

Where P_{check} is the iterated pressure, V_i is the compressible volume of the ith stage, T_{B_i} is the temperature at state B for the ith stage, and N_i is the number of moles of CO_2 desorbed.

Since it is desired for each stage of a system to be the same, equation (12) will determine how much compressible volume each stage requires. The largest volume will then be imposed on each stage of a system, and the ideal gas law will be iterated upon to determine the appropriate temperatures.

Determination of the Temperature at state D

The temperature at state D is determined using two requirements: 1) the free CO_2 gas remaining at the end of state C must be readsorbed and 2) all CO_2 desorbed must be regenerated. As a result, the temperature at state D is readily determined by equation (13). The left side of equation (13) represents

the amount of CO_2 adsorbed from process DA while the right side of the equation represents the amount of CO_2 the adsorbent desorbed from processes AB and BC.

$$x_A - x_D = (x_A - x_C)(\epsilon) \tag{13}$$

Solving the above set of equations for x_D, and then iterating using equation (1) will directly determine the temperature required at state D for each stage.

Results of the Energy Analysis

With all of the necessary states now known, the average power required by the 2-stage, 3-stage and 4-stage systems can be determined using the four different adsorbents.

The average power required by the Grace 544 13X adsorbent is shown in ***Figure 6*** and ***Figure 7***. In ***Figure 6***, the maximum of the output pressure axis is limited to 350 kPa because the two-stage system is either infeasible or sub-optimal past this point. As a result, in an effort to capture the entire pressure range, the power plot in ***Figure 7*** shows only the 3-stage and 4-stage systems. From these plots it is evident that as the adsorption temperature increases, the amount of energy consumed by the Grace 544 13X adsorbent also increases. The primary reason for this is that the adsorbent's isosteric enthalpy of adsorption, as predicted by its Toth model, increases with temperature. This model also predicts that the adsorbent's enthalpy of adsorption decreases with pressure; however, this effect is less pronounced in the figures below.
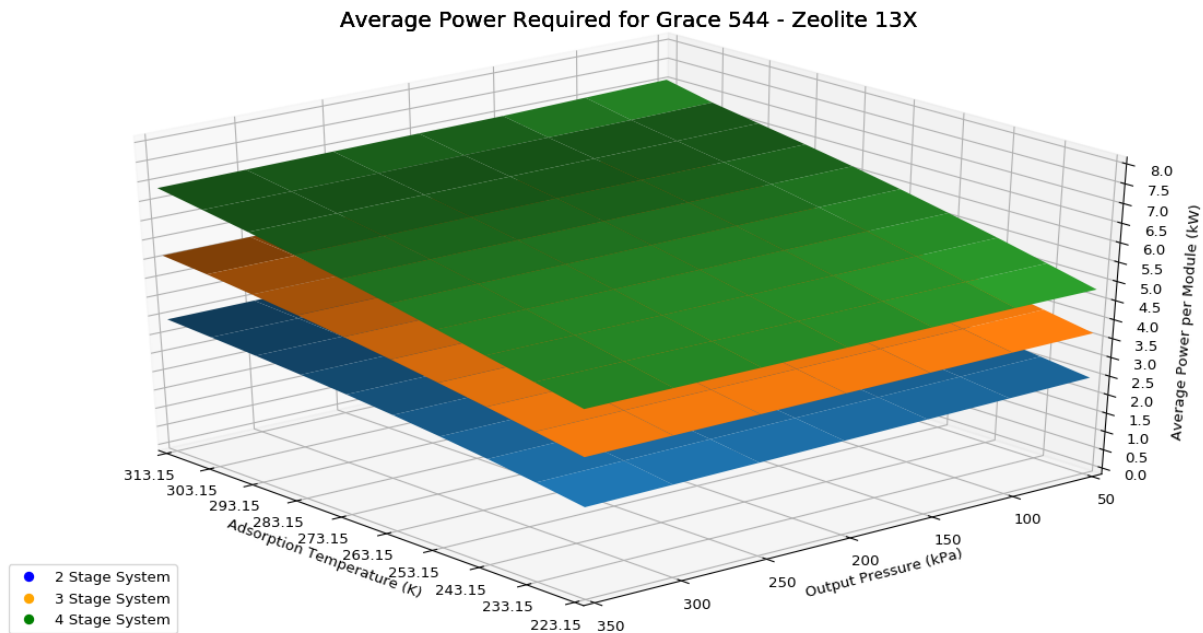

