Atmosphere Revitalization Using Adsorbent Media for Space Exploration Life Support

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Abstract

Atmosphere revitalization is key for providing a habitable cabin environment for crewed spacecraft such as the International Space Station (ISS). Volatile organic compounds (VOCs) are released into the cabin atmosphere via human metabolism, crew activities, equipment offgassing, and process vents. Without active control VOC concentrations may build up in the cabin atmosphere and potentially become deleterious to human health and performance. Photocatalytic oxidation has proven useful in the removal of these VOCs. Sol-Gel Solutions, LLC and the University of Florida have developed Silica-Titania Composites (STC), which are porous, high surface area silica-gel adsorbents impregnated with TiO_2 photocatalytic particles. STC is used in a packed bed reactor irradiated with ultraviolet (UV) light to oxidize VOCs to CO_2 and H_2O. A previous issue with this process is partial oxidation of some VOCs, like ethanol, into unwanted contaminants, like acetaldehyde. The partial oxidation products can build up if further treatment is not utilized and eventually become counterproductive of the entire process. However, it is believed that the porous nature of the STC may provide favorable reaction conditions that minimize partial oxidation product formation.

Photocatalytic Oxidation

Initiation by UV light

$$h\nu > Bg$$
$$\text{Semiconductor} \rightarrow e^-_{CB} + h^+_{VB}$$

Radical Propagation (formation of OH·)

$$O_2 + e^- \rightarrow O_2^-$$
$$h^+ + H_2O \rightarrow OH\cdot + h^+$$
$$O_2^- + h^+ \rightarrow HO_2\cdot$$
$$HO_2\cdot + h^+ + e^- \rightarrow H_2O_2$$
$$H_2O_2 + h\nu \rightarrow 2OH\cdot$$

Termination

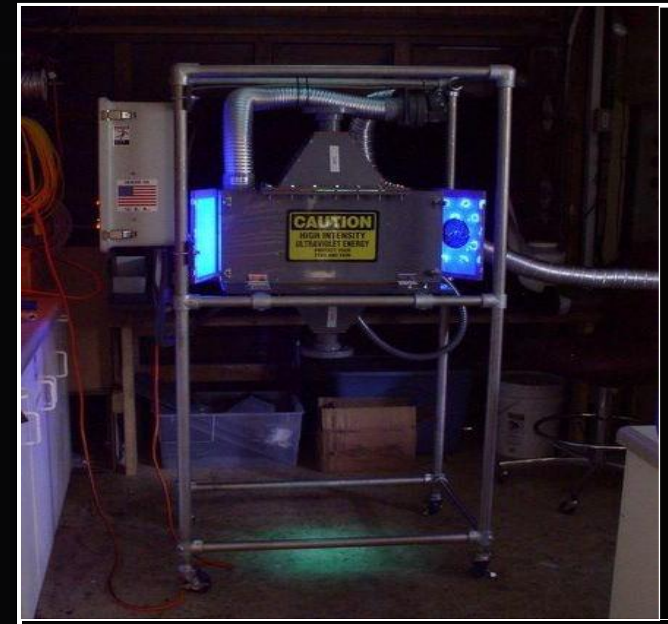
$$\text{VOCs} + OH\cdot \rightarrow CO_2 + H_2O$$

