FUNDAMENTALS OF AIR PURIFICATION

Halogen hydrocarbons must be removed by adsorption prior to catalytic oxidation; catalysts may become adsorbents at some conditions of use

W. R. Calvert
U. S. Navy Engineering Lab.
Annapolis, Md.

The removal of unwanted gases from the atmospheres of submarines becomes necessary when men, materials, and machines are enclosed for long periods of time. Adsorbent can remove unwanted gases such as carbon dioxide and Freon 12 along with vapors such as Freon 11. Water vapor must also be removed. Other gases not readily adsorbed at room temperature, such as Hydrogen, CO, and gaseous C-H-O- compounds, can be converted by catalytic oxidation to moisture and CO_2 which are adsorbable. Since safety in processing plants depends upon the sucessful removal of dangerous airborne materials, the data curves and information presented here may be helpful.

We have learned much about what happens when adsorbents and catalysts are used to treat air. Principle adsorbents used in these studies are 13X molecular sieves and carbon. Principle catalysts are Hopcalite and a platina/alumina catalyst which we refer to as No. 2, because it is the cheaper version, with most of the capabilities of its family of catalysts.

A look at the apparatus

The apparatus used is shown in Figure 1. In the testing, a 1 cu.ft./min. stream is prepared by adding two vapors and four gases to air. After compression, cooling, and condensate knockout, the stream is at 30 lb./sq.in. gauge at room temperature, and has constant vapor content. The adsorption step removes moisture, $CO_2$and two Freons. Heat activated adsorbents and catalysts were studied in this set-up. Bed depth was 5.4 inches; bed volume was 23 cu. in., and the stream velocity through the

Gas Analysis

CO and CO_2 by Nondispersive Infrared Analyzers
H_2 by Gas Chromatograph
Hydrocarbons by Hydrogen Flame Ionization Detectors
Moisture by Aminco % RH Meter

