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A Thermodynamics Analysis for Improvement of Carbon Dioxide Removal Technologies for Space

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The carbon dioxide removal assembly (CDRA) has been used for the past two decades to continually remove carbon dioxide (CO_2) as part of the air revitalization system onboard the international space station (ISS). The CDRA is an adsorption-based system that relies on sorbent materials that require a significant energy input to be thermally regenerated. Additionally, the system faces challenges in reliability and size/weight, so it is being re-evaluated for viability beyond-low-earth-orbit missions. The CDRA removes CO_2 from the cabin air through a cyclical adsorption-desorption process that uses four molecular sieve beds. The main components include two desiccant beds to remove H_2O, two CO_2 zeolite sorbent beds, an air blower, two resistive heaters, and a cooling heat exchanger. Past studies on the CDRA primarily focus on predictive physics-based modeling of the sorbent beds to understand reliability, performance, and sorbent kinetics, with very few performing a thermodynamic analysis of the entire system. This study aims to improve the understanding of component-level losses of the CDRA using exergy destruction analysis and to quantify the losses. We developed a thermodynamics black-box model using a first and second law balances over each individual component over one operational cycle. The results indicate that the molecular sieve sorbent beds are major contributors to lost work within the CDRA. However, the total exergy destruction in the desiccant beds is greater than the sorbent beds. This indicates that the desiccant beds are the largest contributor of losses. Removing water prior to the removal of CO_2 from the flow stream is a necessary step because the zeolite sorbent will preferentially adsorb water. Our findings motivate the use of alternative components that may offer direct separation of water at higher efficiencies.

Nomenclature

$\tilde{e}$	=	Specific Exergy [kJ/kg]
$\tilde{E}_d$	=	Exergy Destruction [kW]
e	=	Specific Energy [kJ/kg]
h	=	Specific Enthalpy [KJ/kg]
s	=	Specific Entropy [kJ/kg-K]
$\dot{Q}$	=	Heat Transfer [kW]
$\dot{W}$	=	Work [kW]
$\dot{\sigma}_{gen}$	=	Entropy Generation [kJ/kg-K]
P	=	Pressure [kPa]
$\dot{m}$	=	Mass Flow Rate [kg/s]
V	=	Volume [m^3]
t	=	Time [s]
T	=	Temperature [°C]
Subscripts		
cv	=	Control Volume
0	=	Reference
b	=	Boundary

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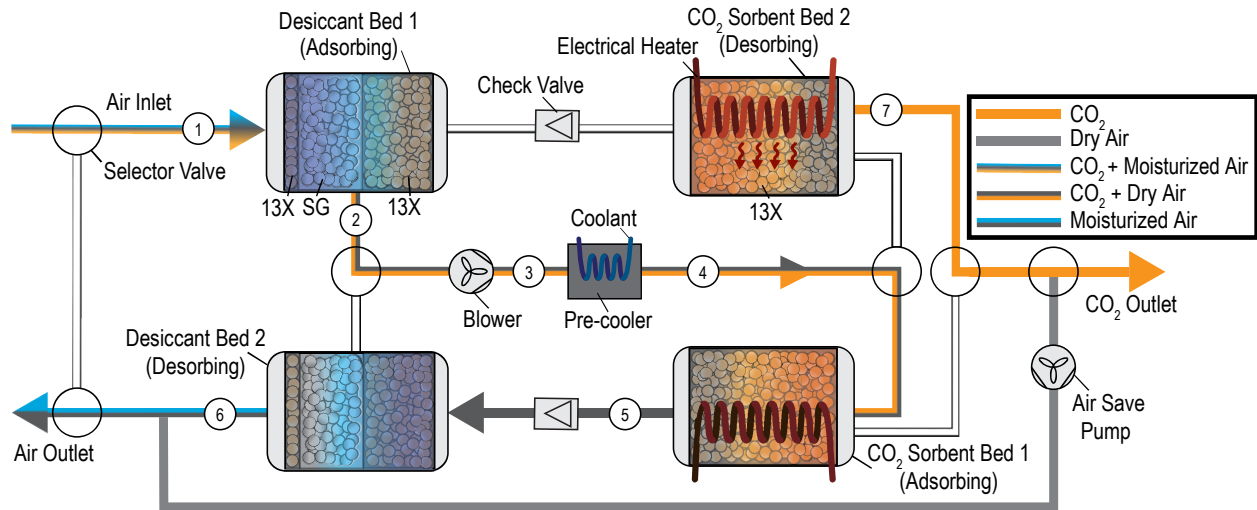[§]Assistant Professor, School of Mechanical Engineering.

