DESIGN AND EVALUATION OF ESCAPE AND CBRN RESPIRATOR CARTRIDGES USING NANO GOLD CARBON MONOXIDE OXIDATION CATALYST

Lisa Croll, Brit Billingsley, Larry Brey, Duane Fansler, and Paul Martinson
3M Company
Saint Paul, Minnesota, USA, 55144

As presented at the 10th International Symposium on Protection against Chemical and Biological Warfare Agents, held in Stockholm, Sweden, 8-11 June 2010

ABSTRACT

This paper will present information regarding 3M's nanogold Carbon Monoxide (CO) oxidation catalyst and the design and evaluation of two individual protection respiratory cartridges that employ 3M's nanogold CO oxidation catalyst. The first is designed for escape applications from environments containing carbon monoxide and the second for chemical, biological, radiological, and nuclear (CBRN) situations.

Catalysts consisting of gold particles supported on metal oxides are known to be effective for CO removal. However, highly active gold catalysts have been difficult to prepare reproducibly by standard techniques. Scale-up of these catalysts has also proven to be difficult. 3M has developed a CO oxidation catalyst with high activity at ambient and sub-ambient temperatures. This catalyst efficiently and safely converts poisonous CO into the much less hazardous carbon dioxide (CO_2). Unlike hopcalite, the traditional catalyst for CO oxidation, the 3M catalyst contains immobilized nanogold which is not deactivated by water vapor during use. This property makes unnecessary the heavy, protective bed of desiccant normally used with hopcalite catalysts. The 3M nanogold catalyst is unique among nanogold catalysts in that it is made using a physical vapor deposition process.

INTRODUCTION AND BACKGOUND

The goal of this project was to design and evaluate individual respiratory protection cartridges that deploy the 3M nanogold CO oxidation catalyst. The steps in the project were: define the cartridge requirements using the appropriate standards, develop cartridge bed designs, assemble prototype cartridges, and evaluate the performance of the prototypes.

Definition of Cartridge Requirements

Relevant global occupational standards were used to define the requirements for two types of respirator cartridges, one intended for escape from CO containing environments and a second that would provide protection from CO during entry into CBRN contaminated environments. For both cartridges, no single standard existed that defined all of the requirements.

The escape cartridge is designed for industrial, mining or commercial escape type applications. While the primary standard defining this escape application was EN 403, the device described in this paper is also capable of meeting U.S. American National Standards Institute (ANSI) 110-2009 including the organic vapor (OV) requirement, and U.S. National Institute for Occupational Safety and Health (NIOSH) industrial 42 CFR 84 escape gas requirements.

The second cartridge is intended for operational CBRN applications. The base standard for evaluating performance of this device for CBRN applications is the U.S. NIOSH 42 CFR 84 CBRN Full Facepiece Air Purifying Respirator (APR) standard. This standard does not include requirements for CO, therefore the CO requirements from the U.S. 42 CFR 84 CBRN Air Purifying Escape Respirator (APER) standard were utilized along with the APR requirements.

Both of the cartridges were designed to have at least 15 minutes of service life for all challenge gases. See Tables 1.0 and 2.0 for the list of gases. The service life for carbon monoxide can be very long, hours or days, because the nanogold is catalytic and its activity for CO oxidation is not limited by sorbent capacity or stoichiometry as is typical of the other challenge gases. The useful life of the nanogold catalyst for carbon monoxide may be limited by accumulation of catalyst poisons during operation of the filter.

<u>Properties of CO catalysts</u>

Commercially available carbon CO catalysts fall into three categories.

- Hopcalite is a good catalyst for CO oxidation but is deactivated by water vapor.
- Supported Platinum (Pt) /Palladium (Pd)/ Tin dioxide (SnO_2) catalysts tolerate water but high Pt/Pd loadings are needed to be effective at high CO levels.
- Nanoparticle gold on oxide supports are very active at high relative humidities, but only recently have been commercially available (Mintek in Randburg, South Africa and 3M)

Each of the traditionally used CO catalysts have significant limitations. While hopcalite is an effective catalyst, it is deactivated by water. Therefore a desiccant bed up-stream of the hopcalite is required. The useful life of such a system is limited by the capacity of the desiccant bed. The Pt/Pd/SnO_2 catalysts require high precious metal loadings and therefore are very expensive materials to be used in this application. Previous technologies for making gold nanoparticle catalysts were challenging to scale up for commercial applications due to their poor reproducibility, and reclaiming unused gold from these solution-based processes can be problematic.