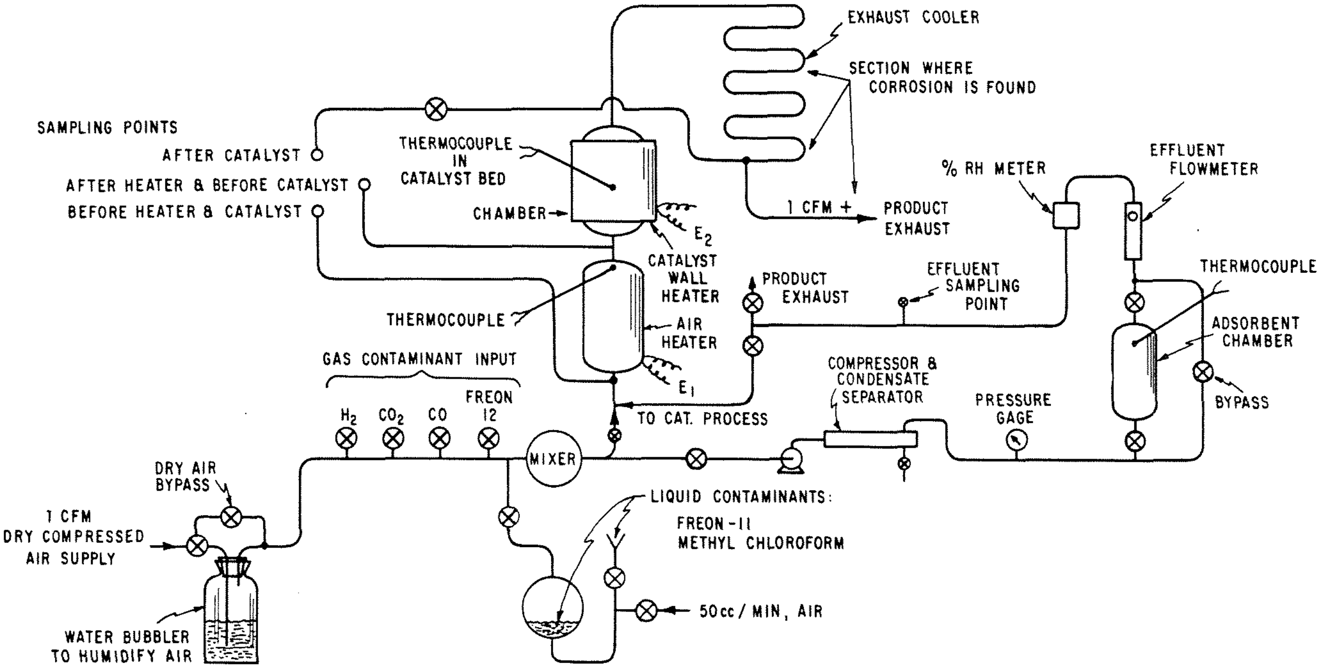

Figure 1. Flow diagram of experimental catalytic and experimental adsorption processes.

chamber was 28.9 ft./min.

Feed stream and effluent were analyzed for CO and CO_2 using the LIRA analyzers. Gas chromatography was employed for analysis for H and the Freons. Moisture was analyzed by the Aminco % RH meter which is very slow but nevertheless very informative. Catalysts were studied while heating and cooling. Bed depth was 3.5 inches; bed volume was 3.8 cu.in.; velocity through the chamber was 140 ft./min. Pressure was 1 atm., and flowrate was 1 cu.ft./min. When Freons and methyl chloroform, which is a common flame retardant solvent, were included in the oxidation studies in this section, corrosion quickly perforated the stainless steel tubing. Hopcalite was the catalyst in these studies.

Figure 2 shows simultaneous adsorption studies with data plotted for molecular sieves and catalysts. Four curves are shown from 13X molecular sieves. Four from Hopcalite are shown in column (b). Five from No. 2 catalyst includes hydrogen which was neither adsorbed nor oxidized by Hopcalite and 13X. Moisture curves are not shown, expecting that you know what they look like.

A look at a bigger curve

A magnification, of the CO_2 curves is shown in Figure 3 with 13X holding effluent % CO_2 at zero for 3½ minutes and the two catalysts are somewhat poorer in this respect. The time at zero will be used to compare adsorbents. Returning to Figure 2, it can be seen that both Freons were adsorbed well by 13X and by Hopcalite with the test ending before the 13X-Freon 11 breakthrough. Adsorption stops in the No. 2 catalyst curves as oxidation starts up.

In the CO curves on Figure 2, CO adsorption by the MnO/CuO gel catalysts is compared with the CO oxidation by the platina/alumina catalyst. The former has a breakthrough, the latter does not. Actually, while the Hopcalite was still active, it oxidized CO and then became inactive as it adsorbed CO_2, moisture, and the Freons.

Hydrogen oxidized readily on the heat activated catalysts and liberated enough heat to elevate the stream temperature to above 200°F. This is the catalyst which oxidizes hydrogen starting at room temperature. Note that the initial hydrogen concentration was 0.7% by volume.

Carbon superior for carbon

Once again the superiority of carbon for adsorbing carbon compounds is shown, Table 1. Carbon dioxide, however, is adsorbed better by the 13X type crystals of sodium aluminosilicate. And CO_2 is our principal adsorbate. The M.S. 544 is bead-like and 13X is extrudate. Both are made from 13X crystals. I have no explanation for the strange difference between the two. With Freons removed from the foul air, we can complete the task by oxidizing CO and H_2.

The curves in Figure 3 warn of desorbate coming off as throughput continues. In this Freon 11 curve from M.S. 544, adsorption A- A, is followed by a rise until the effluent's concentration is nearly double the feed concentration.

Points C for Freon 11, moisture, and CO_2 coincide as common points. The CO_2 curve is half scale. The moisture has approached its feed concentration at point C, loading the adsorbent, and with no desorption of water vapor. The point C for Freon 12 falls short because of displacement of this gas by the Freon 11 vapors.

