Volatile Organic Compounds (VOC) interaction with high and low temperature carbon monoxide/hydrogen oxidation catalysts

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Abstract

Under its duty of care the UK Ministry of Defence (MoD) must ensure that Royal Navy (RN) submarines maintain a safe breathable atmosphere. A key component in this is the high-temperature carbon monoxide (CO)/hydrogen (H_2) burner. This employs a bed of Moleculite®, a copper oxide/manganese dioxide oxidation catalyst at elevated temperature. Although the primary function of the burner is the removal of H_2 and CO an important secondary role is the removal of Volatile Organic Compounds (VOC). This paper presents the finding of an investigation to determine the removal performance of Moleculite® for several submarine atmosphere VOC. Removal of between 61 and 76 % total VOC content was found, suggesting that the CO/H_2 burner has a significant impact on the level of atmospheric VOC. Whilst Moleculite® has been the catalyst of choice for many years, other materials which operate at lower temperatures are of growing interest. Use of these alternatives would provide significant power savings. Low-temperature catalysts have the potential to be poisoned by submarine atmosphere contaminants. The laboratory evaluation of two Johnson-Matthey precious metal catalysts is reported. Results showed that VOC had only a minimal effect on CO and H_2 oxidation performance and that these catalysts had an average VOC removal of 78.5 %. Low-temperature catalysts have potential to replace the currently used high-temperature catalyst with no adverse effect on either CO/H_2 or VOC removal performance.

Introduction

Under its duty of care, the UK Ministry of Defence (MoD) must ensure that Royal Navy (RN) submarines maintain a safe breathable atmosphere. To achieve this, the MoD adopts a rigorous Passive and Active atmosphere control programme which has been discussed in previous SAMAP papers.

The submarine's atmosphere is consistently monitored and controlled within set exposure reference values (detailed in the UK restricted publication BR1326 - Book of Reference for Submarine Atmosphere Control) [1]. These levels are set to ensure that submariner health is not compromised, and so operational capability of the platform is maintained.

The UK has for the last twelve years, run a contract with QinetiQ to provide scientific support to atmosphere control under the Maritime Strategic Capability Agreement (MSCA). The contract objective is to assist the UK MoD in providing assured support to critical capabilities. The life support section for Submarine Atmosphere Control, consists of six specialist scientists which assist the MoD in providing scientific support / evaluation, and targeted and underpinning research on atmosphere management techniques.

Every year the MoD and QinetiQ evaluate areas of interest and potential development opportunities to support submarine atmosphere control. A full scientific programme is developed and contractually agreed, and progress evaluated at quarterly intervals.

The MoD tasked QinetiQ under this contract to evaluate the potential use of preidentified precious metal catalysts for low temperature carbon monoxide (CO) / hydrogen (H_2) removal and subsequent Volatile Organic Contaminants (VOC) removal. This work is reported further in this paper

On RN submarine's, CO and H_2 are removed by a high-temperature catalytic burner. The burner employs a bed of Molecular Products' Moleculite®, a copper oxide/manganese dioxide oxidation catalyst that operates at an elevated temperature.

While the primary function of the burner is the removal of CO and H_2, anecdotally, it has a number of secondary benefits that include the removal of VOC, microbiological contamination, and aerosols. Although there has been some work [2] to measure the contribution made by the burner to the removal of submarine VOC, it is still not fully quantified. Complete thermal oxidation of VOC would normally require temperatures in excess of 1000 °C. Catalytic oxidation can occur at far lower temperatures [3, 4, 5, 6, 7, 8, 9, 10, and 11], however this does not always result in complete VOC degradation. Partial breakdown products can be formed, which contribute to a submarine's VOC load and may be more hazardous to health. This paper details some of the work carried out to quantify VOC breakdown over the Moleculite®.

Moleculite® has been used for many years, however, there has been increasing interest in alternative low-temperature catalysts. The advantage of these catalysts would be a significant reduction in power consumption. Under contract to the MoD, QinetiQ has evaluated several potential alternative low-temperature catalysts for CO and H_2 removal. This work identified a dual-bed catalyst consisting of Johnson-Matthey's (JM) Q1 (palladium on iron oxide) and Q3 (platinum on titanium dioxide) that can oxidise CO and H_2 at 100 °C.