Figure 6: Average power required by the Grace 544 adsorbent to meet the O_2 only requirement. The maximum pressure is limited to show how the 2-stage system performs.
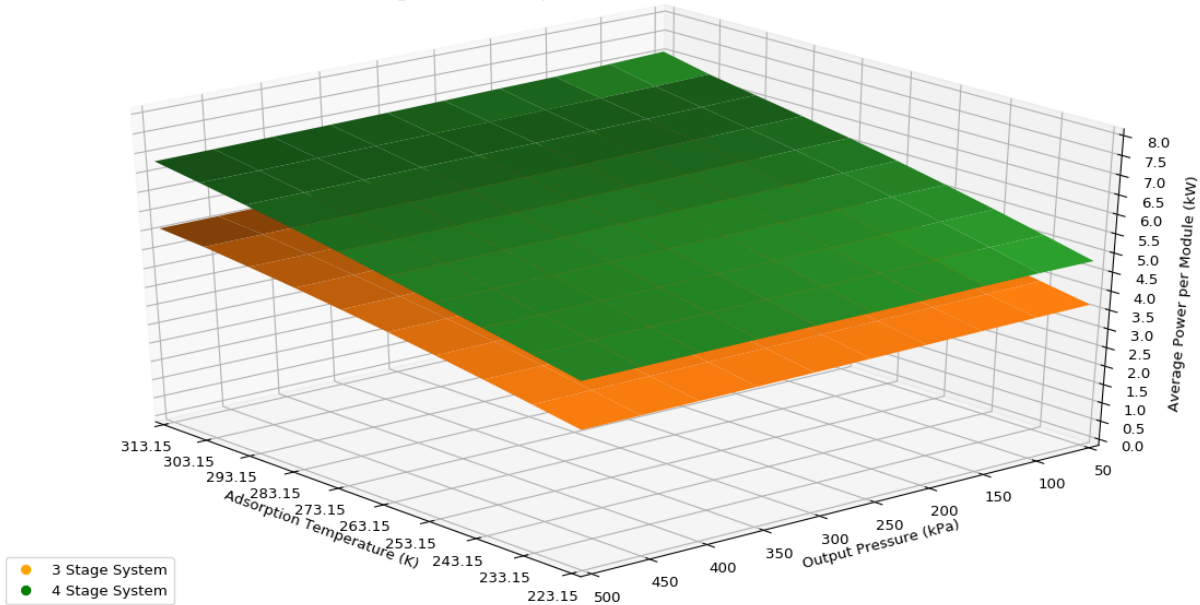
Figure 7: Average power required by the Grace 544 adsorbent to meet the O_2 only requirement. Only the 3-stage and 4-stage configurations are compared for a maximum pressure of 500 kPa.

For the adsorbents considered in this paper, ***Tables 2-4*** show how much power is required to meet a 350 kPa pressure requirement. Select adsorption temperatures were chosen to show how the adsorbents operate in "hot" and "cold" ambient temperatures. In each table, the adsorbent that requires the most power is highlighted in pink while the adsorbent that requires the least amount is highlighted in grey. From these tables, it is readily apparent how desirable it is to reduce the number of stages in a system – not only does the total system mass increase, but the amount of power required by the system greatly increases with increasing stage count.

Table 2: Average power input of a 2-stage system for $P^{Output} = 350\ kPa$.

	Average Power Input (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

Table 3: Average power input of a 3-stage system for $P^{Output} = 350\ kPa$.

Adsorption Temperature	Average Power Input (kW per module) 3-Stage System, $P^{Output} = 350\ kPa$					
	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

Table 4: Average power input of a 4-stage system for $P^{Output} = 350\ kPa$.

