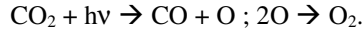


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**Introduction:** One of the critical challenges of human Mars missions is the need for in situ resource utilization (ISRU), in particular oxygen and hydrogen, for consumables (including life support) and for propellant. The Mars Design Reference Architecture further anticipates two main options for human-scale activities: solar and nuclear fission. An additional option, the use of large-scale (1–5 kWe) radioisotope power systems (RPSs) is also considered for backup power needs, as well as for surface transportation applications.

In this paper we evaluate through models and experiments the feasibility of "mining" the Mars atmosphere for oxygen *and* for energy. In particular, we focus on what we envision as the most challenging step: the initial concentration of oxygen and carbon monoxide from minute atmospheric levels to a pressure of 1–10 kPa.

**Background:** Molecular oxygen (O<sub>2</sub>) and carbon monoxide (CO) on Mars results primarily from the solar photolysis of CO<sub>2</sub> (95% of the atmosphere by volume):



The resulting O<sub>2</sub> and CO steady-state concentrations are ~0.16% and 0.06%, respectively. Assuming separation at 200 K, the minimum theoretical extraction work is  $W_{\text{O}_2} = 10.7 \text{ kJ/mol O}_2$  and  $W_{\text{CO}} = 12.3 \text{ kJ/mol CO}$ . Two important comparisons follow: First,  $W_{\text{O}_2}$  is only ~2% of the CO<sub>2</sub> splitting enthalpy ( $\Delta H \sim 570 \text{ kJ/mol O}_2$ ), the current ISRU state-of-the-art. Second, the sum  $\frac{1}{2}W_{\text{O}_2} + W_{\text{CO}} \sim 17.7 \text{ kJ/mol} \ll \sim 283 \text{ kJ/mol}$ , the heat of CO combustion, indicating that an efficient CO + O<sub>2</sub> extraction process could result in energy return on investment EROI > 1, effectively allowing the use of the Mars atmosphere as a fuel/oxidizer source.

In this paper we primarily focus on the separation process for O<sub>2</sub>, as part of a NASA Innovative Advanced Concepts (NIAC) Phase I project. The process, *thermal swing sorption/desorption* (TSSD), is illustrated in Figure 1. TSSD is a two step thermally driven cycle, using a precisely tailored high surface area O<sub>2</sub> sorbent.

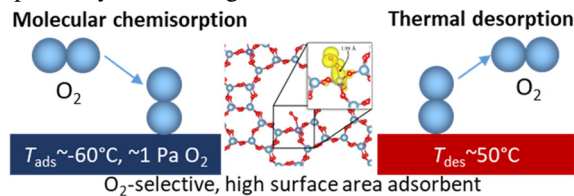


Figure 1. Illustration of the TSSD adsorption/desorption processes. Middle: doped zeolite and its electronic structure.

**Results and discussion:** The most relevant aspect of the separation process is the invested amount and type of energy. Our focus on a primarily thermal input stems from the objective to minimize energy conversion steps, especially for Mars mission scenarios where the primary energy is heat, such as in RPS or nuclear fission.

**Adsorption/desorption model and performance.** In the process description, the occupied fraction of the available adsorption sites is the coverage ( $\theta$ ). In the basic model, there are three terms: (1) the binding energy, (2) sensible enthalpy and entropy of the material (both derived from the heat capacity), and (3) mixing entropy. We employ the Einstein model, with a single Einstein temperature independent of  $\theta$  to represent both the clean, and oxygen-covered sorbent, and to capture the free energy from vibrational modes. A compound energy model determines equilibrium  $\theta$  as a function of gas-phase T and  $p_{\text{O}_2}$ . At equilibrium, the oxygen chemical potential in the condensed and gas phases must be equal. The latter depends on temperature and  $p_{\text{O}_2}$ . The former depends on temperature and  $\theta$ . Thus, at  $T_{\text{ads}}$  and  $p_{\text{O}_2} \sim p_{\text{asd}}$  the system equilibrates at a coverage  $\theta_{\text{ads}}$ . At  $T_{\text{d}}$  and  $p_{\text{O}_2, \text{d}}$ , the system equilibrates at  $\theta_{\text{d}}$ .