One obstacle to the introduction of low-temperature catalysts is their potential poisoning by contaminants in the submarine atmosphere. QinetiQ has exposed the JM catalysts to a range of VOC in laboratory tests. Although it is impossible to completely replicate the complex VOC mix present on-board a submarine, this study exposed the catalysts to several different classes of contaminant, such as, alkanes, aldehydes, and alcohols.

Experimental

High-temperature Moleculite® tests

The laboratory test apparatus is shown in Figure 1. A compressor supplied diluent air which was then divided into a 'dry' flow and a 'wet' flow that had passed through a wash bottle. The required relative humidity (RH) of the challenge air was obtained by controlling the proportion of 'wet' and 'dry' air using flow controllers. The humidity of the challenge air was maintained at around 50 % RH measured at room temperature. The air flow was set to a gas hourly space velocity (GHSV) of 60000 h^{-1} through the catalyst to match that of the high-temperature CO/H_2 burner.

The catalyst was fresh Moleculite® packed to a depth of 0.5 cm in a glass furnace tube. The tube furnace temperature was operated at 280 °C which is the standard operating temperature of the CO/H_2 Burner.
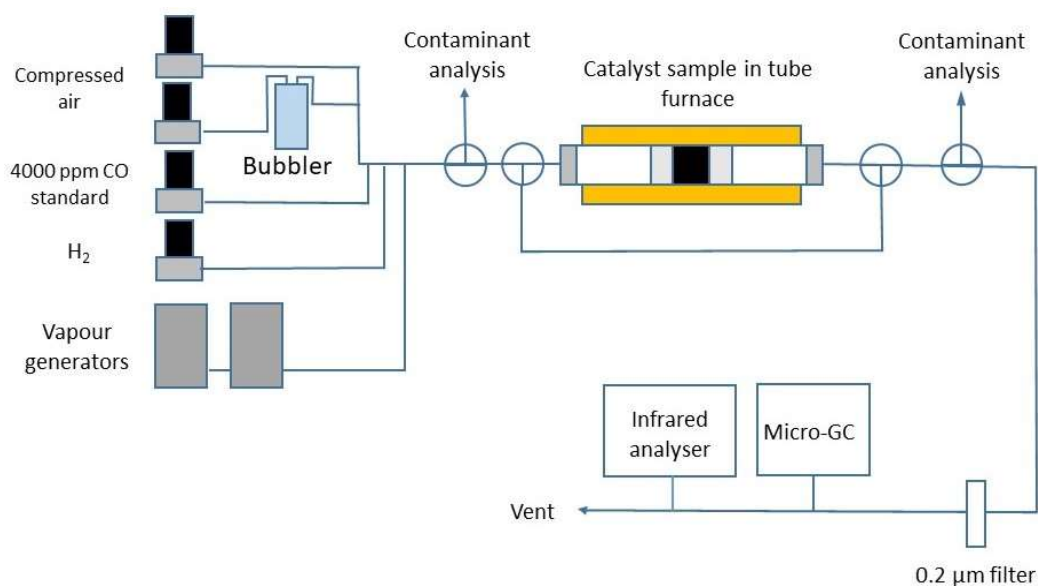
Figure 1: Schematic experimental arrangement for the high-temperature catalyst study

A test gas of 6 ppm CO concentration was produced in the challenge gas by blending a 4000 ppm standard with diluent air. CO was monitored by infrared using either a Thermo Environmental Instruments 48 °C analyser, or a Gasmet DX4040. Test H_2 concentrations were produced by blending the pure gas with diluent air and measured using a micro-GC fitted with a molecular sieve column and thermal conductivity detector.

The test VOC were selected from the list of target contaminants in BR1326 [1]. VOC were produced using two Graseby standard generators, operated at different temperatures to account for the difference in volatility of target compounds. The first generator contained: 2-butanone, benzene and decane and operated at 33 °C, and the second contained: 1, 2, 3-trimethylbenzene, acetophenone and naphthalene and operated at 70 °C. Details of the dimensions of the diffusion devices and the test concentration are shown in Table 1.