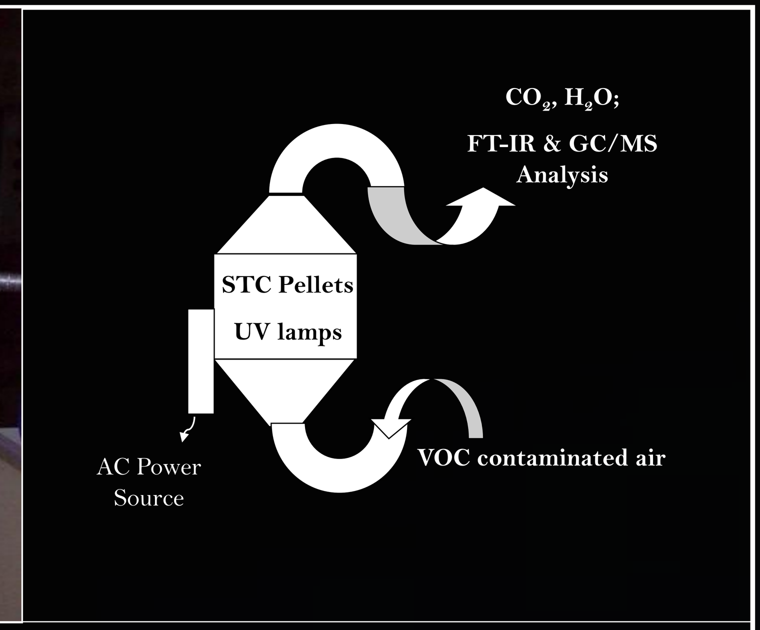
"Prohibition" on Spacecraft

There are regulations set forth by NASA's toxicology group concerning the spacecraft maximum allowable concentration (SMAC) for airborne contaminants. Acceptable concentrations of contaminants differ, usually decreasing, as the potential exposure duration is increased. For example, humans can tolerate about 1000 ppm of ethanol in the air for long duration flights (over 7 days) before it becomes unhealthy. However, the water purification system is very sensitive to polar organic solvents, such as ethanol, and can only withstand a maximum of 5 ppm ethanol. Therefore, the goal is to rid the cabin of as much ethanol as possible.

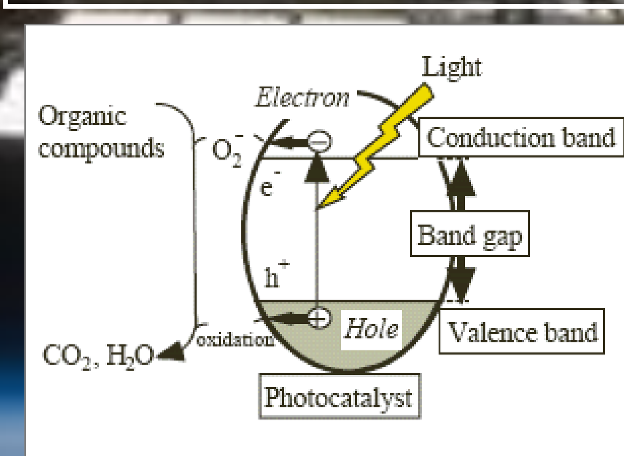
Chemical	1 hr (ppm)	Organ/Effect	24 hr (ppm)	Organ/Effect	7 d (ppm)	Organ/Effect	30 d (ppm)	Organ/Effect	180 d (ppm)	Organ/Effect	1000 d (ppm)	Organ/Effect
Acetaldehyde	10	Mucosa/Irritation	6	Mucosa/Irritation	2	Mucosa/Irritation	2	Mucosa/Irritation	2	Mucosa/Irritation	n/a	n/a
Acetone	500	CNS/Fatigue	200	CNS/Fatigue	22	CNS/Fatigue, headache	22	CNS/Fatigue, headache	22	CNS/Fatigue, headache	n/a	n/a
Carbon Dioxide	20000	CNS/Hyperventilation, headache, visual disturbance	13000	CNS/Hyperventilation, headache, visual disturbance	7000	CNS/Hyperventilation, headache	7000	CNS/Hyperventilation, headache	7000	CNS/Hyperventilation, headache	5000	CNS/Headache
Carbon Monoxide	425	CNS/Depression, CV/Arrhythmia	100	CNS/Depression, CV/Arrhythmia	55	CNS/Depression, CV/Arrhythmia	15	CNS/Depression, CV/Arrhythmia	15	CNS/Depression, CV/Arrhythmia	15	CNS/Depression, CV/Arrhythmia
Dichloromethane	100	CNS/Depression	35	CNS/Depression	14	CNS/Depression	7	Liver/Hepatotoxicity	3	Liver/Hepatotoxicity	1	Kidney/Nephrotoxicity
Ethanol	5000	Eye/Irritation, Mucosa/Irritation, Skin/flushing	5000	Eye/Irritation, Mucosa/Irritation, Skin/flushing	1000	Eye/Irritation, Mucosa/Irritation, Skin/flushing, Liver/Hepatotoxicity	1000	Eye/Irritation, Mucosa/Irritation, Skin/flushing, Liver/Hepatotoxicity	1000	Eye/Irritation, Mucosa/Irritation, Skin/flushing, Liver/Hepatotoxicity	1000	Eye/Irritation, Mucosa/Irritation, Skin/flushing, Liver/Hepatotoxicity
Methanol	200	Eye/Visual disturbance	70	Eye/Visual disturbance	70	Eye/Visual disturbance	70	Eye/Visual disturbance	70	Eye/Visual disturbance	23	Eye/Visual disturbance
2-propanol	400	CNS/Depression, Mucosa/Irritation	100	CNS/Depression, Mucosa/Irritation, Liver/Hepatotoxicity	60	CNS/Depression, Mucosa/Irritation, Liver/Hepatotoxicity	60	CNS/Depression, Mucosa/Irritation, PNS/Decr. Cond'n. velocity	60	CNS/Depression, Mucosa/Irritation	n/a	n/a
Propylene Glycol	32	Eye/irritation, Throat/irritation, Lung/irritation	17	Eye/irritation, Throat/irritation, Lung/irritation	9	Eye/discharge, Nose/Hemorrhage	3	Eye/discharge, Nose/Hemorrhage	1.5	Nose/Epithelium thickening	1.5	Nose/Epithelium thickening
m-Xylene	50	Mucosa/Irritation, CNS/Depression, Eye/Irritation	17	Mucosa/Irritation, CNS/Depression, Eye/Irritation	17	CNS/Neurotoxicity	17	CNS/Neurotoxicity	8.5	Ear/Ototoxicity	1.5	Ear/Ototoxicity