Fig. 1 Schematic diagram of the Carbon Dioxide Removal Assembly (CDRA) operation in one half-cycle. (State 1-2) Air from the cabin enters the through the desiccant bed (adsorbing) where water is adsorbed with the silica gel (SG) and molecular sieve beads (Zeolite 13X). (State 2-4) The heated dry air proceeds to the blower and pre-cooler unit where the temperature of the stream is reduced. (State 4-5) The cooled dry air travels to the CO_2 sorbent bed (adsorbing) where CO_2 is adsorbed from the stream with molecular sieve beads. (State 5-6) The desiccant bed (desorbing) then adds water that was adsorbed in the previous half-cycle back into the stream. The CO_2-free air the exits the CDRA to be returned to the cabin. (State 7) At the same time of the CO_2 adsorption from State 1 to 6, the CO_2 sorbent bed (desorbing) is heated to break the bonds of CO_2, N_2, and O_2 from the molecular sieve. CO_2 exits out of the CDRA to the space vacuum (CO_2 outlet). Afterward, the beds flip roles between adsorbing and desorbing in the next half-cycle. The inactive pipes are used for the next half cycle when the desiccant and sorbent beds alternate functions.

I. Introduction

On the International Space Station (ISS), astronauts have the responsibility of conducting research and experiments within the micro-gravity environment and performing maintenance. The ISS is an orbiting research facility that uses carbon dioxide (CO_2) removal technologies for air revitalization to keep astronauts alive. Being exposed to high levels of CO_2 (>5000 ppm) can cause drowsiness, unconsciousness, and impair cognitive functions, which can put astronauts in life-risking situations [1]. The carbon dioxide removal assembly (CDRA) uses a sorbent-based four-bed molecular sieve technology and has been continuously removing CO_2 in the ISS for over 20 years [2]. The system consists of two desiccant beds, two sorbent beds, a blower, a pre-cooler unit, and electrical heaters (Fig. **??**). In one cycle of operation of the CDRA, all the beds will have dual roles and switch from adsorbing to desorbing functions half-way through the cycle. The CDRA thereby continuously operates in half-cycles of 144 min each to remove CO_2 from the cabin atmosphere and vent it to space [2].