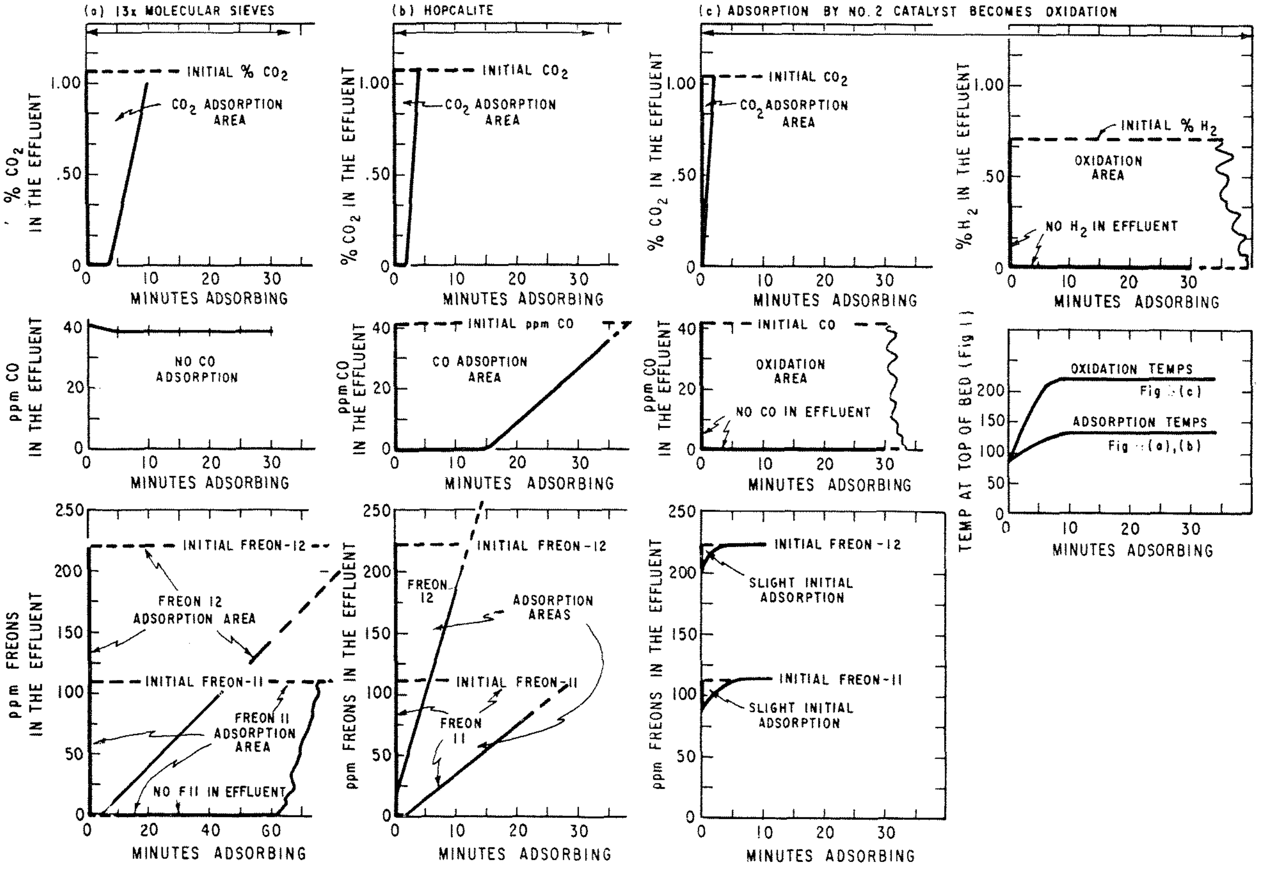

Figure 2. Simultaneous adsorption: curves from study of molecular sieves and catalysts.

