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Environment in Submarine Compartments

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ABSTRACT

The crew operating in the confined environment of a submarine are subjected to discomfort as a result of physiological stress caused by toxic substances which are generated due to engineering, operational and other human activities. The physiological problems of men under prolonged confinement in a submarine have been reviewed. Data on air pollutants monitored during 'cruise' and 'at rest' conditions inside a submarine are given. Threshold limit value (TLV) of trace substances in the confined environment has been discussed. The merits of air purification and air revitalization systems currently employed for control of air pollution have been brought out.

1. INTRODUCTION

The submarine crew are subjected to discomfort due to the generation of toxic gases by various engineering and operational activities. Some of the sources of these toxic gases are batteries, fuels, refrigerants, foodstuffs, degreasing agents, paints, polymers and the metabolic activities of the crew themselves. During snorting, toxic gases such as carbon dioxide, hydrocarbon and oxides of nitrogen are generated. During diving, build-up of carbon dioxide results in the depletion of oxygen. Prolonged exposure of crew to these gases not only impairs his efficiency but also may prove risky. In the recent years, therefore, monitoring of toxic gases in the submarine and their control have become very essential.

2. DISTURBANCE OF NORMAL ENVIRONMENT

Constituents of the normal environment of a submarine are shown in Table 1. There is a gradual decrease in the amount of oxygen and an increase in the amount of carbon dioxide as a result of the respiration of the crew. The relationship between

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Table 1. Normal atmosphere constituents

Gas	(%) by volume
Nitrogen	78.05
Oxygen	20.90
Argon	0.93
Carbon-dioxide	0.03
Other gases	0.09

consumption of oxygen and build-up of carbon dioxide is depicted in Fig. 1. An average rate of consumption of oxygen per man per hour is 27 litres, whereas, the release of carbon dioxide is 25 litres. Addition of oxygen when its concentration decreases to 18 per cent (v/v) and absorption of carbon dioxide when its concentration increases to 1 per cent (v/v) are desirable.

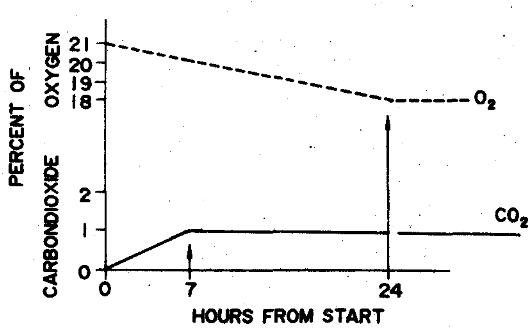

Figure 1. Submarine environment. Arrows indicate increase in CO_2 after 7th hour and O_2 depletion after 24th hour.

3. SOURCES OF CONTAMINATION

The contaminants are generated from materials of construction, operation of the equipment and human physiological activities. In addition, machinery operation, cooking, smoking and charging of batteries produce toxic gases, vapours and aerosols which contaminate the normal atmosphere of a submarine. The possible sources of major contaminants in a submarine are given in Table 2. These can be further categorised into three groups, namely, organic, acidic and alkaline toxic gases and vapours with hetero-atoms of sulphur, nirtogen and halogen and possessing a neutral character (Table 3).

4. MAXIMUM ALLOWABLE CONCENTRATIONS

Maximum allowable concentrations (MAC) of some contaminants reported by the American Conferences of Government Industrial Hygienists[1] which pertain to eight hours daily exposure for five days a week at work places cannot be applied to those working in closed compartments. The situation is a little more complicated since

Table 2. Sources of main contaminants in submarine compartments

Contaminant	Possible source(s)
Carbon monoxide	Burning of oils, smoking
Carbon dioxide	Respiration, burning of organics
Sulphur dioxide	Burning of fuels
Hydrogen sulphide, mercaptans	Burning of fuels
Organics (hydrocarbon)	From fuels, solvents, cleaning agents
Ethylbenzene, xylene, methanol, ethanol	Paints, solvents, lubricating oils
Triaryl phosphate	Compressors, lubricating oils
Freons	Leaks of refrigerants
Chlorine	Freon decomposition
Hydrogen chloride	Freon decomposition
Oxides of nitrogen	Burners
Hydrogen	Batteries
Stibine	Batteries
Sulphuric acid aerosol	Batteries
Ammonia	Scrubbers, sanitary tanks, cooking
Acetaldehyde, acetone, lactic acid, butyric acid, ketones	Humans

