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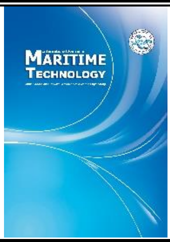

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Review Article

A comprehensive review of air purification technologies in submarine atmospheres

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ABSTRACT

Maintaining a precisely controlled atmospheric environment is paramount for optimizing the operational effectiveness and survivability of military submarines. Early submarines operated with rudimentary atmospheric management, severely limiting submerged endurance. However, the escalating demands of naval warfare, particularly during and following World War I, catalyzed the development of progressively sophisticated air revitalization systems. These advancements enabled extended submerged operations, a key tactical advantage. The advent of nuclear-powered submarines marked a watershed moment, revolutionizing atmospheric control by eliminating the reliance on atmospheric oxygen for propulsion. This technological leap not only transformed submarine propulsion but also spurred the development of highly advanced air purification systems, subsequently influencing conventional diesel-electric submarine designs. More recently, the emergence of air-independent propulsion (AIP) submarines has further underscored the critical importance of efficient and reliable air revitalization, as these platforms strive for prolonged submerged durations. This comprehensive review examines the historical evolution of air purification methods in military submarines, specifically focusing on the pivotal technological advancements that have enabled extended submerged operations and significantly enhanced crew survivability. It highlights the development and refinement of key technologies, including electrochemical and chemical oxygen generation, advanced carbon dioxide removal techniques such as amine scrubbing and solid sorbents, and sophisticated contaminant control strategies utilizing catalytic converters and filtration systems. This review also explores how these advancements have been seamlessly integrated into both nuclear and AIP submarine platforms, detailing the unique challenges and solutions associated with each.

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1. Introduction

To execute the strategic tasks of submarines, it is essential to create conditions that enable humans to perform challenging duties [1]. While there are numerous factors to consider in this environment, a primary requirement is to ensure a physiologically acceptable atmosphere that supports human life and does not adversely affect health or cognitive functions[2, 3]. Table 1 presents the gases present in the atmosphere along with their volume percentages.

Table 1. Normal atmosphere constituents [1].

Gas	(%)by volume
Nitrogen	78.05
Oxygen	20.9
Argon	0.93
Carbon dioxide	0.03
Other gases	0.09

The management of this atmosphere has been a gradual process adapted to the changing strategic needs of submarines and new advances in propulsion technology. This evolution was made possible by a combination of unlimited air-independent power and a stable enclosed space[4, 5]. However, the genesis of the submarine's atmospheric control lay in the submarine's early designs[1]. Common submarine pollutants and their possible sources are listed in Table 2.

Table 2. Air pollutants in the submarine environment and their sources*[1]*.

Contaminant	Possible source(s)
Carbon monoxide	Burning of oils, smoking
Carbon dioxide	Respiration, burning of organics
Sulfur dioxide	Burning of fuels
Organics (hydrocarbon)	From fuels, solvents, and cleaning agents
Ethylbenzene, xylene, methanol, ethanol	Paints, solvents, and lubricating oils
Chlorine	Freon decomposition
Hydrogen chloride	Freon decomposition
Oxides of nitrogen	Burners
Hydrogen	Batteries
Sulfuric acid aerosol	Batteries
Ammonia	Scrubbers, sanitary tanks, and cooking

To ensure the safety of the crew in the short and long term, it is important to specify the permissible composition of the submarine's atmosphere [6]. Table 3 shows the submarine air profile for a typical submarine.

Table 3. Typical submarine air specification for a conventional submarine [2].

Compound	Limit
NO_2	5 ppm
CO_2	5000 ppm
CO	35 ppm
SO_2	2 ppm
Formaldehyde	2 ppm
NH_3	25 ppm
O_3	0.1 ppm

The need for physiologically acceptable air quality was identified in early man-powered submarines. Notable examples were the Hunley and the Alligator[7], the latter of which was the first submarine purchased by the United States Navy (1862). It was 14 meters long and powered by a hand screwdriver and a crew of 16 (or possibly more). Although manpower provided limited speed, it had the advantage of silent movement, which was one of the main requirements of submarines. The short time spent underwater necessitated the control of the internal atmosphere. This was achieved by passing air over the lime with the help of the tail to remove carbon dioxide. Later generations of successful submarine designs incorporated various forms of mechanical propulsion, including steam engines. Batteries were charged by combustion engine generators on the surface. Originally, submarine internal combustion engines ran on gasoline, exposing submarines to fuel fires. Interestingly, these risks were more of a concern than the concentrations of carbon dioxide and oxygen. Later, during World War I, the introduction of diesel engines reduced the risk of fuel fires in submarines, and they were the forerunners of submarines. Of the submarines of World War I, only German-built submarines were equipped with primitive atmospheric control through the use of carbon dioxide absorbers and compressed oxygen cylinders[8].