The resulting outputs of these models are *reversible oxygen coverages*  $\Delta\theta = \theta_{\text{ads}} - \theta_{\text{des}}$  (Figure 2). From  $\Delta\theta$ , assuming a fraction of adsorption-active atoms (1/60), and solid-solid heat recovery effectiveness ( $\epsilon = 0.75$ ), we estimate the separation heat input (Figure 3).

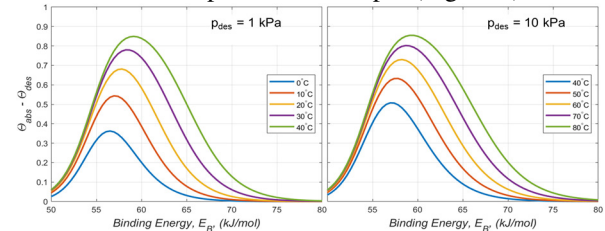


Figure 2.  $\Delta\theta$  vs. binding energy ( $E_b$ ) for adsorption at 200 K (night-time temperature Jezero) and ambient  $p_{\text{O}_2} = 1.18 \text{ Pa}$  (also Jezero). Desorption at  $p_{\text{O}_2} = 1 \text{ kPa}$  and  $p_{\text{O}_2} = 10 \text{ kPa}$ .

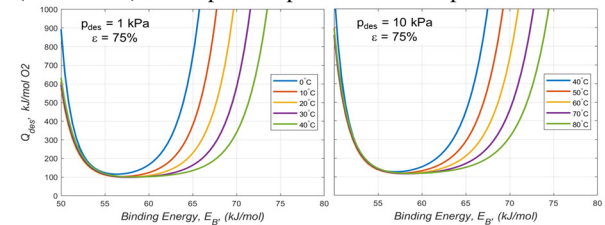


Figure 3. Separation heat input for the conditions in Figure 2.

The most important aspect of the above results is that a sorbent properties and operating parameter space exists, for which the  $O_2$  separation heat input is lower than even the theoretical energy of  $CO_2$  splitting. Of note is also the effect of delivery pressure on the heat input requirement. Heat savings are available for  $O_2$  that need not be substantially pressurized.

**Sorbent materials.** We evaluated two types of sorbents: substituted zeolites and mesoporous metal oxides. For substituted zeolites (Figure 1), starting from the target binding energies ( $E_b$ ) above, we use density functional theory (DFT) and machine learning to identify elements, which when substituted into a zeolite structure (such as ALPO-5), exhibit the desired  $O_2$   $E_b$ . Oxides that are able to release and uptake oxygen into the lattice are plentiful, and our main focus for this materials class was on identifying suitable candidates to synthesize in highly porous form. We measured the oxygen capacity via thermogravimetric analysis (TGA).

The performance of one successful sorbent (mesoporous  $YBaCo_4O_{7+\delta}$ , or YBC114) is shown in Figure 4.

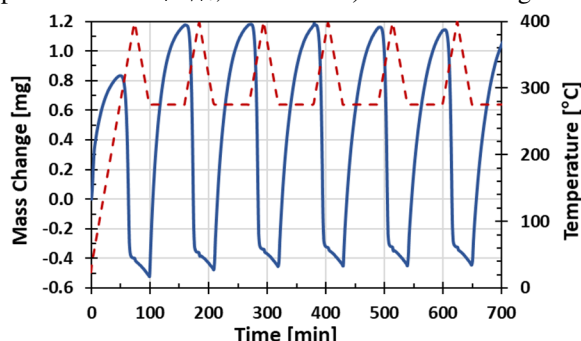


Figure 4. Porous YBC mass change over 5 TGA cycles between oxygen sorption at 20 kPa and desorption in  $N_2$ . The oxygen capacity under this condition is 0.89 mol  $O$ /mol YBC.