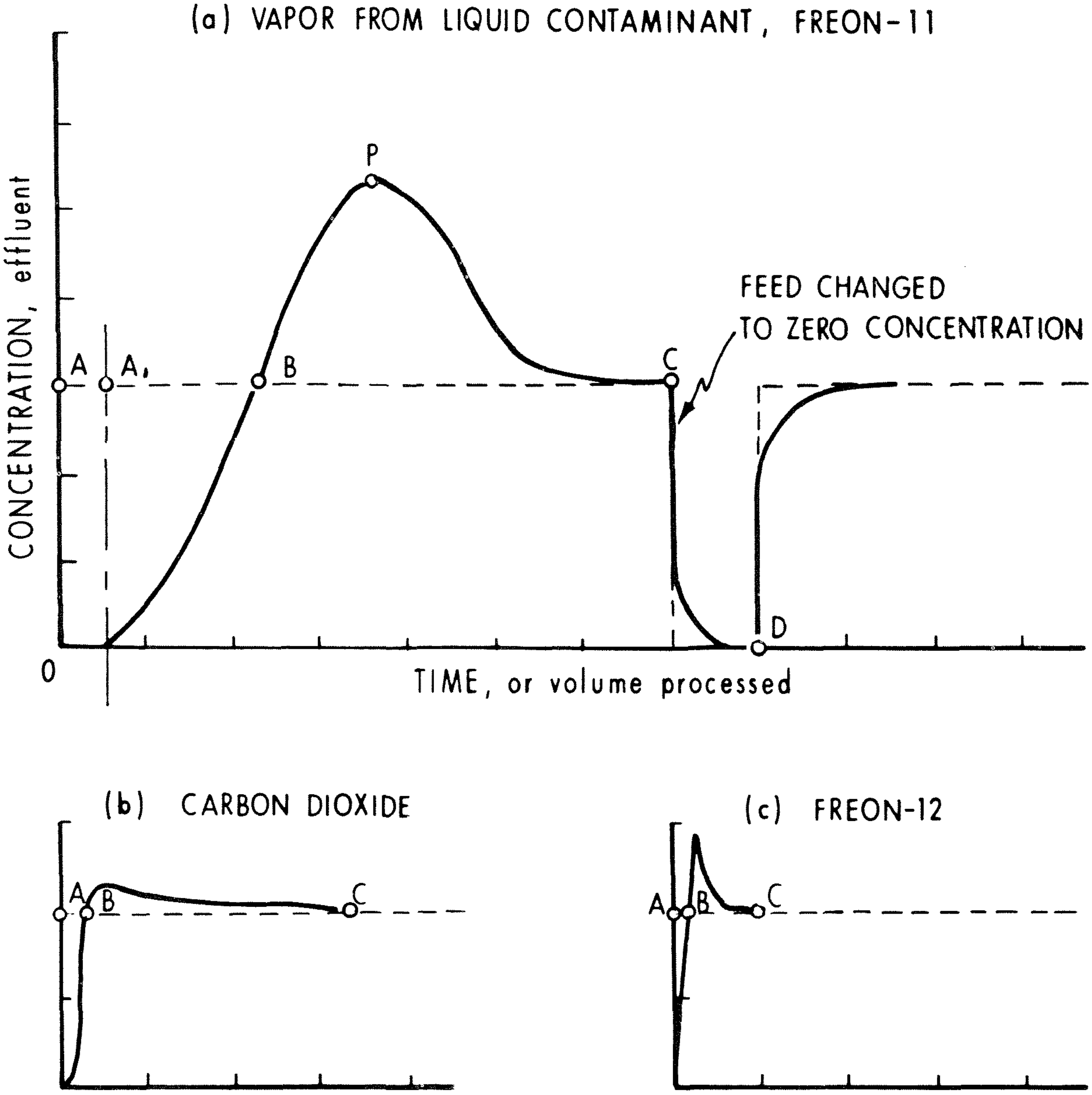

Figure 3. Graphical patterns of adsorption and desorption by carbon and sodium alumin silicate.

When contaminant input was shut off, concentration fell to zero and point D, with no indication of further desorption as would be expected if point C had been a Freon 11 equilibrium point. Heat activation is necessary for further separations, by this adsorbent or any other adsorbent. Carbon gives similar curves with other A - B - C - dimensions. Gas solids chromatography employs this phenomena. Note that A - A is the adsorption period. The shortest period in a set of curves should be used if all contaminants are to be completely removed.

In the absence of heat product from hydrogen oxidation, the CO oxidation by platinum catalyst is different, Figure 4. Adsorption at room temperature is followed by desorption resulting from the heat. This progresses along with improved oxidation until 200F. After heating to 400F, moisture adsorbs as the catalyst cools. The LIRA blank includes moisture interference, errors, and may include CO product from partial oxidation of trace hydrocarbons from the compressed air. In any case this quantity is so small that it becomes insignificant in breathing air.

A CO product may indicate trouble

In plant safety operations a CO product may indicate trouble. Where halogen hydrocarbons are involved, it warns of corrosion due to carbonyls.