Current research efforts for CO_2 technologies are focused on improving sorbent-based technologies [3–5] and a few are exploring other methods such as carbon capture via deposition [6] and ionic liquid-based scrubbers [7]. Research efforts for the CDRA have generally consisted of performance testing of flight hardware operation and performance [2]. Other fundamental studies have focused on understanding and improving sorbent kinetics, performance, and durability [8–12]. Theoretical studies have focused constructing a predictive models of adsorption in the sorbent bed using multi-physics transport simulations [12–14]. In comparison, very few studies have performed thermodynamic analyses of the system. Chow et al. [15] conducted an exergy-based analysis of the environmental control and life support system (ECLSS) aboard the ISS with focus on the oxygen generation assembly (OGA) electrolyzer. Among the subsystems of the ECLSS, the CDRA was included in the analysis. The authors concluded that the OGA was the largest contributor of losses in the air revitalization subsystem, with CDRA being the next largest. This study aims to provide a detailed component-level thermodynamics analysis of the CDRA to help guide innovation in CO_2 removal technologies, especially for future interplanetary travel.
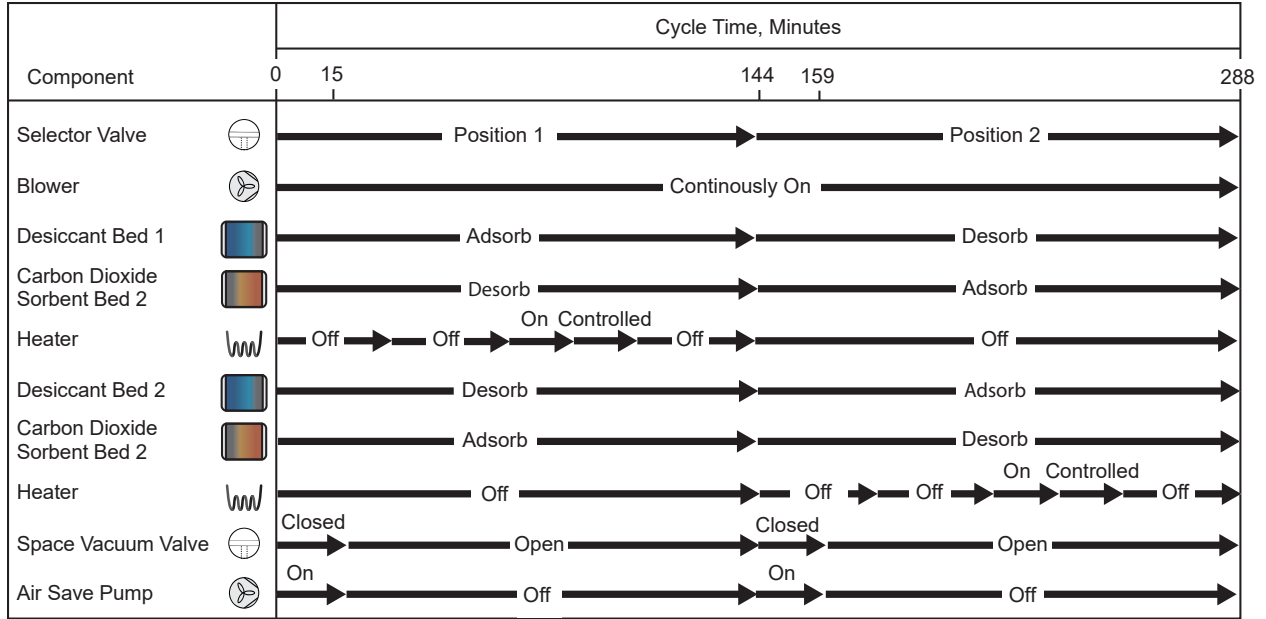
Component		Cycle Time, Minutes					
		0 15		144 159			288
Selector Valve	⊝	Position 1 →→		Position 2 →→			
Blower	⊗	Continuously On →→					
Desiccant Bed 1	▮	Adsorb →→		Desorb →→			
Carbon Dioxide Sorbent Bed 2	▮	Desorb →→		Adsorb →→			
Heater	⟋⟍	Off → Off → On Controlled → Off →		Off →→			
Desiccant Bed 2	▮	Desorb →→		Adsorb →→			
Carbon Dioxide Sorbent Bed 2	▮	Adsorb →→		Desorb →→ On Controlled → Off →			
Heater	⟋⟍	Off →→		Off → Off → On Controlled → Off →			
Space Vacuum Valve	⊝	Closed → Open →→		Closed → Open →→			
Air Save Pump	⊗	On → Off →→		On → Off →→			

Fig. 2 Component operation of the Carbon Dioxide Removal Assembly (CDRA) over a full cycle (Modified from Reference [16]).

II. Modeling Approach

In this section, we discuss the CDRA operation in detail and the thermodynamics basis for the model. We use a black box modeling approach where we apply an exergy balance, derived from the first and second laws of thermodynamics, to the find exergy destruction. A set of general equations are derived that can be applied to each of the components.