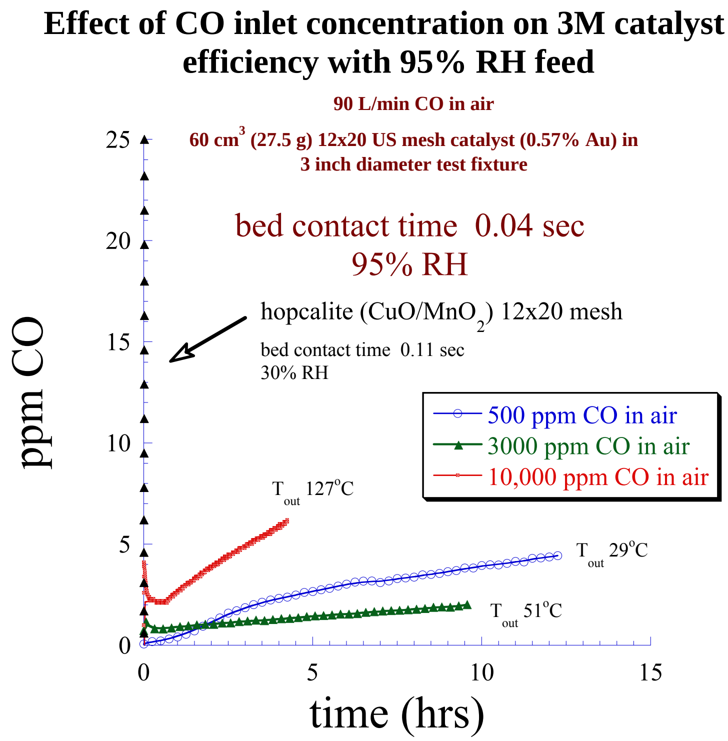
3M's nanogold catalyst has the following features:

- *Efficient removal of carbon monoxide in high humidity*
- *Efficient removal of carbon monoxide below room temperature*
- *Effective in high and low concentrations of carbon monoxide*

<u>Effect of challenge concentration on catalyst performance</u>

Graph 1.0 shows test results for various CO challenge concentrations. Results for a hopcalite catalyst are also shown for comparison. The hopcalite performance is shown by the triangles adjacent to the left axis. The challenge for the hopcalite sample was 3000ppm of CO. The outlet temperatures for the various challenge concentrations are also shown.

Graph 1.0



<u>Effect of cyclic flow on catalyst performance</u>

Certain regulatory standards specify sinusoidal cyclic flow for CO testing. The effect of cyclic flow on catalyst performance is very pronounced and often misunderstood.

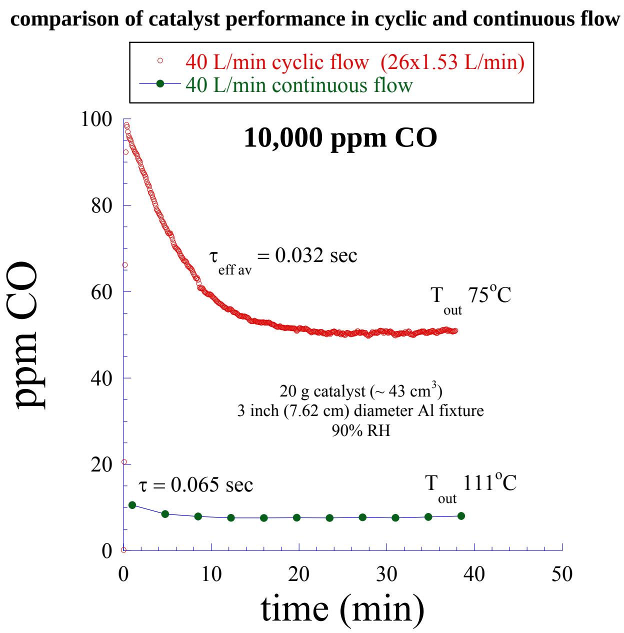
For most gases and the corresponding sorbents, the time to breakthrough of a contaminant through an adsorption bed that contains adsorbent considerably in excess of the critical bed depth is often about the same for a continuous flow and a sinusoidal flow of the same average flow rate. This was demonstrated for respirator cartridges in a series of papers published by Gary Nelson and coworkers in the 1970s, see for example Nelson, Gary O. and Harder, Charles A., 'Respirator Cartridge Efficiency Studies IV. Effects of Steady-State and Pulsating Flow', American Industrial Hygiene Association Journal, 33: 12, 797 — 805, 1972. The performance of adsorption beds is usually dominated by the <u>capacity</u> of the adsorbent for the contaminant and not the kinetics of adsorption. The adsorbent is not picking up contaminant during the "exhalation" part of the breathing cycle so the amount of contaminant adsorbed over the duration of the test is the same for both flow patterns.

