Chapter One

Nanoporous Materials in Atmosphere Revitalization

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1.1 INTRODUCTION

Atmosphere Revitalization (AR) is the term the National Aeronautics and Space Administration (NASA) uses to encompass the engineered systems that maintain a safe, breathable gaseous atmosphere inside a habitable space cabin. An AR subsystem is a key part of the Environmental Control and Life Support (ECLS) system for habitable space cabins. The ultimate goal for AR subsystem designers is to 'close the loop', that is, to capture gaseous human metabolic products, specifically water vapor (H_2O) and carbon dioxide (CO_2), for maximal oxygen (O_2) recovery and to make other useful resources from those products. The AR subsystem also removes trace chemical contaminants from the cabin atmosphere to preserve cabin atmospheric quality, provides O_2, and may include instrumentation to monitor cabin atmospheric quality.

Long-duration crewed space exploration missions require advancements in AR process technologies in order to reduce power consumption and mass and to increase reliability compared to those used for shorter duration missions that are typically limited to low Earth orbit (LEO). For example, current AR subsystems

include separate processors and process air flow loops for removing metabolic CO_2 and volatile organic trace contaminants (TCs). Physical adsorbents contained in fixed, packed beds are employed in these processors. Still, isolated pockets of high carbon dioxide have been suggested as a trigger for crew headaches [1, 2], and concern persists about future cabin ammonia (NH_3) levels as compared with historical flights [3, 4]. Developers are already focused on certain potential advancements. ECLS systems engineers envision improving the AR subsystem by combining the functions of TC control and CO_2 removal into a single regenerable process and moving toward structured sorbents – monoliths – instead of granular material [5]. Monoliths present a lower pressure drop and eliminate particle attrition problems that result from bed containment. New materials and configurations offer promise for lowering cabin levels of CO_2 and NH_3 as well as for reducing power requirements and increasing reliability. This chapter summarizes the challenges faced by ECLS system engineers and scientists in pursuing these goals, and the promising materials developments that may be a part of the technical solution for the challenges of crewed space exploration beyond LEO.

1.1.1   *Development History of AR Systems for Space*

The early human space flight programs -Mercury, Gemini and Apollo- all utilized an expendable, granular lithium hydroxide (LiOH) canister for CO_2 control. Activated charcoal was located upstream of the LiOH in the same canister for odor control. The Skylab vehicle was much larger and missions lasted much longer. A swing-bed molecular sieve system operating on a 15-minute half cycle was used for CO_2 control (see Figure 1, [6]). Charcoal beds operated in parallel with 13X/5A zeolite beds to control odors. Flow rates in various legs of the system are shown in the figure. During desorption of water and CO_2 to space vacuum, flow was maintained in the charcoal and bypass legs of the desorbing side.
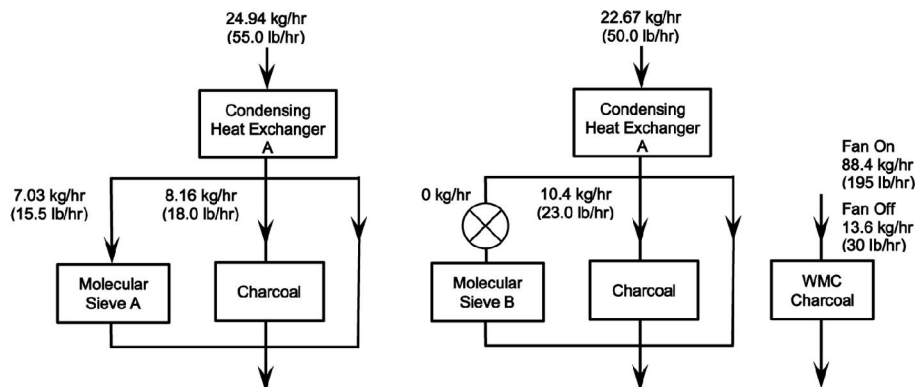

Fig. 1 Skylab AR [7].

On the Shuttle, two radial flow beds containing 2.3 kg of granular LiOH (each) are used for CO_2 control. The LiOH beds produce water so the LiOH bed is followed by a condensing heat exchanger. Lastly, there is a radial-flow ambient temperature catalytic oxidizer containing 0.32 kg of Pt-on-charcoal catalyst (see Figure 2).
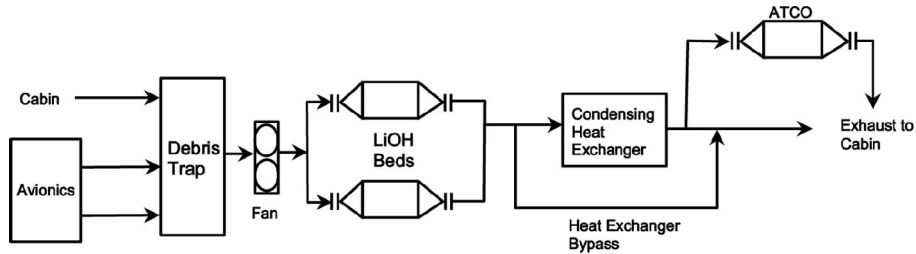

Fig. 2 Shuttle AR. Source: NASA Shuttle Operational Data Book, Volume 1, NASA Johnson Space Center, October 1984