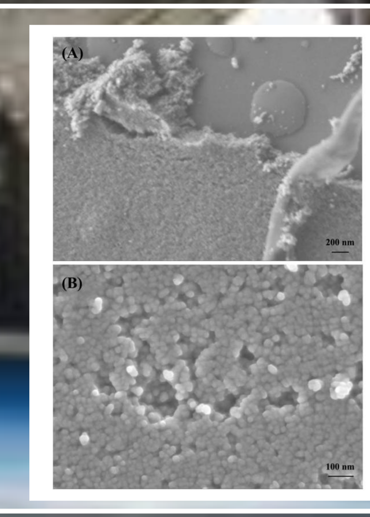
Pilot - Scale Reactor





This pilot-scale photocatalytic reactor is designed such that incoming contaminated air enters the bottom, passes through UV-irradiated STC pellets to activate the oxidation reaction, and the CO_2 and H_2O exit the top for further purification downstream. Both the inlet and exit stream compositions are analyzed using *in situ* gas chromatography and Fourier transform infrared spectroscopy to determine the efficiency of the reacting process.





(Above) Left: Diagram of how photocatalytic oxidation works.
(Above) Middle: UV bulbs that provide enough energy to promote electrons from the valence band to the conduction band.
(Above) Right: Scanning electron micrographs of the TiO_2 thin film on glass substrate at (A)33,000 X and (B)100,000 X magnification, showing thin film thickness (0.2 m) and nano-structured TiO_2 catalyst (20 nm in diameter).