VOC	Diffusion tube capillary		Diffusion chamber temperature (°C)	Concentration (ppm)
	Length (mm)	Diameter (mm)		
2-Butanone	75	1	33	2.1
Benzene	75	1	33	2.5
Decane	15	3	33	1.4
1,2,3-Trimethylbenzene	21	2	70	4.2
Acetophenone	75	5	70	3.0
Naphthalene	75	5	70	1.3

Table 1: Standards generator conditions for the high-temperature Moleculite® tests

Inlet and outlet samples were collected using Tedlar gas bags. A 400ml aliquot of this gas was then sampled onto Carbograph 1-TD sorbent tubes (Markes International) and analysed using thermal desorption/gas chromatography/mass spectrometry (TD/GC/MS) - Markes International Unity/Ultra, Thermo Scientific Trace GC Ultra and DSQ II MS. The GC was fitted with a BPX5 capillary column (SGE, 50 m x 0.2 mm x 1.0 µm film thickness). Stock VOC solutions were produced gravimetrically in methanol (HPLC grade Fisher). Calibration standards were prepared by serial dilutions of these solutions. The analysis of Carbograph tubes spiked with 4 µl of liquid standard was used to produce VOC calibration graphs.

Moleculite® was exposed to the CO, H_2 and the VOC mix for 6 h. As H_2 oxidation is highly exothermic, tests were repeated, using a fresh catalyst bed, for a challenge concentrations of 0.0, 0.5 and 2.0 % H_2.

Low-temperature catalyst tests.

Figure 2 shows the modified experimental arrangement used for the low-temperature catalyst tests. Packed dual-beds of Q1 and Q3 catalyst (5 mm each) were held in place using glass beads in the 18mm diameter test cell. Heating tape was used to maintain the required temperature of the catalyst bed. The voltage across the heating tape was reduced during tests with H_2 in the challenge gas to maintain the temperature constant at 100 °C.
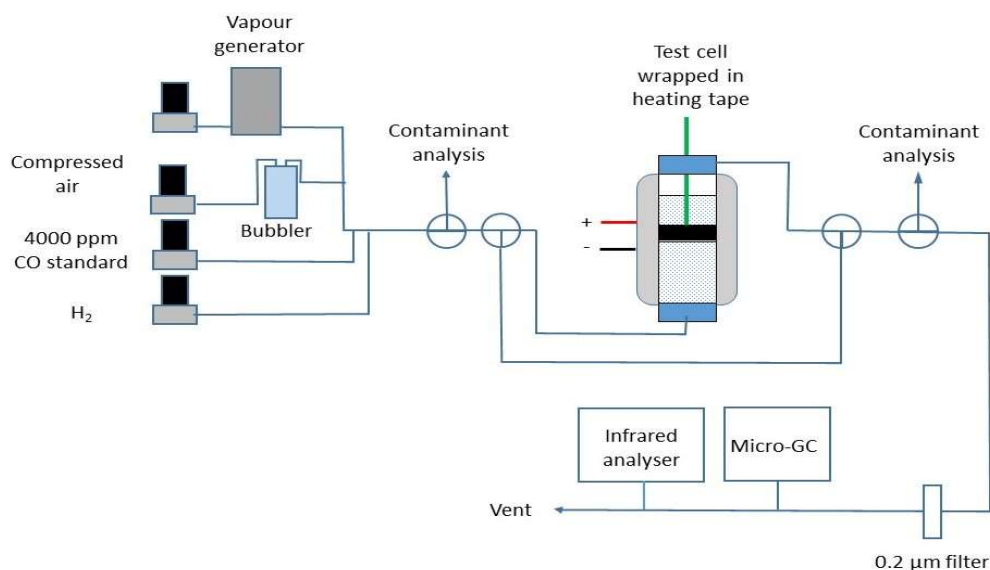

Figure 2: Schematic experimental arrangement for the high-temperature catalyst study

Test VOC were again selected from the BR1326 [2] list of target contaminants. The intent was to expose the catalysts to the low concentration of VOC typically present in a submarine atmosphere rather than the higher submarine action limits. Vapour phase VOC were supplied by the Standards Generator and gases by an additional flow controller. A GHSV of 60000 h^{-1} was used and the challenge gas contained 6 ppm CO and 0.5 % H_2.

VOC measurement, apart from methanol, ethanol and butanol, used the same sampling method as the high temperature catalyst work. A smaller 100 ml sample was transferred to the Carbograph TD1 tube for TD/GC/MS analysis. The other contaminants were measured using either Draeger gas detection tubes or the Gasmet DX4040 analyser.