A. CDRA Component Operation

The CDRA operates in half-cycles of 144 min and completes 10 cycles every 24 hours. It is made up of four fixed-bed molecular-sieve adsorbers that function using temperature and pressure swing adsorption [17]. All of the previously described components in Fig. 1 have operational functions that vary depending on the half cycle. A detailed timeline of the functions of each component is shown in Fig. 2. During one half-cycle, for instance from 0-144 min, two beds are adsorbing H_2O (Desiccant Bed 1) and CO_2 (Carbon Dioxide Sorbent Bed 1) while the other two beds (Desiccant Bed 2; Carbon Dioxide Sorbent Bed 2) are desorbing the species that were adsorbed in the previous half-cycle. The beds switch roles every half-cycle. Fig. 1 colors the air streams based on the species content during the first half cycle from Fig 2. The flow first passes through the adsorbing desiccant bed where all of the moisture content is adsorbed. The temperature of the flow rises as a result of the heat of adsorption. The flow is moved along by a blower into the pre-cooler where the flow is cooled down prior to passing through the adsorbing CO_2 bed. This step increases the efficiency of the CDRA by reducing the process air temperature [2]. Finally, prior to returning to the cabin atmosphere, the flow passes through the desorbing desiccant bed that was adsorbing in the previous half-cycle. At the beginning of the cycle, all of the CO_2 is adsorbed which results in a nearly CO_2-free stream being returned to the cabin. Toward the end of the half-cycle, breakthrough may occur, which is when the adsorbed gas begins to appear at the bed outlet [12], leading to small traces of CO_2 being returned to the cabin.

B. Thermodynamic Modeling

1. Thermodynamic Basis

Exergy was used to quantify the losses of each component of the CDRA. Exergy is a useful property to quantify the available energy and work a system can perform [18]. Exergy destruction represents the lost potential work or exergy destroyed. It is used to identify the areas and magnitudes of lost or wasted energy within the system. A blackbox thermodynamic model was used to apply an exergy balance over each component as its own control volume, as shown
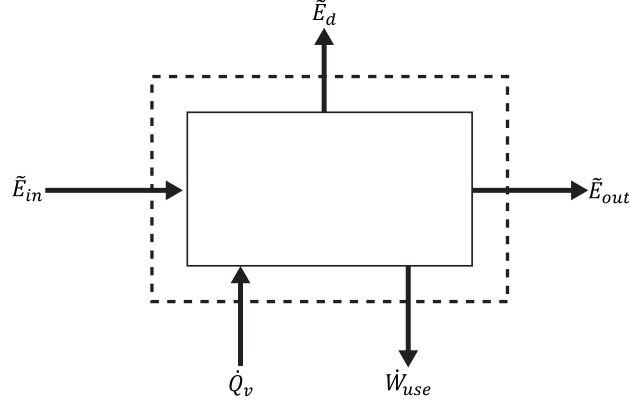
Fig. 3 Exergy, $\tilde{E}_d$, balance over a control volume showing exergy in and out, exergy destroyed ($\tilde{E}$), heat input ($\dot{Q}_v$), and useful work out ($\dot{W}_{use}$).

in Fig. 3 . The exergy balance was derived from the first and second laws of thermodynamics for an open system and used to find the exergy destruction. The first law of thermodynamics for an open system is

$$\frac{dE_{cv}}{dt} = \dot{Q} + \dot{W} + \sum_{inlet} \dot{m}\left(h + \frac{u^2}{2} + gz\right) - \sum_{outlet} \dot{m}\left(h + \frac{u^2}{2} + gz\right) \tag{1}$$

where E is the energy transfer across the control volume (cv), $\dot{Q}$ and $\dot{W}$ are rate of heat transfer and work, respectively, h is specific enthalpy, $u^2/2$ and gz, are specific kinetic energy and potential energy, respectively. The second law of thermodynamics is given by

$$\frac{S_{cv}}{dt} = \frac{\dot{Q}}{T_b} + \dot{\sigma}_{gen} + \sum_{inlet} \dot{m}s - \sum_{outlet} \dot{m}s \tag{2}$$

where s is the specific entropy, $\dot{\sigma}_{gen}$ is the rate of entropy generation, and T_b is the temperature at the boundary. The exergy balance is then derived by combining Eqn. 1 and Eqn. 2 and is given by