On the U.S. Segment of International Space Station (ISS), CO_2 control is achieved using a molecular sieve swing-bed system consisting of two water-removal beds and two CO_2 removal beds. The equipment is called the Carbon Dioxide Removal Assembly (CDRA) [8], or the Four Bed Molecular Sieve (4BMS). Desiccant beds are separate from CO_2 removal beds to enable water recovery and avoid venting water to space. Water is a valuable resource on extended missions. ISS operates in a water-save mode; water removed from air to facilitate CO_2 adsorption is returned to the same air downstream for astronaut comfort.
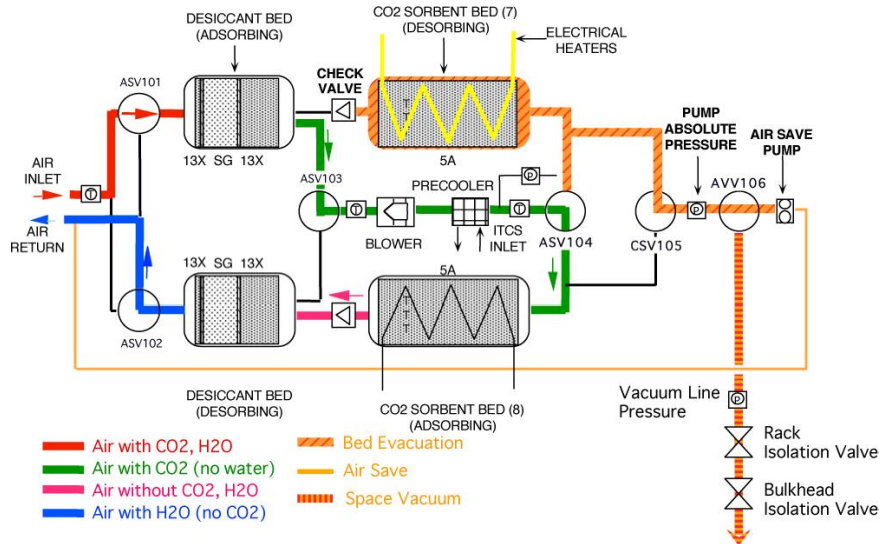

Fig. 3 ISS Carbon Dioxide Removal Assembly (CDRA) schematic [8].

1.1.2 *Design Challenges and Considerations*

Factors Influencing a Combined Trace Contaminant/Carbon Dioxide Removal System:

On board the ISS U.S. On-orbit Segment (USOS), TCs are removed using physical adsorption, chemical adsorption, and thermal catalytic oxidation. The TC control equipment employs a large packed bed of granular activated carbon (GAC) to remove high molecular weight volatile organic compounds (VOCs) from the cabin atmosphere. The GAC is treated with phosphoric acid (H_3PO_4) to remove NH_3. A packed bed containing thermal oxidation catalyst is located downstream of the GAC bed. The catalytic oxidation process removes light hydrocarbons such as formaldehyde (CH_2O) and methane (CH_4) as well as carbon monoxide (CO). A fixed bed of granular LiOH located downstream of the catalytic oxidation subassembly removes any acidic oxidation products from the process air stream. The carbon bed and LiOH bed are expendable and periodically refurbished. The system is shown schematically in the Figure 4.
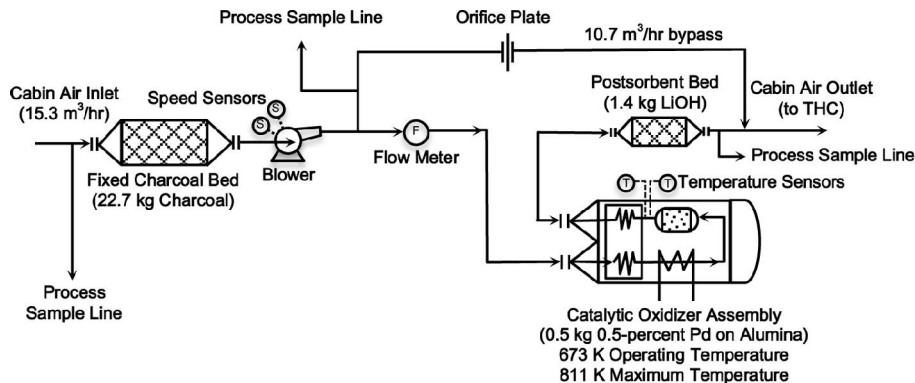

Fig. 4 ISS TCCS [9].

In a parallel air purification process, CO_2 removal is accomplished via physical adsorption in a combined vacuum-swing/temperature-swing system that periodically vents CO_2 to space. As mentioned above, the ISS CDRA consists of four packed beds — two containing silica gel and zeolite 13X desiccant media and two containing zeolite 5A CO_2 sorbent media. Flow rates and bed sizes of the current TC and CO_2 removal systems are very different. These differences are driven by cabin air quality requirements such as maximum allowable concentration and contaminant generation rates, as well as the chemical and physical parameters of the system, such as surface area, porosity, and kinetics. Compounds produced at higher rates or consumed via inherently slow reactions require larger systems or higher throughput. Ammonia removal dictates the GAC bed size and flow rate while methane (CH_4) and carbon monoxide (CO)

sets the catalytic oxidizer size and flow rate. The GAC bed for the ISS TC control equipment has a contact time of ~12 s and the thermal catalytic oxidation bed has a contact time of 0.67 s, reflecting the varying process flow rate and bed volumes. By comparison, process air flow through the CO_2 sorbent beds has resulted in a 1.6 s to 4 s contact time [10]. One amine-based CO_2 removal process under development employs a 0.25 s contact time. Historically, there has been a range of flow requirements needed to meet the cabin air quality specifications. Some overlapping middle ground exists such that one regenerable AR subsystem could incorporate both the TC and CO_2 removal functions in a new configuration, potentially incorporating shorter residence times and desorption cycles. This new vision necessitates an evaluation of newer and reversible sorbent materials.

Toxicology Considerations:

Recently, for health and wellness reasons, NASA toxicology experts have lowered the spacecraft maximum allowable concentration (SMAC) for NH_3 to 7 ppm [11]. Carbon dioxide has also been subject to scrutiny as a contaminant in space cabins, concurrent with its examination as a terrestrial greenhouse gas. Pockets of high CO_2 concentration have been suggested as the trigger for crew-reported headaches. NASA has lowered the 180-day SMAC for CO_2 from 7,000 to 5,000 ppm. Lower levels of CO_2 are clearly better, more closely approximating the terrestrial environment and contributing to fewer physiological responses.