Table 2 lists the contaminants, their measured concentrations, and the exposure times. A miscalculation of the required standard generator conditions resulted in a higher than planned concentration of butan-2-one. After the first aldehyde and ketones test, the butan-2-one diffusion vial was removed from the generator and oven temperature raised to increase the concentration of benzaldehyde and acetophenone.

VOC	Exposure duration (h)	Concentration (ppm)	
Alcohols: Methanol Ethanol Butanol	168	1.90 0.99 1.56	
Alkanes: Decane Nonane	168	0.36 0.82	
Aromatics: Toluene Ethyl-benzene Para-xylene	168	2.25 0.55 0.78	
Aldehyde and ketones: Butan-2-one Benzaldehyde Acetophenone	96	Low Temp. 33.2 0.43 0.14	High Temp. - 0.65 0.39
Chlorinated: 1,1,1-Tricholorethane 1,1,1-Trichloroethylene Tetrachloroethane	168	4.93 1.16 0.16	
Siloxanes: Hexamethylcyclotrisiloxane Octamethylcyclotetrasiloxane Decamethylcyclopentasiloxane	168	0.25 0.11 0.07	
Hydrogen sulfide	21	0.05	
Ammonia — Test 1	7	1.80	
Ammonia — Test 2	14	3.10	

Table 2: Experimental conditions for the low-temperature catalyst tests

Results

High temperature Moleculite® tests

The percentage removal of analytes was calculated using the equation below.

$$Removal = \frac{[analyte]_{inlet} - [analyte]_{outlet}}{[analyte]_{inlet}} \times 100$$

The average percentage removal of the six test VOC during the 6 h experiment are shown in Table 3.

VOC	Inlet concentration (ppm)	Outlet concentration (ppm)	Average removal (%)
2-Butanone	1.148	0.023	98
Benzene	0.895	0.474	47
Decane	0.251	0.073	71
1,2,3-Trimethylbenzene	0.081	0.015	82
Acetophenone	0.031	0.006	81
Naphthalene	0.012	0.003	75
Average VOC percentage removal			76

Table 3: High-temperature Moleculite® results

The results in Table 3 show that the measured inlet VOC concentrations was less than that expected from the reduction in weight of the diffusion tubes (Table 1). This may indicate VOC adsorption within the test apparatus. The total VOC challenge concentration was about 2.4 ppm. Benzene had the lowest removal of 47 % probably due to the inherent stability of the aromatic ring structure.

The results of this study were in agreement with those of the sole submarine Minor Trial from 1984. During this trial the VOC removal efficiency of the high-temperature burner was 70 – 80 % [2].

Table 4 contains the results of experiments to determine the effect of H_2 in the inlet air.

VOC	0.0 % H_2	0.5 % H_2	1.8 % H_2
	Average removal (%)		
2-butanone	79	80	76
benzene	46	26	25
decane	66	65	55
1,2,3-trimethylbenzene	71	77	72
acetophenone	72	79	79
naphthalene	68	71	-
Average VOC removal	67	66	61

Table 4: Effect of H_2 concentration on VOC removal by Moleculite®

The results in Table 4 show that, apart from benzene, H_2 had little effect on the removal of the VOC. It is unclear why the breakdown of benzene was so much less. The fresh catalyst bed in the 0.0 % H_2 experiment had a lower VOC removal efficiency than that used for the earlier experiment (Table 3). It is possible that this was due to differences in the packing density of the catalyst bed.

In addition to measuring the reduction of target VOC, outlet samples were analysed for partial breakdown products. These results indicated that none of the target VOC were incompletely oxidised. Given the very low challenge concentration, it is possible that the concentration of partial breakdown products was below the limit of detection of the analytical procedure.

Low-temperature catalyst tests

Table 5 shows the CO and H_2 oxidation performance of the low-temperature dual catalysts prior to and after exposure to atmosphere contaminant compounds.

Contaminants		Exposure duration (h)	Average removal (%)			
			Pre-exposure		Post-exposure	
			CO	H_2	CO	H_2
Alcohols		168	98.4	100.0	100.0	100.0
Alkanes		168	100.0	100.0	100.0	100.0
Aromatics		168	100.0	99.3	99.9	100.0
Aldehydes and ketones		192	99.4	97.3	99.5	98.1
Chlorinated		168	100.0	96.0	100.0	100.0
Siloxanes		168	98.3	95.0	100.0	88.4
Hydrogen sulfide		7	99.3	98.5	100.0	100.0
		14			100.0	100.0
		21			100.0	100.0
Ammonia	Test 1	7	100.0	100.0	100.0	43.9*

Contaminants		Exposure duration (h)	Average removal (%)			
			Pre-exposure		Post-exposure	
			CO	H$_2$	CO	H$_2$
	Test 2	14	100.0	100.0	100.0	100.0

*Averaged result

Table 5: Effect of atmosphere contaminants on low-temperature CO and H$_2$ oxidation

These results show that exposure of the catalysts to most contaminants did not adversely affect CO and H$_2$ oxidation. The only exceptions to this were found during the ammonia and siloxanes exposure experiments.