$$\frac{\tilde{E}_{cv}}{dt} = \left(1 - \frac{T_0}{T_b}\right)\dot{Q}_{cv} + \left[\dot{W}_{cv} + P_0\frac{dV_{cv}}{dt}\right] - \tilde{E}_d + \sum_{in} \dot{m}_{in}\tilde{e}_{f,in} - \sum_{out} \dot{m}_{out}\tilde{e}_{f,out} \tag{3}$$

where $\tilde{E}$ is the exergy, P_0 is the reference pressure, T_0 is the reference temperature, dV_{cv}/dt is the time rate of change of system volume, $\tilde{E}_d$ is the exergy destruction, and $\tilde{e}_f$ is the specific flow exergy given by,

$$\tilde{e}_f = (h - h_0) - T_0(s - s_0) + \frac{u^2}{2} + gz \tag{4}$$

Where h_0 and s_0 are the reference enthalpy and entropy, respectively. By combining Eqn. 2 and 3, the exergy destruction, $\tilde{E}_d$ can also be expressed in terms of the entropy generation,

$$\tilde{E}_d = T_0\dot{\sigma}_{gen} \tag{5}$$

The simplifying assumptions are as follows: steady-state operation, constant heat of adsorption, neglect changes in kinetic and potential energy, adiabatic beds (perfectly insulated), state points averaged over one half-cycle, constant moles adsorbed, and no breakthrough. Applying the simplifying assumptions, the equations reduce to an expression for the exergy destruction specific to each component type, as introduced in the following section.

C. Component Specific Exergy Destruction Equations

The thermodynamics basis is used to generate general equations to find the exergy destruction for the adsorbing beds, desorbing beds, blower, and the pre-cooler. The general form of the exergy destruction for the adsorbing beds is given by

$$\tilde{E}_{d,bed} = T_0 \left(\frac{\sum_{outlet} (m_i s_i)_{@T_{outlet}} - \sum_{inlet} (m_i s_i)_{@T_{inlet}} + \frac{\dot{Q}_{lat,i}}{T_b}}{t_{hc}} \right) \tag{6}$$

where i indicates the species (either H_2O, CO_2, N_2, or O_2), m is the mass, $\dot{Q}_{lat}$ is the latent heat of adsorption, and t_{hc} is the duration of one half-cycle. The entropy, s, is evaluated at the corresponding inlet or outlet temperature (T_{inlet} and T_{outlet}, respectively). Prior to desorption of the CO_2 beds the air save pump is operated for a short amount of time to return any excess air (N_2 and O_2) back into the cabin. We neglect the air save pump and consider only the work input from heating the CO_2 sorbent bed. The exergy destruction for the desorbing CO_2 sorbent beds is given by

$$\tilde{E}_{d,CO_2} = \dot{W}_{cv} \tag{7}$$

where $\dot{W}_{cv}$ is the heat applied by electric heaters to increase the bed temperature and thereby the rate of desorption of the CO_2 molecules from the sorbent bed. Because there is no adsorption in the blower, the mass term can be pulled out of the summation to yield the expression for exergy destruction as

$$\tilde{E}_{d,blower} = T_0 m \ \frac{\sum_{outlet} (s_i)_{@T_{outlet}} - \sum_{inlet} (s_i)_{@T_{inlet}}}{t_{hc}} \tag{8}$$

A heat exchanger relationship is used for the pre-cooler [18],

$$\tilde{E}_{d,pre-cooler} = \dot{m}_{air} \left[(h_{inlet,air} - h_{outlet,air}) - T_0 (s_{inlet,air} - s_{outlet,air}) \right] +$$
$$\dot{m}_{coolant} \left[(h_{inlet,coolant} - h_{outlet,coolant}) - T_0 (s_{inlet,coolant} - s_{outlet,coolant}) \right] \tag{9}$$

where the subscript *air* refers to the process air flow within the CDRA and the subscript *coolant* refers to the fluid in the pre-cooler used to cool down the process air flow. The coolant used in the CDRA is water. The inlet and outlet of each component is treated as a state point with a fixed temperature and pressure values obtained from literature, summarized in Table 1.

Table 1   Temperature and partial pressure at each state point for one half-cycle.