Table 3. Classification of important contaminants

Group I *C, H, O* compounds	Group II Acid or alkaline type	Group III Neutral gases
Benzene, Toulene, Xylene, Acetaldehyde, Methyl ethyl ketone, Acetone, Hexane, Pentane, Methane	Chlorine, Hydrogen, Fluoride, Ammonia, Nitrogen dioxide, Hydrogen chloride, Sulphur dioxide, Hydrogen sulphide, Carbon dioxide	Vinyl chloride, Trichloro-ethylene, Freons, Stibine

the MAC for toxic substances in the closed environment has been arrived at by examining the effect of individual gases. This does not relate to a mixture of gases, a complex situation encountered in the confined spaces of the submarine. La Belle *et al.*[2] reported that the synergistic effects of mixed gases were more pronounced and greater than the effects of the individual components. Fairchild *et al.*[3] have reported antagonistic action of toxic compounds. For example, sulphur compounds offer protection against ozone toxicity. The interaction of toxic compounds results in the formation of new reaction products which add to the complexity of establishing tolerance limits of trace substances in the closed environment. Situations like these emphasize the urgency of toxicological studies on mixtures of toxic substances. The MACs specified for exposure in submarine operations are given in Table 4. The

Table 4. Maximum allowable concentrations of toxic gases in submarine compartments[28,29]

Contaminant	MACs
Carbon monoxide	100 ppm
Carbon dioxide	0.5%
Hydrocarbons (HC)	500 ppm
Sulphur dioxide	5 ppm
Chlorine	1 ppm
Stibine	0.1 ppm
Hydrogen	2%
Freon (Dichlorodifluoro methane)	1000 ppm
Ammonia	100 ppm

standard values are modified by a factor of at least 10 in order to ensure proper environmental safety in submarine compartments.

The emperical equation for the members of a group exposed simultaneously to more than one pollutant can be given by[1]:

$$\sum_{i=1}^{n} \left(\frac{C_i}{SMAC_i} \right) = 1$$

where, *i* is one of a toxicological group of *n* contaminants, SMAC is the individual maximum allowable concentration based on toxicity, and *C* is the maximum allowable concentration of each contaminant in the mixture. For example, the individual MACs are 20 ppm for *X* and 40 ppm for *Y*. If these two contaminants are present at the same time and are limited to concentrations of 15 ppm for *X* and 10 ppm for *Y*:

$$\sum_{i=1}^{n} \left(\frac{C_i}{SMAC_i} \right) = \frac{15}{20} + \frac{10}{40} = 1$$

It is logical that the individual maximum allowable concentrations should be reduced to the modified values that are pertinent to physiological action.

5. TOXICITY OF INDIVIDUAL AIR CONTAMINANTS

Carbon monoxide (*CO*) is a colourless and odourless gas and has great affinity for haemoglobin which is about 240 times more than that of oxygen. *CO* impairs the transport of oxygen at the tissue level. Carboxy haemoglobin levels of 4 per cent and above are undesirable. An exposure to 100 ppm *CO* for 2.5 hrs cause significant decrease in visual perception, manual dexterity, ability to learn and perform certain intellectual tests.[4] Carbon monoxide also causes peripheral atherosclerotic disease in man,[5] which develop leg pain even after short walking. *CO* is formed in the body through the breakdown of haemoglobin at a rate of 10 cc per day.[6,7] For a free air volume of lm^3 per man, 25 ppm of *CO* level would be reached in less than five days, if the *CO* is not removed continuously.

The toxic effects of carbon dioxide are well known. An increase in CO_2 causes an increased rate of breathing and high concentrations paralyze the respiratory centre resulting in asphyxiation and death. An exposure to 0.5 per cent CO_2 will cause deeper and faster breathing, whereas, 2-3 per cent of carbon dioxide in the air increase ventilation by 50 and 100 per cent. Five per cent CO_2 causes about 300 per cent increase in ventilation and breathing becomes laborious. 10 per cent of CO_2 in air can be endured for a few minutes only.[8] At 12-15 per cent exposure of CO_2, unconsciousness and death may take place. The recommended maximum allowable concentration for CO_2 is 5000 ppm.

Hydrocarbons and other organic compounds are produced by the incomplete combustion of fuel and other carbon containing substances. These organic compounds in the gaseous or particulate form include methane, propane, formaldehyde, benzene, acrolein, etc. Aliphatic hydrocarbons are basically inert and have no demonstrable effects except at very high concentrations.[9] However, aromatic hydrocarbons are very irritating. National Academy of Sciences,[10] USA reports that chronic exposures to some aromatic hydrocarbons are responsible for leukopenia and anemia; and benzene, toulene or xylene at concentrations above 100 ppm may cause fatigue, weakness, discomfort, confusion, skin paresthesias, etc. Benzo *a*-pyrene, a combustion product of fuels is carcinogenic.