In the first ammonia exposure experiment H$_2$ oxidation initially dropped to 67.8 % then declined over time to 16.5 % (averaged oxidation 43.9 %). Heating the catalyst in contaminant-free air at 100 °C restored the H$_2$ removal to 69.0 %. The second ammonia exposure experiment was conducted using fresh catalyst and this maintained 100 % H$_2$ for 14 h. The catalysts used in these experiments came from the same batches and it is unclear why results were so variable.

After the siloxane experiments, a baseline performance test using fresh catalyst had degraded H$_2$ removal. This was attributed to residual siloxane within the test apparatus. After thorough cleaning of the apparatus, H$_2$ removal using a second sample of fresh catalyst beds remained lower (67 %) than expected (100 %). An and extended purge of the catalyst at 100 °C with contaminant free air removed all remaining siloxane from the system and restored the H$_2$ removal efficiency to 100 %.

The percentage removal of the target atmosphere contaminants during the low-temperature catalyst experiments are shown in Table 6.

Contaminant		Outlet concentration (ppm)	Percentage removal (%)
Methanol		0.00	100.0
Ethanol		0.00	100.0
Butanol		0.00	100.0
Decane		<0.01	97.2
Nonane		<0.01	98.8
Toluene		0.24	89.3
Ethyl-benzene		0.04	92.7
p-Xylene		0.12	84.6
Butan-2-one		0.40	98.8
Benzaldehyde		<0.01	98.5*
Acetophenone		<0.01	97.4*
1,1,1-Tricholorethane		1.84	62.7
1,1,1-Trichloroethylene		0.03	97.4
Tetrachloroethane		<0.01	93.8
Hexamethyltricyclosiloxane		0.13	48.0
Octamethylcyclotetrasiloxane		0.08	27.3
Decamethylcyclopentasiloxane		<0.01	85.7
Hydrogen sulfide		0.00	100.0
Ammonia	Test 2	0.57	81.6
Average contaminant removal			78.5

* High temperature experiment

Table6: Test cell outlet concentration of contaminants and breakdown products

These results show >80% removal of most contaminants and an overall average removal of 78.5%. The exceptions were 1,1,1-tricholorethane, hexamethyltricyclosiloxane and

octamethylcyclotetrasiloxane. Analysis of samples of the outlet air found no partial breakdown products.

During the second ammonia experiment the outlet air was monitored for oxides of nitrogen (NO_x). Table 7 shows the concentration of nitric oxide, nitrogen dioxide and nitrous oxide in catalyst inlet and outlet air.

	Ammonia (ppm)	Nitric oxide (ppm)	Nitrogen dioxide (ppm)	Nitrous oxide (ppm)
Inlet	3.08	0.23	0.13	0.36
Outlet	0.57	0.00	0.05	0.25

Table 7: Ammonia and NO_x concentrations during second ammonia test

These results shows that although the catalysts removed 81 % of the ammonia in the inlet air, there not a proportionate increase in the NO_x concentrations of outlet air. Further work has been recommended using a more sensitive NO_x chemiluminescent analyser to determine the fate of ammonia on these catalysts.

Conclusions

The high-temperature catalyst Moleculite® oxidised most VOC. Laboratory experiments showed average total VOC removal of the six test compounds was 61 – 76 %. These finding indicate that the CO/H_2 burner makes a significant contribution to controlling VOC in the atmosphere on RN submarines.

The low-temperature catalyst study showed that the CO and H_2 removal performance of a dual-bed of JM Q1 and Q3 catalysts was unaffected by the majority of submarine atmosphere contaminants. This system could potentially form the basis of a future low-temperature CO/H_2 burner. The catalysts had an average contaminant removal of 78.5 % suggesting that this important secondary function would not be lost in a low-temperature precious metal burner.

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