Carbon Dioxide – Our Common "Enemy"

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Abstract

Health effects of brief and prolonged exposure to carbon dioxide continue to be a concern for those of us who manage this pollutant in closed volumes, such as in spacecraft and submarines. In both examples, considerable resources are required to scrub the atmosphere to levels that are considered totally safe for maintenance of crew health and performance. Defining safe levels is not a simple task because of many confounding factors, including: lack of a robust database on human exposures, suspected significant variations in individual susceptibility, variations in the endpoints used to assess potentially adverse effects, the added effects of stress, and the fluid shifts associated with micro-gravity (astronauts only). In 2004 the National Research Council (NRC) proposed revised Continuous Exposure Guidelines (CEGLs) and Emergency Exposure Guidelines (EEGLs) to the U.S. Navy. Similarly, in 2008 the NASA Toxicology Group, in cooperation with another subcommittee of the NRC, revised Spacecraft Maximum Allowable Concentrations (SMACs). In addition, a 1000-day exposure limit was set for long-duration spaceflights to celestial bodies. Herein we examine the rationale for the levels proposed to the U.S. Navy and compare this rationale with the one used by NASA to set its limits. We include a critical review of previous studies on the effects of exposure to CO_2 and attempt to dissect out the challenges associated with setting fully-defensible limits. Past methods of CO_2 removal in spacecraft are summarized and recent experiences with management of CO_2 aboard the International Space Station (ISS) with 13 persons aboard are described. This includes the tandem operations of the Russian Vozduk and the U.S. Carbon Dioxide Removal System. A third removal system is present while the station is docked to the Shuttle spacecraft, so our experience includes the lithium hydroxide system aboard Shuttle for the removal of CO_2. We discuss strategies for highly-efficient, regenerable removal of CO_2 that could meet the 1000-day SMAC of 0.5%, which would apply to long-duration voyages to Mars.

Introduction

Carbon dioxide is the major pollutant produced by humans as a byproduct of metabolism. A typical human exhales about 1 kg/day. Substantial resources must be employed to control this pollutant in sealed environments such as submarines and spacecraft. The magnitude of those resources increases as the acceptable level of CO_2 is decreased. Therefore, it is essential that we set CO_2 exposure levels in a rationale way, based on solid evidence, to ensure that we are not going to waste resources, yet we are able to protect the crew from the adverse effects of CO_2 exposure.

The problem of setting safe exposure limits is confounded by many factors. Have the appropriate endpoints been assessed and at levels that are sensitive enough for our purposes? Is there consensus about what constitutes an adverse effect and what is simply a measurable effect with no significance? There must be data on the inter-individual diversity of adverse responses.

We must know whether the physiological changes induced by confinement or absence of gravity could affect sensitivity to CO_2. The database regarding CO_2 suffers from a paucity of robust data. Experience in spaceflight, especially when circumstances force us to permit an unexpectedly high exposure to CO_2 can be a learning experience. Control of CO_2 by regenerable systems requires sophisticated hardware that can be vulnerable to failures. Expendable systems are more robust, but these cannot be the basis for long-term missions to distant celestial bodies. Our goal in this paper is to examine the limits and methods of control in a quasi-integrated way to better understand tradeoffs in the management of CO_2.

## Critical Review of the Toxicity Database on Carbon Dioxide

This discussion will be confined to data obtained while humans are exposed to CO_2. A high-quality study will have the following characteristics: 1) at least 10-12 test subjects, 2) exposures lasting at least 30 days to assess long-term effects, 3) frequent and sophisticated measures of endpoints that show subtle degradation of health or performance, 4) post-exposure follow up of subjects to assess any residual adverse effects, 5) robust statistical design that facilitates population susceptibility measurements and assessment of inter-individual variability, and 6) assessment of adverse effects at three exposure levels. For this particular compound, adverse effects associated with abrupt increases in CO_2 may be important. A few of these characteristics can be found in some studies; however, most studies we are aware of fall far short of meeting the standards above. For example, a table in the SMAC document lists six major human studies published between 1967 and 1988.[1] None of the studies involves more than 8 subjects, only one has 30-day exposures, and most endpoints were crude measures of adverse effects. Newer studies are summarized in Table 1. Like their earlier counterparts, these studies consistently fall short of meeting criteria for studies that could be useful for setting exposure standards or discerning inter-individual susceptibility.