Adsorption Temperature	Average Power Input (kW per module) 4-Stage System, $P^{Output} = 350\ kPa$					
	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	1.77	5.55	1.92	6.04	2.06	6.47
BASF Zeolite 13X	1.80	5.64	1.93	6.07	2.05	6.45
Grace 522 Zeolite 5A	2.26	7.00	2.22	6.92	2.19	6.84
VSA10 LiX	1.96	6.15	2.12	6.67	2.27	7.12

For the temperature ranges considered in *Tables 2-4*, the Grace 522 5A adsorbent requires the most power until higher temperatures cause the VSA 10 LiX adsorbent to require more. The 13X adsorbents actually require the least amount of power and they have similar values to each other. Since the Grace 522 5A adsorbent already requires the most mass for the target pressures considered in this paper, it is therefore the worst performing adsorbent in this paper. This is further reinforced by *Table 5*, where the worst-case total masses and the average power required are tabulated for the higher pressure targets using a 3-stage configuration. Here, the Grace 522 5A adsorbent has comparable values of power to the 13X adsorbents, however the significant difference in mass makes it the least competitive.

Between the three other adsorbents, the VSA 10 LiX requires the most power; however, it also requires the least amount of mass. As shown by *Figure 5*, the difference in total mass between these adsorbents is around 0.5 kg for the lower target pressures. This difference increases to around 1.0 kg for a target pressure of 500 kPa; therefore, it is not entirely evident which material is the best performing out of the four because the thermodynamics of the adsorbents and the pump hardware have been neglected in this analysis. For the 2 stage case in *Table 2*, the differences in power input for the O_2/CH_4 mission may be comparable enough to assert that the VSA 10 LiX performs the best; however, further analysis is required to make a conclusive decision.

In meeting the high pressure targets, the amount of power required by a single TSA pump is substantial. For a target pressure of 350 kPa, a TSA pump can require anywhere from 2.80 kW to about 7.12 kW of power to meet the O_2 only requirements depending on the adsorbent used and the number of stages in a pump. As mentioned before, it is desirable to use the least amount of stages not only because the

total system mass decreases but the total power input also decreases significantly. However, this cannot be done unless a better adsorbent is either selected or developed. Such a material will adsorb more CO_2 at lower pressures and be able to desorb more at the target pressures. Since the adsorption and desorption processes constitute a majority of the energy cost, a direct reduction can also be made by selecting an adsorbent with smaller enthalpies of adsorption.

Table 5: Average specific power input by the 3-stage in order to meet the O_2 only requirements

Output Pressure	300 kPa		400 kPa		500 kPa	
Comparative Parameters (per module)	Worst-Case Total Mass (kg)	Average Power Input (kW)	Worst-Case Total Mass (kg)	Average Power Input (kW)	Worst-Case Total Mass (kg)	Average Power Input (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

Conclusion

In this analysis, four adsorbents were analyzed for various pressure and temperature conditions using a TSA pump concept. Using the works by Rapp et al. and PNNL as a guide, the optimal inter-stage pressures for 2-stage, 3-stage and 4-stage systems were determined in order to meet the mission requirements and to determine the total adsorbent mass required by each configuration. For all four adsorbents, it was found that a 2-stage system would either be infeasible or sub-optimal for high pressure requirements like 500 kPa. To appropriately meet these high target pressures, the designer would need to increase the stage count of the system to increase effective desorption. However, the total system mass will increase as additional hardware is incorporated into the system. In the latter part of this paper, the average power required to run the multi-stage configurations was also determined and compared for each adsorbent using an idealized cycle consisting of isobaric and isochoric processes.

From the comparison study, it was found that the VSA 10 LiX adsorbent required the least amount of mass while the Grace 522 5A adsorbent required the most to meet the mission requirements. In addition, it was found that the Grace 544 13X and BASF 13X adsorbents required the least amount of power while the Grace 522 5A and VSA 10 LiX adsorbents required the most. Since the Grace 522 5A adsorbent already requires the most mass for the range of operation, it performs the worst out of the four. Although the VSA 10 LiX adsorbent has the highest power input, it may still perform better than the 13X adsorbents depending on its thermodynamics. As a result, further analysis is required in order to conclusively determine which material is the most competitive.