Desorption Dynamics and Vacuum Stability Considerations:

The effect of vacuum exposure on sorbents must be understood. On board ISS, NH_3 is removed with Barnebey-Sutcliffe Type 3032 4×6 mesh GAC, which is periodically replaced. Type 3032 activated carbon was treated with H_3PO_4 and is no longer commercially available. It will likely be replaced with a similar material, and could be susceptible to acute vacuum exposures because some future crewed spacecraft design architectures have no airlock. Therefore an emergency extravehicular activity (EVA) would require cabin depressurization. For such spacecraft design architectures the sorbent material must be vacuum-stable. Similarly, in vacuum-venting systems such as the ISS CDRA, vacuum is necessary during desorption to remove CO_2 from the beds. Temperature is often used with vacuum desorption to enhance desorption kinetics, but most granular sorbent materials are inherently poor thermal conductors, making the process very inefficient. Thermal desorption from some new engineered materials, however, can be driven by directly-applied electrical current, offering a potential reduction in the power requirement and simplifying the thermal design challenge.

Opportunities for Spacecraft Resource Conservation:

Beyond these challenges and considerations, there are opportunities for power savings and reliability improvements in the AR subsystem design. Across all categories of target contaminant, engineered structured sorbents – monoliths – offer the promise of lower pressure drop (and fan power), while minimizing the problem of particle attrition. Packing retention mechanisms typically use force (e.g., springs, clamps) to keep bed particles fixed within the flow circuit. The packing force, the flow itself, and reactant particle volume changes all contribute to particle attrition and the production of fines, which can be carried downstream and affect valve sealing surfaces and equipment such as fans and heat exchangers. Some sorbent substrates also allow for more efficient heating. NASA has pursued the development of monolithic adsorption systems for trace contaminants, CO_2, water vapor, and targeted TC catalytic oxidation. Those systems might appear in a 3-tiered swing-bed system such as the one shown below in Figure 5, NASA's concept for a Next Generation Atmosphere Revitalization system.
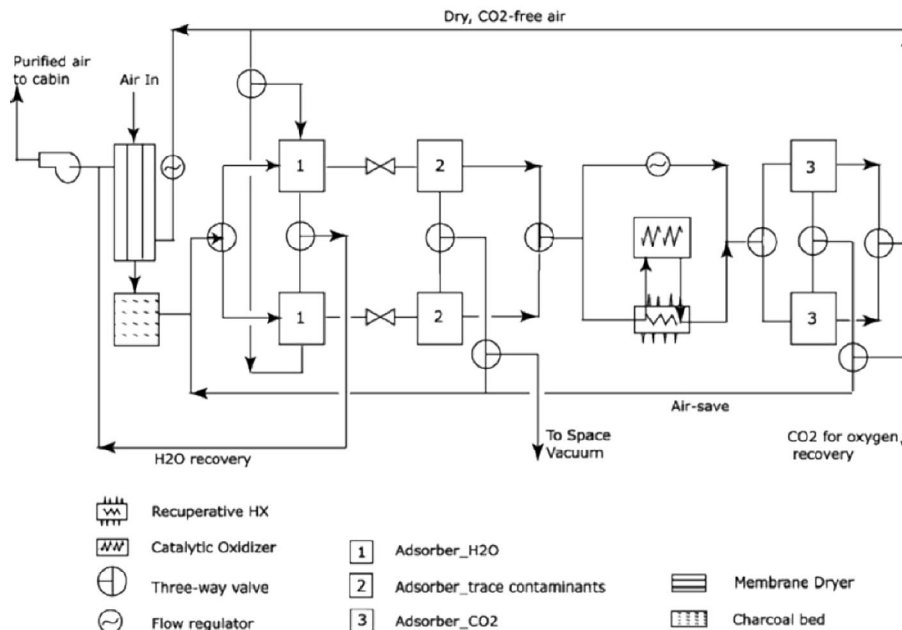

Fig. 5 Next Generation ARS [5]

Lastly, in pursuit of loop closure, there are additional needs for specific gas separations. For example, one CH_4 processor produces a mixture of acetylene (C_2H_2) and hydrogen that would require separation and selective adsorption systems using nanoporous materials offer a promising means for accomplishing this.

The Center for Advanced Nanoscale Materials (CaNM) at the University of Puerto Rico and NASA have been working to address many of these challenges. The remainder of this chapter describes specific materials development efforts, experimental results and future plans.

1.2   MICROPOROUS MATERIALS

Porous adsorbent materials are usually classified according to the International Union of Pure and Applied Chemistry (IUPAC) definitions. That is, microporous (< 20 nm), mesoporous (2 – 50 nm) and macroporous (50 nm) materials. Among these, only the first two classifications are usually considered in fixed bed type applications due to their inherent large specific surface area. The following sections will therefore focus in summarizing relevant properties of some microporous and mesoporous materials that are currently been used and/or could be considered for AR.