Table 1. Studies of CO_2 effects on humans published since 1995

Concentration	Duration of Exposure	No. Subjects	Findings	Reference No.
2.5%	~1/2 hour	3	Decreased depth perception only	2
2.5%	~1/2 hour	3	Decreased ability to detect motion	3
0.7 and 1.2%	20 d	4	Transient increase in cerebral blood flow, headaches at higher concentration	4
0.7 and 1.2%	26d	4	Slight decrement in tracking at highest concentration, no change in mood or performance at lower concentration	5
0.7 and 1.2%	26 d		No alteration in sleep quality	6
0.5% average	101 d sub.	122	No distinct alteration in sleep quality	7

Rationale for Submarine Exposure Limits from the NRC

For many years the U.S. Navy has asked the NRC to recommend a panel of exposure limits for submariners. Exposures to CO_2 are among those that must be limited. In 2004 the NRC recommended the exposure limits shown in figure 1, which also shows NASA's limits developed in 2008.
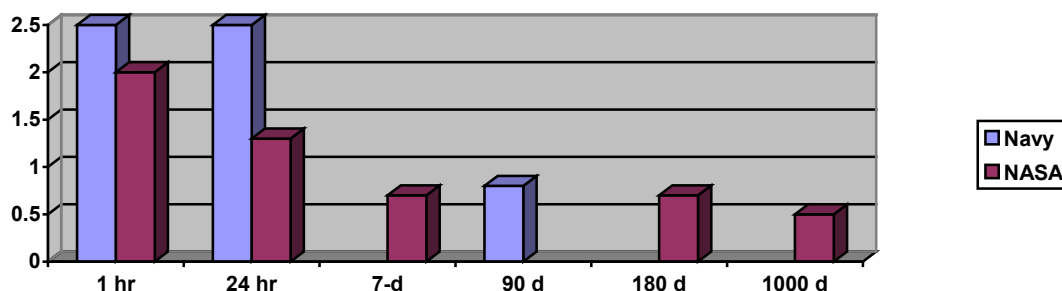
Figure 1. Exposure limits (%) proposed for various times in submarines and adopted by NASA in cooperation with the National Research Council (% CO_2 vs. time of exposure).

The basis of the values recommended to the U.S. Navy by the NRC is much different than the basis for the limits adopted by NASA. The NRC, beginning with a LOAEL (lowest observed adverse effect level) of 2.5% for visual effects,[2,3] calculated a continuous exposure guidance level (CEGL) as follows:

$$CEGL\ (90d) = LOAEL\ (visual)/3 = 2.5\%/3 = 0.8\%$$

The factor of 3 was applied for "limited data." For 1 h and 24 h, the committee felt that no factor of 3 was needed, hence the emergency exposure guidance levels (EEGLs) were both set at 2.5%.

Rationale for NASA Spacecraft Limits

As shown in Figure 1, the limits for spacecraft are typically lower than limits suggested for submarines by the NRC for a given time of exposure. The 1 h SMAC was set based on the collective observation that at 2% we would expect no more than mild headache and hyperventilation in the first hour of exposure. The 24 h SMAC was left unchanged from 1.3%, and it was noted that this makes some sense in view of the NRC recommendation of 2.5% to the U.S. Navy. The difference can be attributed to the reality that astronauts will need to repair the CO_2 removal system (a relatively sophisticated task), whereas, submariners could engage additional scrubbers or possibly surface.

The 1000-d SMAC for CO_2 was set at only 0.5% because of anecdotal reports that some ISS crewmembers seem to exhibit behavioral changes when concentrations exceed 0.5%. A mission of 1000-d is likely to involve highly confined space and close crew contact. Behavioral deficits could not be tolerated during such a mission; however, the weight and power demands for CO_2 scrubbing also become more of an issue for such distant flights. The SMAC is a compromise between these realities.