However, this is not the case for filters that remove contaminants catalytically. A catalyst bed (for which performance is entirely dependent on kinetic factors) gets no benefit from "resting" during the exhale cycle. In fact, at high CO concentrations, the cooling that occurs in the reaction zone when no CO is being oxidized can decrease catalyst performance.

The EN403 30 L/min cyclic flow (20x1.5) has a *peak* flow rate of about 94 L/min (πX30). The average flow seen by the catalyst *when air is flowing* is not 30 L/min but 60 L/min (since for 1/2 of the time, the flow is zero). So the effective bed contact time in cyclic flow is 1/2 the bed contact time in continuous flow.

Graph 2.0 illustrates the effect on catalyst performance of continuous and cyclic flow patterns. Here 20 g of catalyst was tested at 40 L/min average flow (NIOSH) using both continuous and sinusoidal flow patterns. Catalyst performance is much better for the continuous flow pattern. The effect of cyclic flow on catalyst performance must be considered when designing a catalyst bed for a gas filter.

Graph 2.0



EXPERIMENTAL

<u>EN 403 Escape Cartridge</u>

The cartridge bed design that was developed for the EN 403 escape cartridge consists of a bed of protective catalyst/sorbent, in this case hopcalite, upstream of a bed of 3M nanogold catalyst. The bed design was determined based on the required service life performance for three key gases; CO, cyclohexane and hydrogen cyanide (HCN). The 3M nanogold catalyst consists of a 12 x 20 mesh bed of activated carbon coated with titanium dioxide particles onto which the nanogold islands are deposited. In addition to CO removal, the activated carbon substrate provides organic vapor service life. The protective catalyst/sorbent is a mixed oxide of copper and manganese, usually referred to as hopcalite. The hopcalite in this application is not primarily functioning as a CO oxidation catalyst but as a protective layer for the nanogold catalyst. Even in the presence of moisture, hopcalite still is an effective sorbent for certain gases, such as SO_2, H_2S, HCN, ammonia and other potential catalyst poisons that may be present in an escape situation. The total cartridge sorbent volume, consisting of the hopcalite and catalyst, is 125ml.

EN 403 escape cartridges were assembled into cartridge bodies that were approximately 100 mm in diameter and utilized a DIN 40 attachment to the facepiece. The cartridges included NIOSH P95 particulate filter elements. Packaged assembled cartridges were environmentally conditioned per EN 403 for 72 hours at 70ºC dry, 72 hours at 70 ºC and 95% RH, 24 hours at -30ºC and then rough handled as required by EN 403. The resulting cartridges had excellent CO filtration capability. When challenged with 7500 ppm CO, the maximum outlet concentration was <5 ppm CO during the first 15 minutes. After 30 minutes the breakthrough remained under 5 ppm CO. The CO service life of the catalyst can be quite long if the catalyst is protected from compounds that can poison the catalyst such as H_2S and SO_2. The protective hopcalite layer provides such protection. In other 3M tests, the nanogold catalyst was still effective after 72 hours exposure to CO in air.