As seen by *Tables 2-5*, the adsorbents considered in this paper require substantial power in order to meet the mission requirements. Since this paper's analysis only encompasses an idealized case describing adsorption and desorption processes, the actual power required by the TSA pump will be larger. The cycle time, for example, affects the amount of adsorbent required and, therefore, the total

system mass. As the cycle time increases, the amount of adsorbent and system hardware also increases; thereby, introducing additional parasitic mass that will increase energy costs and also affect the performance of the heat exchanger. Nevertheless, this paper shows that adsorption and desorption processes are highly energy intensive and significant effort must be made to make the TSA pump more feasible for a Mars ISRU system. As shown above, one way to directly reduce energy costs is to select adsorbents with lower enthalpies of adsorption. Further reductions can be made by selecting adsorbents with characteristics tailored for a mission on Mars. Such adsorbents will extract more CO_2 at lower pressures and retain less particles at higher pressures while using lower desorption temperatures. This results in a system with lower energy consumption and with higher effective desorption rates than the ones considered in this paper. In addition, these adsorbents will allow the TSA pump to meet higher pressure targets using lower stage counts; thereby, reducing the total system mass and the required power input.

Future Work

In this paper, we looked at a system level cycle analysis dealing with CO_2 mass requirements for a proposed TSA pump. We acknowledge that a more detailed component modeling description needs to be performed. A Thermal Desktop / Sinda / Fluint model is currently being developed which describes the TSA pump as a transient, one-dimensional system. This will incorporate all of the major adsorption and heat transfer physics present in the TSA pump, but still allow rapid analysis (desktop level computer). Many assumptions made in this paper will be revisited in the thermal desktop analysis and further analysis involving the TSA cycle time and other design parameters will be conducted to help characterize and size a Mars TSA pump. We are assuming, at this time, three-dimensional, Computational Fluid Dynamics (CFD) analysis (cluster / supercomputer level) will only be needed to answer questions about heat transfer working fluid flow uniformity and Mars atmospheric air inflow within the TSA pump.

In an effort to reduce energy costs, recuperation strategies that take advantage of the TSA pump's thermally activated processes will be studied. Local strategies between different modules and stages, as well as system-wide strategies involving other subsystems of the ISRU system will be explored. There is high potential for power saving on the entire ISRU oxygen (and or fuel) plant thermal budget as the chemical plants that generate the chemical products are similarly energy intensive.

Acknowledgements

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Nomenclature

Parameter	Description
P	Pressure (kPa)
P_i	The ith stage output pressure (kPa)
P^{Output}	Output Pressure (kPa)
P^{Mars}	Martian Ambient Pressure (set to 7 torr)
T	Temperature (K)
T_A, T_B, T_C, T_D	Temperature at State A,B,C, and D, respectively
$T^{adsorption}$	Adsorption Temperature (K)
$T^{desorption}$	Desorption Temperature (K)
x_A, x_B, x_C, x_D	Adsorptive capacity (moles-CO_2/kg-sorbent) at states A, B, C, and D, respectively
R	Universal Gas Constant (J/(mol-K))
V	Compressible Volume (m^3)
ϵ	Efficiency of CO_2 transfer out of a stage (e.g. 95% transferred to the next stage)
$Q_{desorption}$	Energy due to desorption (kJ)
$Q_{adsorption}$	Energy due to adsorption (kJ)
Q_{in}	Heat flowing into a system (kJ)
Q_{out}	Heat flowing out a system (kJ)
U	Internal Energy (kJ)
h	Specific enthalpy (kJ/mol)
$\overline{\Delta h}$	Average Change in Enthalpy (kJ/mol)
u	Specific internal energy (kJ/mol)
J	Objective Function
n	Amount of CO_2 desorbed in moving from state A to state C (mol/kg-sorbent)
n^{target}	Target amount of CO_2 to desorb (mol/kg-sorbent)
N	Moles CO_2 (moles)
M_{CO_2}	Molecular Weight of CO_2 (kg/kmol)
$m_{co2}^{required}$	Required CO_2 throughput (kg/cycle)
m_{stage}^{worst}	Worst-Case stage mass (kg)
m_{stage}	Adsorbent mass in a single stage (kg)
a, b, t	Toth model curve-fit parameters
$q_{desorption}$	Specific Energy due to desorption (kJ/mol)
$q_{adsorption}$	Specific Energy due to adsorption (kJ/mol)
q_{st}	Isoteric Heat of Adsorption (kJ/mol)

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