Methods for Scrubbing Carbon Dioxide in Spacecraft

Two methods are employed in controlling CO_2 levels in manned spacecraft – adsorption and chemical reaction. During the NASA's Mercury, Gemini, and Apollo Programs, the carbon dioxide removal systems used lithium hydroxide (LiOH) canisters.[9] In the presence of water, CO_2 reacts with lithium hydroxide to form the more innocuous compound, lithium carbonate. In these vehicles, two canisters of lithium hydroxide pellets were mounted in a parallel configuration. However, operationally, only one canister was used at a time. As the lithium hydroxide in the canister was depleted, the air-flow was diverted to the second canister and the first canister replaced. Due to the simplicity and effectiveness of the lithium hydroxide-based CO_2 scrubbing system, a very similar system was adopted for use on the Space Shuttles. The CO_2 removal system in Skylab was a complete departure from the previous NASA programs and served as the precursor to the current system used on the ISS. Skylab employed a regenerative CO_2 removal system using canisters of molecular sieves, specifically 5A zeolite, to adsorb CO_2 from the Skylab atmosphere. Two canisters of zeolite were used such that one canister was regenerated by vacuum desorption into space while the second canister removed CO_2 to ensure continuous removal.

Figure 2. US LiOH canister on ISS and Shuttles.

One major drawback of a lithium hydroxide-based system is the inability to regenerate. Ultimately, this leads to stowage issues since it requires roughly 1.5 kg of lithium hydroxide to scrub the CO_2 released by one crew member in one day.[10] As such, manned spacecraft built for longer mission durations, e.g., Skylab, Russian Mir, and the ISS, use LiOH as a supplement to regenerative CO_2 scrubbing systems. The current LiOH canisters used on ISS and on the Shuttle contain 3 kg of lithium hydroxide pellets, take up approximately 6 L in volume, and are certified for a 2.4 year lifetime (Figure 2). Because Shuttles rely solely on LiOH for scrubbing CO_2, some shuttle flights to ISS are unable to carry enough LiOH canisters for the duration of the mission due to their weight and volume requirements. Under these circumstances, LiOH canisters on-board ISS are used to augment the Shuttle supply and are replenished at a later date. Like the US Shuttle, LiOH canisters are also used to scrub CO_2 in the manned Russian transport vehicle, Soyuz. Russian-supplied LiOH canisters are also on-board ISS, and are almost twice as large as the US canisters. US LiOH canisters can be used in the Russian system using an adapter. ISS LiOH canisters are separated into two categories – contingency reserve and stockpile. Contingency reserve is defined as the number of LiOH canisters required to support 3 crew members for 15 days in the event of an off-nominal situation.

Generally, the goal of ISS CO_2 control is to maintain the level of CO_2 below 6 mmHg. If CO_2 levels rise, actions will be implemented according to CO_2 levels and/or CO_2-related crew symptoms. These actions range from a simple change in crew activity to minimize crew exertion, to supplementing CO_2 scrubbing with LiOH canisters, or even donning of breathing masks and isolating the affected area until CO_2 levels return to nominal levels.