Table 1 summarizes the EN 403 escape cartridge results for the key gases. The tested cartridges met the 15 minute service life requirement. The 125 ml sorbent volume in the cartridge met the requirements of EN 403.

TABLE 1.0 EN 403 Escape Cartridge Results

All at 25ºC

Challenge Agent	**Challenge Concentration (ppm)**	**Breakthrough Concentration (ppm)**	**Air Flow Rate (L/min)**	**Relative Humidity (%)**	**Service Life (Minutes)**
Hydrogen Cyanide	400	10*	30 ± 1	70 ± 5	20
Cyclohexane	500	5	30 ± 1	50 ± 5	44
Acrolein	100	0.5	30 ± 1	70 ± 5	44
Hydrogen chloride	1000	5	30 ± 1	30± 5	>70
Carbon Monoxide	2,500 ± 10%	200+	30 ± 1 cyclic#	90± 5	2 ppm max in 15 mins ∞
Carbon monoxide	5,000	200+	30 ± 1 cyclic#	90± 5	4 ppm max in 15 mins ∞
Carbon monoxide	7,500	200+	30 ± 1 cyclic#	90± 5	7 ppm max in 15 mins ∞
Carbon monoxide	10,000	200+	30 ± 1 cyclic#	90± 5	8 ppm max in 15 mins ∞

* total of HCN and C_2N_2
+ 5 minute moving time weighted average
# 20 respirations/minute with a sinusoidal wave form
∞ See Graph 1.0 for an example of service life over extended period of time

Operational CBRN + CO Cartridge

The CBRN / CO cartridge bed design is similar to the EN 403 escape cartridge in that it uses a hopcalite bed to protect the catalyst. In addition, the cartridge contains a CBRN capable multigas carbon bed upstream of the hopcalite which in turn is upstream of the nanogold catalyst. The total volume of the cartridge is 335 ml. For this CBRN cartridge the hopcalite layer also protects the catalyst from nitrogen compounds that may off gas from the carbon. The key gases that determined the cartridge size for the CBRN / CO cartridge were cyanogen chloride, ammonia, SO_2 and CO.

Table 2.0 provides the cartridge service lives for the key gases as well as other gases. Prior to testing the packaged cartridges were environmentally conditioned for 3 weeks of diurnal temperature cycling, 3 days at -32 ºC, 5 days of humidity followed by 36 hours of Mil-Std-810F, 514.5 vibration.

TABLE 2.0 CBRN / CO Cartridge Results

Challenge Agent	**Challenge Concentration (ppm)**	**Breakthrough Concentration (ppm)**	**Air Flow Rate (L/min)**	**Relative Humidity (%)**	**Temp ºC**	**Service Life (Minutes)**
Ammonia	2500	12	64	25 ± 5	25	25.7
SO_2	1500	5	64	25 ± 5	5	22.8
Hydrogen cyanide	940	4.7‡	64	80 ± 5	25	100
Formaldehyde	500	1	64	25 ± 5	25	>60
Hydrogen sulfide	1000	5	64	80 ± 5	25	>69
Nitrogen dioxide	200	1ppmNO_2 or 25ppm NO	64	80 ± 5	25	32
Cyclohexane	2600	10	64	80 ± 5	25	41
Carbon monoxide	3600	500	64	90 ± 5	25	1 ppm max in 15 mins ∞
Carbon monoxide	3600	500	64	90 ± 5	0	70 ppm max in 15 mins ∞
Carbon monoxide	6000	500	64	90 ± 5	25	1 ppm max in 15 mins ∞
Carbon Monoxide	6000	500	64	95	0	30 ppm max in 15 mins ∞

‡ total of HCN and C2N2

∞ See graph 1.0 for an example of service life over extended period of time.

The CBRN cartridge met the 15 minute requirement for all of the challenge gases.

CONCLUSIONS

The test results of these two cartridges confirm that the nanogold CO oxidation catalyst is a viable CO filtration technology for respiratory protection cartridges. The results also demonstrate that it is possible to design cartridges that meet existing respiratory protection standards in addition to providing protection from carbon monoxide.