1.2.1   *Zeolitic Adsorbents*

Zeolites are inorganic porous materials with frameworks generally comprised of silicon and aluminum tetrahedra and with a multi-dimensional and interconnected pore system. The structure net charge is usually balanced with extra-framework cations that also serve as adsorption sites depending on their ultimate location. For example, cation locations in zeolite type-A (LTA) vary according to Figure 6. The cations located in site S I are inaccessible to even molecules such as CO_2 given the small dimensions of the Sodalite cage windows surrounding these [12].
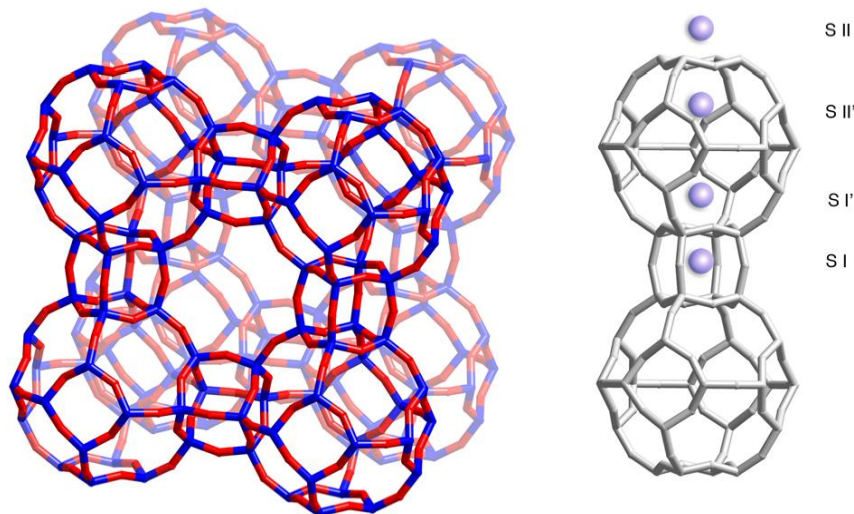

Fig. 6 Zeolite type A (LTA) unit cell (left) and cation locations (right)

The average pore size of LTA zeolites depends on the nature of the extra-framework cation. For example, sodium-containing LTA (Na^+-LTA; 4A Zeolite), the average pore diameter is ca. 0.4 nm (4 Å) and the unit cell contains about 12 extra-framework cations. Only a fraction of these cations are available for interaction with adsorbates (i.e., cations occupy site S II). NASA currently employs Ca^{2+}-LTA (5A Zeolite) for CO_2 removal on board the ISS as part of the CDRA system (see Figure 3), due to its excellent adsorption capacity at room temperature and ease of regeneration. A set of equilibrium isotherms and associated isosteric heat of adsorption profile are shown in Figure 7.
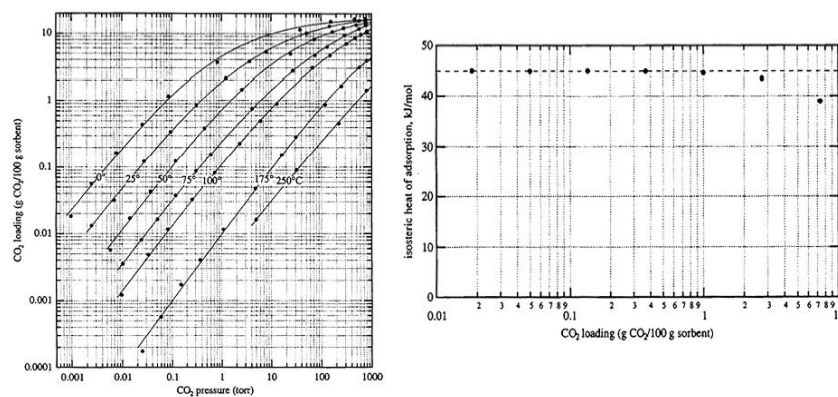

Fig. 7 Adsorption isotherms of CO_2 on Ca^{2+}-LTA at different temperatures (left) and isosteric heat of adsorption (right) [13].

According to the isosteric heat profile, the surface-adsorbate interaction is at the physisorption level, which is suitable for onboard regeneration using vacuum and/or a moderate temperature swing. One of the main limitations of LTA materials, however, is its high degree of hydrophilicity due to coordination of multiple water molecules to cations. The typical water vapor loading at room temperature and about 50% relative humidity is ca. 22-wt% and complete removal usually requires temperatures greater than 350°C. In fact, one of the main challenges of the CDRA system used in the ISS (Figure 3) is to avoid water vapor from reaching the CO_2 adsorption bed (i.e., Ca^{2+}-LTA). Furthermore, applicable SMACs for CO_2 will be lower for longer manned-space missions, and adsorption processes that utilize LTA zeolites will require more generation cycles to compensate for the decrease in working capacity, as evidenced by the lower CO_2 uptakes at lower partial pressures (see Figure 7).

For several decades, we have seen a great effort in the field of crystal growth, leading to the discovery of hundreds of new topologies with frameworks whose composition and nature depart considerably from the one exhibited by zeolites. This offers an excellent window of opportunity to tailor-make adsorbents with properties more suitable for space applications, including lower hydrophilicity, and specific surface interactions to provide better CO_2 working capacities at

lower partial pressures. Recently, Hernández-Maldonado and co-workers reported a strontium-based silicoaluminophosphate (Sr^{2+}-SAPO-34) designed with these challenges in mind [14-17].