Propene added to the steam gives odor trouble because of endothermic quenching of the catalyst when there is not enough heat to drive the oxidation to completion, Figure 5. Other hydrocarbons will do this, too. A large variety of products from such oxidation is possible. Acetylene may be one of them.

Fundamentals which have been demonstrated are as follows;

- Catalysts may become adsorbents at some conditions of use.
- Useful adsorption was shown to be a function of "time at zero concentration in the effluent."
- Gases have the least time at zero.

- Halogen hydrocarbons must be removed by adsorption, prior to catalytic oxidation, to avoid corrosion and toxic products
- Hazardous products may form when endothermic gases and vapors enter the catalytic reaction.
- In a mixed system of gases and vapors, displacement desorption occurs. This could be a considerable hazard when the desorbed mixture is explosive. There are ways to avoid such hazards.

Table 1. Adsorbent study results

Adsorbent Sample	**Minutes, Effluent at Zero Concentration**					
	1.0% CO	**Freon 11 100 ppm**	**Freon 12 200 ppm**	**40 ppm CO**	**0.7% H2**	**Catalytic Oxidation**
Navy Charcoal	2	240 *	90 *	0	0	None
LiOH H_2O	120+	0	0	0	0	None
Silica-gel 407	¼	15	½	0	0	None
Alumina H-151	½	½	½	0	0	None
Molecular Sieves 544	12	120+	50+	½	0	None
Molecular Sieves 522	8	0	0	0	0	None
Molecular Sieves 13X	3½	60+	5+	0	0	None
Molecular Sieves 5A	8	0	0	½	0	None
Molecular Sieves 4A	3	0	0	0	0	None
Molecular Sieves AW 500	5½	0	0	0	0	None
Catalyst $Cu/A\ell_2O_3$	½	½	½	2	0	Poor
Catalyst $Pd/A\ell_2O_3$	½	½	½	0	0	Poor
Catalyst $Cu\text{-}Cr/A\ell_2O_3$	¼	¼	. . . ¼	0	0	Poor
Catalyst 0.2 $Pt/A\ell_2O_3$	—	—	—	∞	∞	Excellent at 220 F
Hopcalite MnO/CuO	1½	½	¼	15	0	Poor

Notes: + The plus sign denotes time beyond the testing period.

* The asterisk denotes prolonged adsorption due to purge cycling.

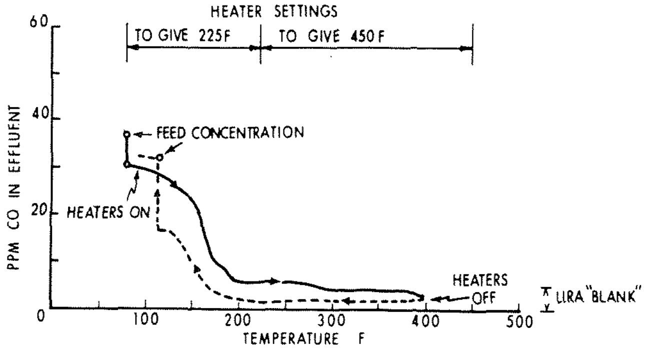

Figure 4. Low temperature catalytic oxidation of carbon monoxide by a Pt/Al_2O_3 catalyst.

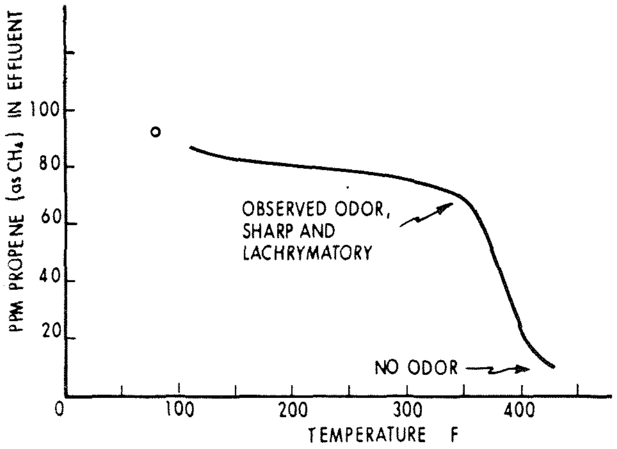

Figure 5. Incomplete initial oxidation of CH CH:CH by a Pt/Al_2O_3 catalyst.