Most of the studies on effects of oxides of nitrogen have been focused on nitrogen dioxide (NO_2) as other oxides of nitrogen react in air to produce nitrogen dioxide.[11] Nitrogen dioxide causes irritation of eyes and nose[12,13] at concentrations between 10 and 15 ppm. High incidence of respiratory illness of families residing in 0.06 to 0.1 ppm NO_2 areas has been reported.[14] Shy[15] *et al.* have studied its effects on children resulting in significant decrease in the pulmonary functions of youngsters exposed to high levels of NO_2 as compared to controls. World Health Organisation reports[16] that exposure to nitrogen dioxide levels of 0.7 to 2.0 ppm for 10 minutes gives rise to an increase in inspiratory and expiratory flow resistance; inhalation of 1.6 to 2.0 ppm nitrogen dioxide concentration for 15 minutes causes a significant increase in total airway resistance.

Sulphur dioxide is a colourless gas with pungent odour and can form SO_3, H_2SO_4 and later sulphates. It causes various respiratory problems like asthma, chronic bronchitis and emphysema. It affects lung functions, irritates eyes, and increases mortality.[17-20] Lawther, *et al.*[19] reports the minimum pollution level leading to a significant response to be about 0.19 ppm (500 μ g/m^3) of SO_2.

Chlorine boils at –35 °C. It is an irritant to the respiratory passages.[21] Exposure to chlorine causes burning of the eyes, cough, and respiratory distress. Tracheobronchitis, pulmonary edema and pneumonia may also develop due to prolonged exposure to chlorine.

Hydrazine is a liquid and boils at 114 °C. It is highly irritating and toxic. Injury to lungs, liver and kidneys has been reported[21] due to inhalation of the vapour of hydrazine. It is absorbed through the skin and causes dermatitis.

Stibine is one of the toxic hydrides, produced during battery charging, due to the presence of antimony in battery grids. Schaefer[22] has reported that stibine concentration above 0.1 ppm is injurious to human health.

Formaldehyde is a colourless and highly reactive gas.[23] It is a component of cigarette smoke and diesel exhaust.[24] Symptoms of mucous membrane and respiratory tract irritation have been associated with formaldehyde exposure. However, it also disturbs memory, mood equilibrium, vegetative functions and sleep.[24] Nasal and eye irritation and lacrimation have been reported[25] at lower concentrations of formaldehyde (i.e., 2-4 ppm).

Freons are colourless hydrocarbon vapours used as refrigerants in air conditioners. They have a very low toxicity.[26]

6. EFFECTS OF TOXIC GASES ON MATERIALS

The generated gases affect submarine construction materials adversely in many ways. They induce corrosion of metals, deterioration of machinery, linoleum and lacquer and also fading of colours. It is noteworthy that the presence of moisture, movement of air and presence of other pollutants play a role in the deterioration of materials. For instance, sulphur dioxide with carbon particles produces rapid corrosion than corrosion caused by sulphur dioxide alone. The surface deterioration of glass and ceramic materials caused by air pollutants is also a well recognised problem onboard submarine. It is worthwhile to note that the resistance of electrical contact increases due to air pollutants. It is due to the build-up of particulate materials and to the formation of reaction products on the contact surface. The effects of toxic gases on materials are illustrated in Table 5.

7. MONITORING OF TOXIC GASES IN CLOSED COMPARTMENTS OF A SUBMARINE

7.1 Instruments

'Comowarn' and 'Warnex' (M/s. Dragerwerk, AG Lubeck) were employed for monitoring carbon monoxide and hydrocarbons, respectively. Chemical detector tubes prepared in NCML were employed for monitoring of stibine and chlorine.

Polymeter equipped with long range carbon dioxide tube (M/s. Dragerwerk AG Lubeck) was also employed.

Table 5. Effects of toxic gases on materials

Gas(es)	Effect(s) on Material(s)
SO_2 and acid gases	Spoilage of surface, corrosion of machinery, loss of metal varnishing, loss of tensile strength
SO_2 acid gases sticky particulates	Discolouration
Acid gases	Change the surface appearance
SO_2, NO and oxidants	Fading of colours
SO_2 and H_2S	Spoil tanks, refrigerators, etc.
CO and Cl_2	Damage sensitive machinery
HC and Cl_2	Fading of colours, linoleum, lacquers, etc.
SbH_3 and H_2S	Spoil the absorbents
Hg	Spoils compasses

CO_2, O_2 and H_2 meters fitted in the submarine were utilised for monitoring of these gases periodically during sea trials.