SAPO-34 materials have a framework made of oxygen-bridged silicon, aluminum and phosphorous centers all in tetrahedral coordination [18-21]. These at the same time form a 3-D interconnected pore network with windows of about 4 nm (4 Å) in diameter, similar to those found in Ca^{2+}-LTA zeolites. A typical SAPO-34 unit cell and associated extra-framework cation locations [22, 23] are shown in Figure 8. Loading of strontium via ion-exchange processes (liquid or solid phase) usually results in about one or two Sr^{2+} ions per unit cell. Due to charge balancing and repulsion criteria, these cations are found in S II and S II' positions, which is desired for interaction with adsorbates. Figure 9 shows CO_2 equilibrium isotherms at different temperatures and the associated isosteric heat of adsorption of Sr^{2+}-SAPO-34 adsorbents. When compared to the results corresponding to Ca^{2+}-LTA at 25°C (see Figure 7) and a CO_2 partial pressure of ca. 1 Torr (or 1300 ppm), the Sr^{2+}-SAPO-34 adsorbents display a 60% increase in equilibrium adsorption capacity. Even more important is the fact that the observed average heat of adsorption is quite similar for both sorbents, which indicates that the SAPO-34 based material might be suitable for regeneration schemes such as the one employed in the CDRA system. Studies performed by Ishikawa and co-workers have found that the interaction between the CO_2 and Sr^{2+}-SAPO-34 arises from a chemical bond of ionic character and that charge donation leads to reduction of the positive charge on the metal cation [16], which results in a lower CO_2 adsorption energy (i.e., physisorption). Therefore, it should be experimentally possible to design an improved system for ultra-deep removal of CO_2 by varying the silicoaluminophosphate composition in the Chabazite-like framework to control the CO_2 adsorption capacity.
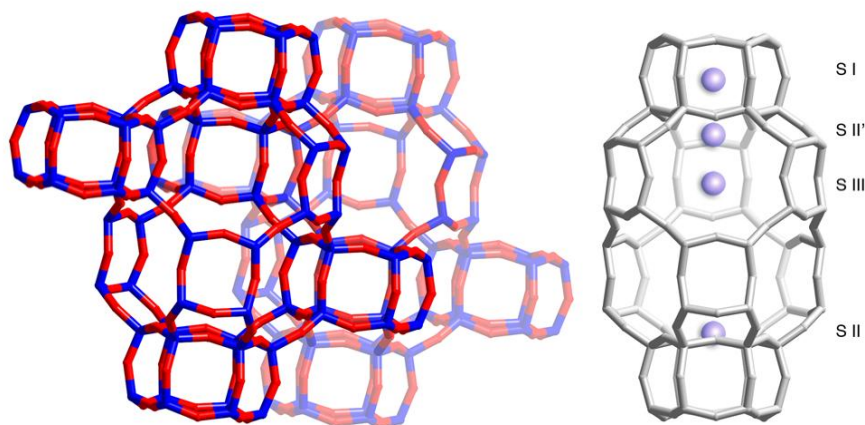

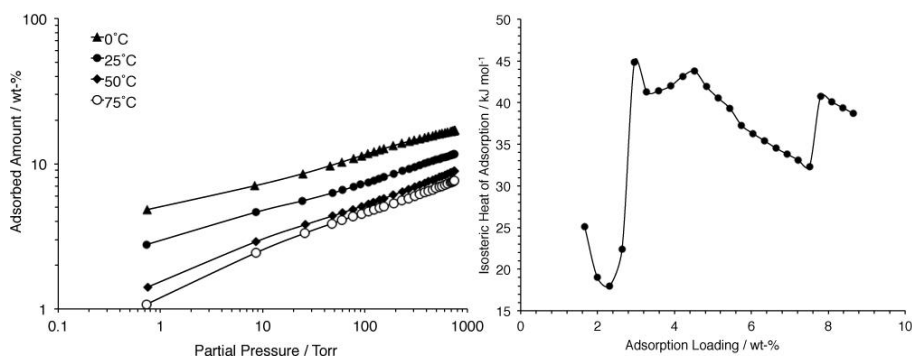Fig. 8 SAPO-34 unit cell (left) and cation locations (right)

Fig. 9 Adsorption isotherms of CO_2 on Sr^{2+}-SAPO-34 at different temperatures (left) and isosteric heat of adsorption (right). Source: Data reprinted with permission From [15]. Copyright 2008 American Chemical Society.

An important aspect to be considered when designing porous adsorbents for CO_2 removal in closed-volume applications is the kinetics governing the adsorption process. Tests performed by Hernández-Maldonado and co-workers for a step loading of 1000 ppm CO_2 concentration indicate a diffusion half time of ca. 0.2 seconds, which should be suitable for fixed bed type processes without sacrificing much working capacity. In fact, tests performed using a small scale fixed bed CO_2 adsorption system at NASA Ames Research Center indicate that Sr^{2+}-SAPO-34 materials display a breakthrough time of ca. 200 minutes during treatment of a stream of nitrogen containing 1300 ppm CO_2 (see Figure 10). For a detection limit of 2 ppm CO_2, the aforementioned data corresponds to a loading of ca. 2.6 wt-%, which matches well with the equilibrium amount observed at similar conditions (see Figure 9) and, therefore, evidences that there are no apparent resistance to diffusion of CO_2.

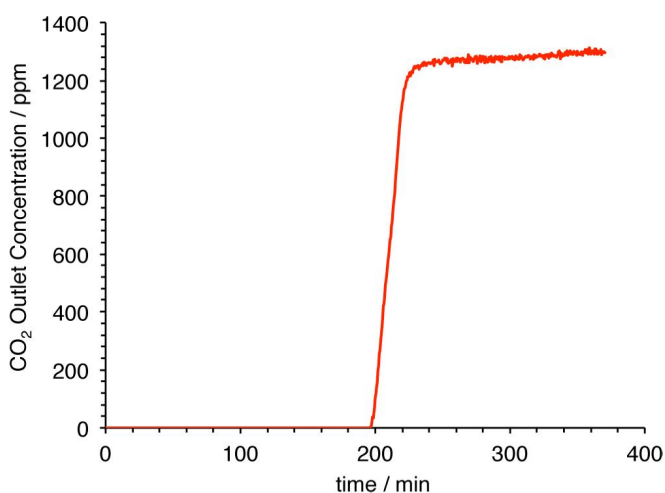Fig. 10 CO_2 breakthrough curve in Sr^{2+}-SAPO-34 at 25°C. Carrier gas was N_2 at 0.5 L/min.