The importance of porosity for a (nominally) bulk sorbent such as YBC can be seen in Figure 5, which compares porous and non-porous sorption times.

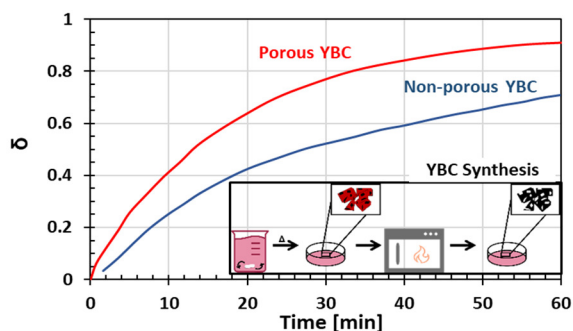


Figure 5. Oxygen uptake vs. time for porous and non-porous YBC. Inset: YBC synthesis.

**System design.** An important element in the TSSD process is the need for mechanical work for ambient air movement and dust filtration. Mechanical work (or electrical input) are of special concern for RPS-powered

cycles, owing to their low heat-to-electricity efficiency. Put simply, heat as an input is much preferable, and electrical/mechanical input should be heavily minimized.

With the above tradeoff in mind, we have created a conceptual design for the  $O_2$  separator, based on a reverse Tesla turbine, that can bring the pressure drop to  $< 20$  Pa (and as low as 2 Pa), and avoids the need for dust filtration entirely, bringing mechanical input to a level much lower than the thermal input.

**The Mars Air Refinery.** While our present models and experimental results are specific to  $O_2$  separation, there is no *a priori* reason to preclude their extension to CO at similar heat/energy input. Rather, being the more reactive of the two species, CO is generally easier to separate from a gas mixture.

Taking the separation energy (primarily heat) inputs as  $\sim 50$  kJ/mol  $O$ , and  $\sim 100$  kJ/mol CO, and a CO heat of combustion of  $\sim 283$  kJ/mol, an EROI greater than unity appears well within reach. A Mars Air Refinery (Figure 6) would separate CO and  $O_2$  from the atmosphere, and use part of the products to generate heat for its operation (after an initial input of external startup energy). The remaining CO +  $O_2$  ( $\sim 130$  kJ for every mole of originally separated CO) would be available for storage, electricity generation (e.g. in a fuel cell), and various downstream consumables, services, propellant, for  $H_2$  production from water ice, etc.

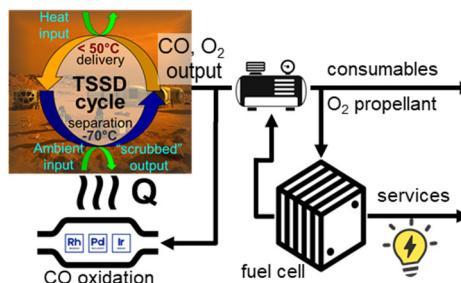


Figure 6. Simplified schematic of the Mars Air Refinery.

**Conclusions:** Our theoretical models and experimental results indicate the feasibility of thermally-driven  $O_2$  sorption separation from the Mars atmosphere at a fraction of the primary energy input required by electrolytic  $CO_2$  splitting. More broadly, the feasibility of separating both  $O_2$  and  $CO_2$ , at a EROI  $> 1$ , for true "energy independence" on Mars also appears within reach.

**References:** [1] I. Ermanoski, E. B. Stechel, Sol. Energy 198 (2020) 578 [2] S. Wilson, E. B. Stechel, I. Ermanoski, C. Muhich, J. Phys. Chem C, 125 (2021), 1269 [3] C. England, J. D. Hrubec, NIAC/USRA Final Report, 2001