The primary CO_2 removal system for the ISS is the Russian Vozdukh located in the Service Module of the Russian On-Orbit Segment (ROS). The Vozdukh houses two desiccant beds and three adsorbent beds, and can operate at a maximum flow-rate of 27 m^3/hour. Cabin air is drawn into Vozdukh and passed through the desiccant beds to remove water thereby increasing the CO_2 removal efficiency of the adsorbent beds. As one adsorbent bed saturates, another can be placed in-line while the saturated bed is heated and the captured CO_2 (and any remaining water adsorbed by the bed) are vacuum desorbed to space. If all three adsorbent beds are used, two beds are operated in tandem and the third bed operates in the opposite mode. The Vozdukh can be operated in a fully automatic mode maintaining CO_2 levels at a preset level. It can also be operated in a semi-automatic mode which allows operation of Vozdukh at reduced capacity decreasing power needs and wear and tear on the various subsystems. Based on technical specifications, operating Vozdukh at 100% capacity can maintain CO_2 levels below 6 mmHg with a crew of 6, with CO_2 removal rates up to 120 L of CO_2/hour. However, based on recent on-orbit testing, this capacity has decreased and CO_2 levels below 6 mmHg can be maintained with a crew of only 3.[11] Evaluation of this result is currently being reviewed by Russian engineering.
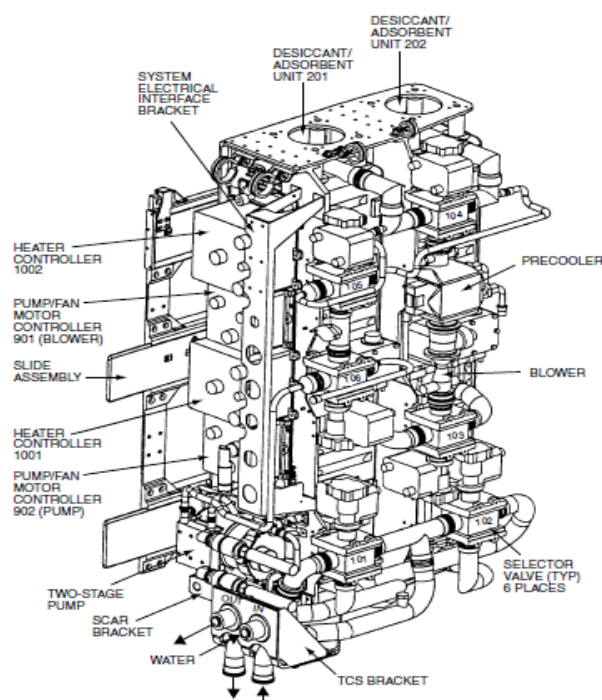
Figure 2. Isometric view of CDRA.

During Vozdukh maintenance, Shuttle docked operations, or off-nominal situations, a redundant CO_2 removal system resides in the US On-Orbit Segment (USOS) known as the Carbon Dioxide Removal Assembly (CDRA) (see Figure 2).[12] CDRA resides in the Atmosphere Revitalization (AR) Rack in the US Lab. In addition to the CDRA, the AR Rack also houses the Trace Contaminant Control System (TCCS) and the Major Constituents Analyzer (MCA). Based on technical specifications, CDRA is capable of providing CO_2 scrubbing for 4 crew members plus animals equal to 1.25 human equivalents. However, on-orbit performance has shown CDRA capable of maintaining CO_2 levels well below 6 mmHg for up to 9 crew members. CDRA utilizes two sets of desiccant and adsorbent beds. As one adsorbent bed saturates, the bed is vacuum desorbed to space while the second adsorbent bed is placed in-line to continue carbon dioxide removal. Cabin air is drawn into CDRA and passed through a desiccant bed by a fan downstream of the bed. After water removal by the desiccant bed, the dry cabin air is passed through the adsorbent bed to remove carbon dioxide.

Prior to reintroduction into the ISS atmosphere, the CO_2-scrubbed air is passed through the second desiccant bed to re-humidify the air. The adsorbent bed is packed with 5A zeolite and its construction is similar to the desiccant bed. Within the zeolite material of the adsorbent bed are strips providing heat to the bed during desorption to space vacuum. To facilitate maintenance, CDRA was constructed in a modular fashion. Examples of the various modules or orbital replacement units (ORUs) include the desiccant bed/CO_2 sorbent bed ORU, the heater controller ORU, and selector valve ORUs. Each ORU can be removed and replaced on-orbit to minimize downtime of the system. In the event maintenance is required to either CDRA or Vozdukh, LiOH canisters are deployed to provide additional CO_2 scrubbing if required.