Zeolites have garnered NASA interest in recent years with regard to their capacity to reversibly adsorb ammonia gas. Ammonia has traditionally been

removed with phosphoric acid treated GAC, which has a capacity of between 2-4% by weight, and must be replaced periodically. NASA's ISS GAC is no longer available. Given that a new material must be identified and that NASA seeks to use regenerable swing-beds for combined CO_2 and trace contaminant control, transition metal ion-exchanged Y-zeolites offer promise. That conclusion is based on the data published by Liu and Aika [24] which documented capacities for reversible ammonia adsorption of 7.03 and 6.49 mmol/g on Co-Y and Cu-Y, respectively at 323 K (~11% by weight). Luna and Hernandez-Maldonado prepared small quantities of these ion-exchange zeolites and pressed pellets ranging in size from 20 to 40 mesh. Figure 11 shows the ammonia weight gain in mg/g of a 1 gram sample of each of these materials subjected to a 500 sccm, 50 ppm (NH_3 in nitrogen) mixture. The current ISS carbon is shown for comparison.
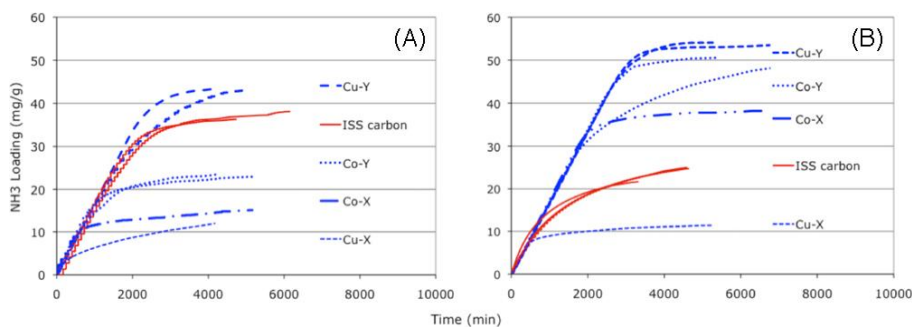

Figure 11. Ammonia loading on Cu- and Co-exchanged X and Y zeolites. Barneby-Sutcliffe 3032 granular activated carbon, used on ISS for ammonia removal, is shown for comparison. (A) with 40% relative humidity and (B) in dry nitrogen.

Although zeolites and zeolitic materials offer attractive CO_2 adsorption characteristics for purification processes necessary in long term missions, their powder nature gives rise to handling problems even when employed in combination with clay-based substrates. The alternative would be the development of zeolitic membranes synthesized by means of secondary growth techniques [25-32] or the use of metal-based frameworks/substrates. The latter will be thoroughly discussed later in this Chapter.

1.2.2 *Amine Based Adsorbents*

The notion of an amine embedded adsorbent originated from amine scrubbing, which has been used to remove CO_2 from natural gas and hydrogen since 1930, when it was patented [33, 34]. The process involves a reaction between the CO_2 with aqueous amine via a zwitterion mechanism to form carbamates [35]. Despite improvements in recent years, there are still many challenges related to scrubbing methods. These include considerable energy requirements for solvent regeneration and corrosion control. However, embedding of the amine onto the surface of a porous material makes it feasible for space related applications as discussed below.

Between the *Skylab* and Shuttle space flight programs, amine compounds gained a CO_2 removal role. Earliest concepts were steam-desorbed [36, 37]. The current regenerable "solid" amine sorbent has undergone a lengthy development, and stems from the use of liquid amines for industrial CO_2 capture and for CO_2 control onboard submarines. Aerospace technologists sought a solution that would retain the basic chemistry of the liquid phase amine-CO_2 system but eliminate the difficulties associated with corrosive solutions and with micro-gravity liquid management [38, 39]. These sorbents are prepared by immersing high surface area plastic beads in an amine solution and subsequently drying. The amine bonds covalently with the plastic but weakly with CO_2 and water. Various post-treatments have been evaluated for improved performance.

The Shuttle program experimented with a vacuum-swing, amine-based CO_2 removal process via detailed test objectives (DTO) during several flights as part of the Extended Duration Orbiter efforts in the 1990's [39-47]. This process, the Regenerable CO_2 Removal System (RCRS) employed the Hamilton Sundstrand HSC and HSC$^+$ sorbent media. This media required the presence of atmospheric moisture to effectively remove CO_2. The units were not designed to control atmospheric moisture as the condensing heat exchanger performed that function. LiOH was used as the functional backup during the DTOs. The experience gained with amine-based CO_2 removal during the Extended Duration Orbiter DTO activities gave rise to an improved sorbent that addressed various technical issues involving lifetime stability and functional redundancy issues [46-48]. An amine-based AR subsystem process architecture was selected for the Crew Exploration Vehicle (CEV), the flagship crew transport vehicle of the Constellation program [49].

The CEV system consists of thermally linked beds of a proprietary sorbent, designated SA9T, alternately exposed to cabin air for removal of CO_2 and water vapor, and to vacuum for desorption [50, 51]. SA9T sorbent, small diameter amine-loaded polymethylmethacrylate (PMMA) beads, are poured into beds containing a brazed aluminum foam support structure. The aluminum foam serves as a conduction path for the heat of adsorption to move from the adsorbing bed toward the desorbing bed, thereby maintaining near-constant temperature and obviating the need for active temperature control. The CEV's CO_2 removal system is regenerable; that is, the sorbent material is not consumed. However, SA9T sorbent attracts both water and CO_2, and therefore both resources are lost upon vacuum desorption. Because the cost of this loss is unacceptable over a long period of time, amine-based systems are not a candidate for long-term missions. However, the same material has been proposed for use in the portable life support system of space suits [52, 53], again with a loss of resources deemed acceptable to the mission.

These amine materials for CO_2 removal have been found to have some affinity for trace contaminants at the expense of CO_2 [54-56], and to lose CO_2 capacity and offgas NH_3 over time [45]. Nevertheless, solid amines are a proven means of CO_2 removal for short duration space missions where recovery of CO_2 and water is not a mission objective.