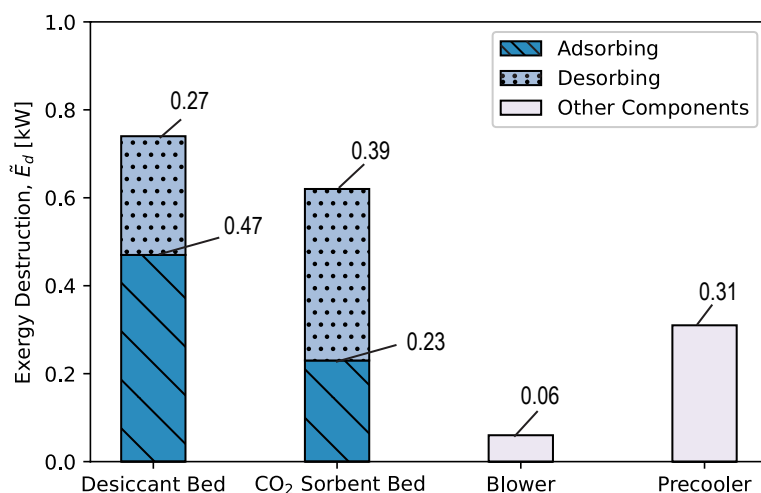| State Point	1	2	3	4	5	6
T [$°C$]	10 [16]	29 [13]	35 [16]	10 [13]	29 [13]	30 [16]
P_{CO_2} [kPa]	0.71	0.71	0.71	0.71	-	-
P_{Air}	85.56	85.56	85.56	85.56	85.56	85.56
P_{H_2O}	24.8	-	-	-	-	24.8

Fig. 4 Exergy destruction of the Carbon Dioxide Removal Assembly (CDRA) components.

III. Results and Discussion

The results of the exergy destruction analysis of each component is shown in Fig. 4. The molecular sieve beds contribute most of the lost work of the system. We further conclude that the desiccant beds together have the highest total exergy destruction. This is explained by water having a higher heat of adsorption than CO_2. (40 kJ/mol for CO_2 and 55 kJ/mol for water [13]). The heat of adsorption is affected by the intermolecular forces between the adsorbate (molecules being adsorbed) and adsorbent (the molecular sieve) [19]. Water has a greater interaction strength with the molecular sieve compared to CO_2, and thus would release more energy. Because the thermodynamic model used fixed-state temperatures, it is highly affected by temperature rises within the system. Water removal is a necessary step because the CO_2 sorbent bed would otherwise preferentially adsorb water over CO_2 due to the molecules being similar in diameter [20]. If any water molecules pass through to the CO_2 sorbent bed, it will decrease the effectiveness of the CDRA. If the sorbent selectivity to CO_2 could be improved to reduce the need for desiccant beds, it would significantly improve CDRA performance. In summary, water adsorption is the largest destroyer of exergy owing to a high heat of adsorption, but is a necessary air stream pre-treatment for sorbent-based CO_2 removal from the cabin atmosphere. This motivates the use of alternative components that may offer direct separation of water at higher efficiencies.

IV. Conclusion

In this study, a thermodynamic model of the carbon dioxide removal assembly (CDRA) was developed to understand and quantify the main sources of component-level losses, so as to help guide innovations and future improvements within the system and CO_2 capture technologies in general. A black-box modeling approach was used and each component was treated as its own control volume. Exergy destruction (or lost work), derived from the first and second law of thermodynamics, was calculated for each of the following components: desiccant beds, CO_2 sorbent beds, a blower, and a pre-cooler. It was found that the desiccant beds were the major source of lost work in the system. This can be explained by water having a higher heat of adsorption than CO_2 and the thermodynamic model being dependent on state-point temperatures. However, water removal is a necessary step because the sorbent material will preferentially adsorb water over CO_2. Dramatic energy savings are possible if water vapor can be removed more efficiently, or if adsorbents can selectively remove CO2 without absorbing water. The model could be improved by accounting for transient changes in heat and mass transfer of the beds, as well as quantifying exergy destruction as a function of CO_2 levels throughout the day.

Acknowledgments

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