Experimentation

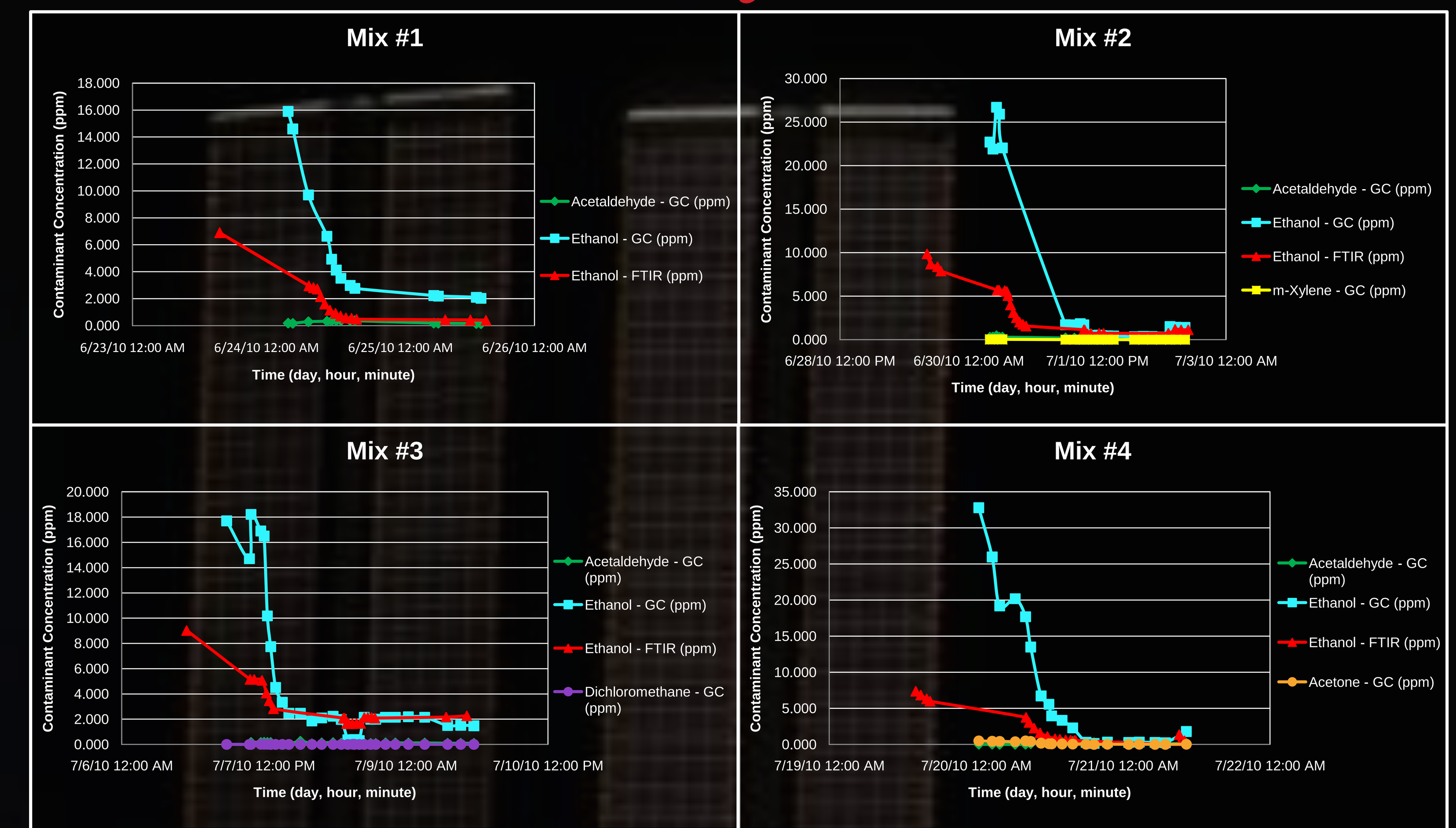
The Regenerative Environmental Control and Life Support System (ECLSS) Module Simulator (REMS) served as the structure for regulating testing operations. Various atmospheric conditions were managed and monitored by LABVIEW to keep testing procedures consistent and accurate. Below are the nominal ambient testing conditions for VOC removal with the PCO reactor.

- Humidity – 30%
- Contaminant concentration – charged up to about 9 ppm before testing
- Injection – 4 mL of contaminant
- Air flow rate – 50 cfm
- Temperature – between 212° and 228 ° F for diffusion of contaminant; room temperature for testing

Following are the contaminant mix components used for comparative testing:

- Mix #1 – Ethanol
- Mix #2 – Ethanol, *m*-Xylene
- Mix #3 – Ethanol, Dichloromethane
- Mix #4 – Ethanol, Acetone
- Mix #5 – Ethanol, Acetaldehyde, Methanol, 2-propanol, Propylene Glycol, *m*-Xylene, 2-butoxyethoxyethanol, Dichloromethane, Acetone, Formic Acid, & Acetic Acid

Efficiency Results



In previous tests with different reactor and catalyst setups, the formation of partial oxidation products, such as acetaldehyde from ethanol, has been an issue. Using this experimental setup, one can see that in all four mix solutions, the concentration of contaminants decreased over the time that the PCO unit was employed with minimal acetaldehyde formation. Also, the lack of increase in concentration over time indicates that the catalysts have not become deactivated by the reaction.

Conclusions

The Sol-Gel Solutions photocatalytic oxidation reactor and its complimentary STC catalyst are a viable solution for controlling VOCs aboard crewed spacecraft. The unit performs well in oxidizing the contaminants into CO_2 and H_2O with a small amount of partial oxidation products, such as acetaldehyde. The process is also sustainable because the catalysts do not become deactivated by the VOCs because of the photocatalytic oxidation and can be used for long periods of time. Future work includes running the experiment with mix #5 and performing a collaborative data analysis to view the efficiency in different situations and compared to other reactor/catalyst setups.

References

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2. Levine, L. H. *et al.* Development of a Photocatalytic Oxidation-based TOC Analyzer Part II: Effect of Reactor Design and Operation Parameters on Oxidation Efficiency of VOCs, SAE 2009-01-2545.
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Acknowledgements

Special thanks to Dr. Frank Six, Dr. Gerald Karr, and the NASA MSFC Academy for the opportunity to do this research and to the MS Space Grant Consortium for funding. Much appreciation is also extended to my PI Jay Perry, mentors Joseph Scott, Ken Frederick, David Howard, and all of the ECLSS department for help and support.