1.2.3 *Metal Organic Frameworks*

Metal organic frameworks (MOFs) allow the synthesis of tailor-made materials with predetermined, tunable porosity and designed chemical nature of pore surface [57-61]. Among the wide variety of porous MOFs described in the recent literature, there are some eye-catching examples of large pore sizes [62-65], flexible frameworks [66], and post-synthetic modified materials [67]. On the other hand, MOFs are not as robust as zeolites and zeolite-like materials and often collapse after a few cycles of pressure and/or temperature swings.

A wide variety of MOFs with pores larger than the kinetic diameter of CO_2 (3.3 Å) have been shown to sorb the latter efficiently. Zeolitic imidazolate frameworks (ZIFs) in particular outperform most other sorbents at ambient conditions [68]: The Zn-containing ZIF-78, with pore diameter of 4.4 Å and BET surface area of 950 $m^2 g^{-1}$, absorbs ~83 L CO_2 per 1 L of sorbent (~ 11.7 wt-%) at 273 K and ambient pressure [69]. The CO_2 sorption capacity of MOFs can be improved by the incorporation of NH_2-functionalities; A Zn-aminotriazole-based MOF absorbs > 15 wt-% at 273 K, ~1 atm [70], while an ethylenediamine functionalized Cu-containing MOF has shown a large increase of its CO_2 sorption capacity at 298 K compared to a non-functionalized analogue [71]. A cobalt(II)-adeninate, bio-MOF-11, with pore diameter of 5.8 Å, performs even better absorbing 20.9 wt-% at 298 K and 1 bar [72].

The storage capacity of MOFs increases dramatically at high pressure: A Cu-based MOF uptakes 35.8 wt-% at 298 K and 15 bar [73], while the Zn-containing MOF-177 adsorbs 59.6 wt-% at 32 bar (BET surface area, 4500 $m^2 g^{-1}$) and MOF-200 and MOF-210, with BET surface areas of 4530 and 6240 $m^2 g^{-1}$, adsorb ~71.5 wt-%, respectively, at 298 K and 50 bar (Figure 12) [62, 74].

Fig. 12. High-pressure CO_2 isotherms of MOF-5, -177, -200, -205, and -210 at 298 K [62]. Needs copyright.

Fig. 13. X-ray structure of CO_2 binding in MOF $Zn_2(Atz)_2(ox)\cdot(CO_2)_{1.3}$ (Atz, 3-amino-1,2,4-triazole; ox, oxalate) at 173 K. (A) The role of the amine group of Atz in binding CO_2-I is depicted. The H atoms of the amine group (located crystallographically) H-bond to oxalate O atoms, directing the N lone pair toward the $C(\delta+)$ atom of the CO_2 molecule. H-bond distances shown are for H-acceptor interactions. (B) Both crystallographically independent CO_2 molecules are shown trapped in a pore, showing the cooperative interaction between CO_2-I and CO_2-II molecules. The CO_2…NH_2 interaction is represented as a dotted purple bond, and the CO_2…CO_2 interaction is indicated as a dotted yellow bond. (C) This panel shows the other interactions present. The CO_2-I…Ox interactions are shown in orange, and the CO_2…NH_2 hydrogen bond interactions are shown in green. For clarity, H atoms are shown in purple [70]. ==Needs copyright==.

An increase of CO_2 sorption capacity has been observed as the number of metal ions present per unit volume of the sorbent increases [75]. In addition, low-temperature X-ray crystallographic evidence shows that CO_2 is physisorbed on the pores of MOFs through end-on O···M interactions with coordinatively unsaturated metal cations, or side-on interactions between amine or hydroxyl

groups and the carbon atom of CO_2 (Figure 13) [70]. Theoretical work has also focused on interpreting the experimentally determined isosteric heats of CO_2 adsorption in terms of dipolar interactions [76].

Current experimental work at the University of Puerto Rico involving the systematic modification of pendant groups and lattice charge in Cu- and Ag-based MOFs, coupled with density functional theory (DFT) calculations of CO_2 sorption energies on their pore surfaces, is pursuing an in-depth understanding of the role of weak van der Waals interactions.

1.3 Microlith®-Based Structured Adsorbents

Regardless of sorbent material or target contaminant, containment of particles in packed beds presents challenges. Compressive forces and particle density changes contribute to particle attrition and the creation of dust. Dust can interfere with valve operation and increase system pressure drop. Implementation of Engineered Structured Sorbents (ESS) is a potential alternative to the traditional packed bed system for the environmental control applications that addresses these challenges. This approach offers the inherent performance and safety attributes of molecular sieve, zeolites (e.g., aluminosilicate) and other sorbent materials capable of effectively removing CO_2, H_2O, and organic contaminants with greater structural integrity, regenerability, and process control. Precision Combustion, Inc. (PCI) and NASA's Marshall Space Flight Center (MSFC) have been developing one ESS approach based on the Microlith® technology [77] to meet the requirements of future, extended human spaceflight explorations [78-82]. The Microlith®-based ESS consist of metal substrates that provide structural integrity (i.e., less partition of sorbents compared to the pellet-based system) and enhanced thermal control during the adsorption/desorption process. This offers improved durability and efficiency over current, state-of-the-art, pellet-based systems. This particular ESS concept also offers a unique internal resistive heating capability that has shown potential for shorter regeneration times and reduced power requirement compared to conventional systems [79-81].

The Microlith® technology, patented and trademarked by PCI [77], consists of a series of ultra-short-channel-length, low thermal mass metal meshes as shown in Figure 14. It replaces the long channels of conventional monoliths with a series of short channel length substrates. Whereas in conventional honeycomb monoliths a fully developed boundary layer is present over a considerable length of the device, the very short channel length characteristic of the mesh-type substrate avoids boundary layer buildup. A Computational Fluid Dynamics (CFD) analysis (Figure 14) illustrates the difference in boundary layer formation between a monolith and mesh-type elements. Since heat and mass transfer coefficients depend on the boundary layer thickness, minimizing boundary layer

buildup enhances transport properties. Additionally, the mesh-type substrate can pack more active surface area into a small volume, providing increased adsorption area for a given pressure drop. The effectiveness of the Microlith® technology and the long-term durability of sorbent and catalyst coatings have been rigorously demonstrated in space station cabin air cleaning application [78-84] and other catalytic applications, including engine exhaust after-treatment [85], combustion, and fuel processing [86-88].