7.2 Monitoring

Monitoring of toxic gases namely, CO, CO_2, H_2, SbH_3, Cl_2 and hydrocarbons has been conducted in the closed compartments of a submarine during its 'cruise' and when it was berthed at shore for engineering maintenance work. Maximum values obtained during 'sea trials' and 'at shore' are summarised in Tables 6 & 7 respectively. Results show that levels of CO_2 and hydrocarbons are more than MAC in sea trials and levels of CO and hydrocarbons at shore are more than MAC.

Table 6. Levels of toxic gases : sea trial experiences

No. of days cruise	:	6 days (125 hrs)
No. of crew	:	96
Temperature of sea	:	32.5–35°C
Maximum diving depth	:	60 meters
Maximum submergence period	:	300 minutes

Toxic gas	MAC	Maximum value obtained
CO	50 ppm	35 ppm
CO_2	0.5%	1.5%
HC	0.05%	1.25%
SbH_3	0.1 ppm	Nil
Cl_2	0.1 ppm	Nil
O_2	18-22%	20%
H_2	2%	0.5%

Table 7. Levels of toxic gases : submarine at shore

No. of days : 35 days

Activity : Engineering maintenance and battery charging

Toxic gas	MAC	Maximum value obtained
CO	50 ppm	140 ppm
CO_2	0.5%	0.33%
HC	0.05%	0.75%
SbH_3	0.1 ppm	Nil
Cl_2	0.1 ppm	Nil
H_2	2%	0.4%

8. AIR PURIFICATION SYSTEMS

In order to enable a submarine to remain submerged for a longer period, air purification equipments are essential. Air purification equipments can be categorised mainly into two classes; one that produces desirable gases and another which removes undesirable contaminants. In submarines, it is imperative to remove various gases namely oxides of carbon, nitrogen and sulphur, hydrogen, hydrocarbons, etc. and to generate vital gas, i.e., oxygen. Some air purification systems are as follows.

Absorption on soda lime.
Absorption on Lithium hydroxide.
Absorption on charcoal.
Reaction with peroxides.
Liquid amine scrubbers (MEA).
Solid amine absorption (TEA).
Catalytic oxidation.
Bio systems.
Electrodialysis.
Solid Polymer Electrolysis (SPE).

9. AIR REVITALIZATION CHEMICALS

Total air revitalization chemicals offer an attractive alternative to other methods.[27] These chemical systems are relatively light, occupy very little space and use a nominal support of energy. The air revitalization chemicals are capable of producing oxygen and absorbing carbon dioxide. The revitalization system can be evaluated on the basis of :

(i) Theoretical oxygen yield and carbon dioxide absorption per unit mass (or volume) of chemical.
(ii) Chemical reactivity to breathing atmosphere.
(iii) Physical state.
(iv) Commercial availability.
(v) Toxicity and hazards in use.
(vi) Beneficial side reactions.

Air revitalization chemicals can be classified into three main groups, i.e. peroxides, superoxides and ozonides. Properties of these compounds are summarised in Table 8.

Table 8. Theoretical properties for air revitalization compounds[27]

Compound	Chemical formula	Kg O_2 evolved per kg chemical	Kg CO_2 absorbed per kg chemical	Kg chemical needed for 0.85 kg O_2	SRQ*
Lithium peroxide	Li_2O_2	0.35	0.96	2.43	1.94
Sodium peroxide	Na_2O_2	0.21	0.56	4.05	1.94
Lithium superoxide	LiO_2	0.61	0.56	1.39	0.67/1.33
Sodium superoxide	NaO_2	0.43	0.40	1.98	0.67/1.33
Potassium superoxide	KO_2	0.34	0.31	2.50	0.67/1.33
Calcium superoxide	$Ca(O_2)_2$	0.46	0.42	1.85	0.67†
Lithium ozonide	LiO_3	0.73	0.39	1.16	0.4/0.8
Sodium ozonide	NaO_3	0.56	0.31	1.52	0.4/0.8
Potassium ozonide	KO_3	0.46	0.25	1.85	0.4/0.8

* SRQ (system respiratory quotient) : The ratio of the volume of CO_2 absorbed to the volume of O_2 released by a chemical system.

For those chemicals having two system respiratory quotients, the first order is the CO_2 absorption by carbonate formation only and the second is for bicarbonate formation only.

† Calcium does not form a bicarbonate.

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