Recent Experience with Scrubber Failures

During a recent Shuttle mission to ISS (STS-128/2J/A), problems arose controlling the temperature of a CO_2 sorbent bed during desorption.[13] Cycling through on-ground Power On/Off commands had no effect, suggesting a failed heater controller. The bed eventually reached its maximum temperature limit, tripping the remote power coupling (RPC) to the bed. Loss of CO_2-removal capability by CDRA during Shuttle docked operations could potentially shorten the Shuttle mission, negatively impacting all subsequent Shuttle missions. One option was to operate CDRA manually from Mission Control Center – Houston (MCC-H) and to implement a software patch removing or disabling software-related limitations that prevented CDRA to operate in auto mode using an alternate heater controller. A software patch would have to be written, tested on-ground and on-orbit prior final implementation. Another option was to replace the heater controller. Due to the time and resources required for such an operation, all the required tasks scheduled for this mission would not be completed. Also, since the problem was not yet fully understood at that time, there was a risk that the heater controller may not be the problem after all. It was decided to operate CDRA manually and implement a software patch. Within a 24-hour time period, a software patch was written and tested, and then prepared for final implementation. After verifying the functional aspects of the software patch on-obit, it was finally implemented to the CDRA control software on ISS allowing CDRA to operate in auto mode. As a result, there were no impacts to the Shuttle mission, and all the planned tasks were completed. After completion of the mission, the heater controller ORU was replaced and the suspected heater controller ORU was returned to ground on the next Shuttle flight for testing, tear-down, and evaluation. As can be seen from this recent event, the management of CO_2 levels in manned spacecraft can have a significant impact on the entire manned program.

Controlling CO_2 on manned spacecraft not only relies on robust systems, but also requires the ability to measure CO_2 levels in a reliable manner. Several systems throughout ISS are used to monitor CO_2 levels using various techniques. Table 2 lists the methods available on ISS, their measuring range, and associated errors in the measurement. At this point in the lifetime of ISS and with three CO_2 removal systems already on-board ISS, developmental work on CO_2 scrubbing for ISS is currently limited to the re-design of the desiccant and adsorbent beds. A recurring issue with both beds is the management of fine particles of zeolitic material generated from the pellets. A few years after CDRA activation in February, 2001, it was determined that fine particles of zeolitic material were escaping the bed assembly and depositing in key components downstream.[14] The loss of some pellets due to this breakdown has no perceptible effects on the CO_2-removal performance of CDRA.

Table 2. CO_2 measuring capabilities on ISS.

ISS Segment	Analyzer	Technique	Analytes	CO_2 Analysis
US Lab	MCA	Mass spectrometry	O_2, N_2, CO_2, H_2, H_2O, and CH_4	0-15 mmHg $\pm$ 0.45 mm Hg
US Lab	CDM	Infrared spectroscopy	CO_2	0.10% $\pm$ 0.03% 2.00% $\pm$ 0.10%
Russian Service Module	SM Gas Analyzer [ИК0501]:	Electrochemical	CO_2, O_2, H_2O	0-25 mmHg $\pm$ 1.25 mm Hg
Russian Functional Cargo Block	FGB Gas Analyzer [ИК0502]:	Electrochemical	CO_2, O_2, H_2O	0-25 mmHg $\pm$ 1.25 mm Hg

However, components downstream of the beds, e.g., pumps and valves, can be severely impacted to the point of irreversible damage. A two-pronged approach was adopted to resolve the fine particle containment. As a "quick-fix", in-line filters were added on-orbit unit just prior to key components prone to damage from fine particles. Periodically, crew is required to clean the filter units much in the same manner as the HEPA filters are cleaned monthly. In addition to this effort, the desiccant/adsorbent bed ORU was re-designed to prevent escape of fine particles. The re-designed ORU consisted of improved static and dynamic seals plus the addition of fixed screens just beyond the dynamic seal as redundant means of capturing fine particles from the bed.

The Constellation Program is planning to implement a regenerative, amine swing-bed system in the next-generation crew vehicle, *Orion*, and in the lunar lander, *Altair*. Similar to CDRA and Vozdukh, the amine swing-bed system employs two CO_2-adsorbing beds, one of which is regenerated by desorption to space vacuum while the second bed is placed in-line for CO_2 removal. Whereas CDRA and Vozdukh used zeolites for adsorbing CO_2, the amine swing-bed system will use an adsorbent material comprised of interleaved layers of beads coated with a proprietary amine compound noted for its affinity for CO_2 and water. Since CO_2 and water will be removed by the swing-bed system, humidity inside the vehicle can also be controlled without the need for condensing heat exchangers, thus simplifying the vehicle cooling system. Testing of an amine swing-bed CO_2 removal system under conditions and loads expected in *Orion* and *Altair* is ongoing.

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