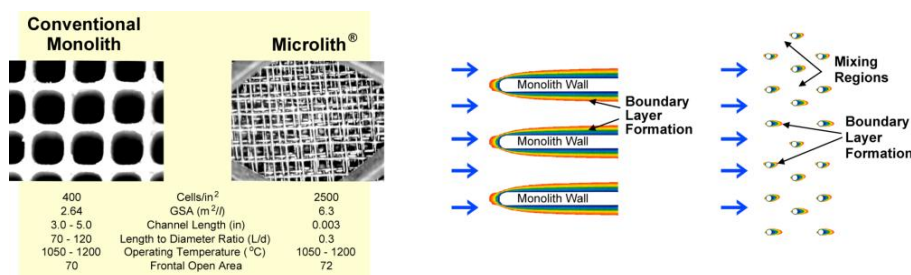| Conventional Monolith		Microlith®
400	Cells/in²	2500
2.64	GSA (m²/l)	6.3
3.0 - 5.0	Channel Length (in)	0.003
70 - 120	Length to Diameter Ratio (L/d)	0.3
1050 - 1200	Operating Temperature (°C)	1050 - 1200
70	Frontal Open Area	72

Fig. 14. Physical characteristics of conventional monolith and short-channel-length Microlith® screens, and CFD analysis of boundary layer formation for a conventional monolith and a linear stack of three mesh-type Microlith® elements.

The development of zeolite and other sorbent coating protocols on the mesh-type substrate requires rigorous evaluation of washcoat formulations in order to produce an adherent, durable coating. The substrate geometry poses unique challenges in the development of sorbent coatings. The washcoats must be capable of being readily applied, and the resulting coatings must have a high degree of adhesion and cohesion and must be sufficiently abrasion resistant in order to withstand routine handling and multiple thermal cycles. At the same time, the formulation must retain the desired chemical and physical characteristics of the sorbents to achieve the expected adsorption capacity and removal efficiency. Washcoats that allow for rapid application of sorbent coatings for high-volume production have been developed. Scanning electron microscopy (SEM) micrograph of the sorbent-coated Microlith® substrates is shown in Figure 15, indicating uniform coatings with a complete coverage around the Microlith® strands.

Several Microlith®-based regenerable adsorption modules have been examined at NASA-MSFC for performance evaluation and optimization. A 1-person load CO_2/trace contaminant adsorber prototype was evaluated to demonstrate the potential of the mesh-type structured sorbent technology for cabin air-cleaning applications. In 2008, a complete 1-person Microlith®-based ESS system, which consisted of a residual drier (i.e., moisture removal module), CO_2 removal module, and trace contaminants removal module was designed and developed. Figure 15a shows an example of the Microlith®-based ESS adsorber design and Figure 15b shows one of the adsorber modules mounted on

the test rig. Performance evaluation at NASA MSFC indicated the capability of removing the targeted 1 kg CO_2/day with an average power requirement of 40 Watts and a 20-minute regeneration period [81]. The adsorption capacity and CO_2 removal efficiency were stable over the 20-hr test and after subjecting the modules to at least 60 thermal cycles (i.e., adsorption-desorption cycles) [81]. Finally, a 4-crew two-leg Microlith®-based ESS system was developed to study continuous CO_2 removal at a rate of 4 kg CO_2/day. These modules are being examined for performance demonstration, system optimization, and long-term durability.
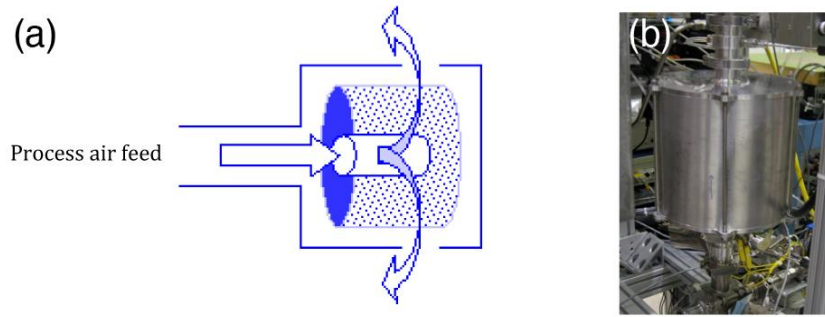

Fig. 15. (a) Simplified Microlith®-based ESS adsorber design and (b) Adsorber module on the test rig.

1.4 Closing Remarks

It is quite evident that the technology and processes used to provide life support systems in space related endeavors have evolved considerably in response to the arrival of new SMACS and emerging space exploration mission challenges. As we proceed to plan for long-term missions (i.e., Mars exploration) it is imperative to accomplish highly efficient resource recovery for these future space exploration vehicle and habitat platforms. Highly efficient resource recovery that in effect "closes the mass loop" requires complex systems engineering that incorporates unique technical solutions. Fortunately, there has been considerably gain in the knowledge of bottom-up design of adsorbents to deal with the stringent atmospheric (i.e., CO_2 and NH_3) and processing requirements, including the design of third-generation porous frameworks that provide structural flexibility and surface interactions that can be controlled by an external variable. Furthermore, we have seen substantial advancement at the engineering level as well, such as the ESS approach that has the potential to significantly enhance the performance of current and future sorbent and catalyst materials

that will enable AR subsystem architectures that will posses lower operational costs.

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