2. World War II generation submarines

World War II submarines, like their predecessors, were semi-buoyant. They were designed primarily for surface operations and, like any other surface ship, were equipped with keels and had guns mounted on deck. They achieved maximum speed on the surface and were slow when immersed. Generally, these submarines remained underwater during the day to avoid visual detection, appearing at night to recharge batteries and perform operations for surface navigation. Work for 1 hour or at a speed of 2 knots for 36 hours. The strategy of deep diving and silence was often used to avoid detection by sonar as well as to avoid depth bombs. In many cases, this required long-term diving c ourses. This allowed a submarine without a carbon dioxide removal system to stay underwater for 15 hours [9] before the concentration of carbon dioxide with a normal crew increased to 3 percent. In the same period, oxygen concentrations dropped to 18% in the absence of supplemental oxygen. These concentrations represented the acceptable limits set by the Royal Navy Admiralty Directives for the operation of air purification equipment on submarines [10].

2.1. Air Purification in World War II generation submarines

As radar clarity improved during World War II, longer dive times were required. The Allied submarines were poorly prepared for this and had few air purification measures. As a result, crew efficiency was severely affected during long dives. For example, it was not uncommon for CO2 levels to exceed 3% and for crews to have difficulty performing physical tasks or even conversing or lighting matches[10]. German and Italian submarines were better served due to their carbon dioxide removal system, oxygen supply, and basic air monitoring. Carbon dioxide was available to British submarines in the early years of the war. It came in 1 form of soda lime, contained in trays, and was distributed throughout the submarine [11]. According to the medical advice of the Royal Navy at the time, compressed oxygen was not carried. In the final years of World War II, the Royal Navy had both the means to remove carbon dioxide and produce oxygen in submarines, but for some reason, it was reluctant to use these resources against the Germans and Italians, preferring to tolerate poor air quality [10]. Due to the lack of space in submarines, there is not always a desire to carry additional equipment unless perfection is necessary. Apart from this, the German and Italian navies had a long-standing culture of air purification practices in submarines. There may also be a greater need for these submarines for a longer period as Allied anti-submarine operations improve. However, after an increase in the number of reports of debilitating health effects (such as headaches and thinking disabilities) experienced on British submarines during long-term scuba diving on May 2, the Royal Navy's attitude changed.[11] Both lithium hydroxide and soda lime are used in submarines to remove carbon dioxide. The higher reaction is lithium hydroxide. It is a mixture of calcium-4 hydroxide and sodium hydroxide (approximately 3-5%) [12].

An intermediate of lithium hydroxide monohydrate is involved in the reaction of carbon dioxide with anhydrous lithium hydroxide [12].

$$LiOH(s) + H_2O\ (g) \rightarrow LiOH{\cdot}H_2O \quad (1)$$

$$LiOH{\cdot}H_2O(s) + CO_2\ (g) \rightarrow Li_2CO_3(s) + 3H_2O\ (g) \quad (2)$$

In the presence of gaseous carbon dioxide, a more complex reaction with soda lime occurs [10]:

$$CO_2\ (g) + Ca\ (OH)_2(s) \xrightarrow{H_2O} CaCO_3(s) + H_2O\ (l) \quad (3)$$

The reaction can be broken down into several steps with the following relative reaction rates:

$$CO_2\ (g) + H_2O \rightarrow CO_2 \quad (4)$$

$$CO_2\ (soln) + NaOH \rightarrow NaHCO_3 \quad (5)$$

$$NaHCO_3 + Ca\ (OH)_2 \rightarrow CaCO_3 + NaOH + H_2O \quad (6)$$

$$CO_2\ (soln) + Ca\ (OH)_2(s) \rightarrow CaCO_3 + H_2O \quad (7)$$

In 1944, the Royal Navy installed oxygen candles on the HMS Thule mixed with iron filings, rated Oxygen. These emitted electrically ignited almost pure sodium chlorate in a highly exothermic reaction [10]. Figure 1 shows an example of upgraded oxygen candles.

Figure 1. Self-Contained O2 Candle [13].

The reactions are as follows [10]:

$$NaClO_3 \rightarrow 2NaCl + 3O_2 \quad (8)$$

$$Fe + O_2 \rightarrow 2FeO \quad (9)$$

Several adverse reactions occur in the presence of water, which produce traces of chlorine-containing compounds that are eliminated by the reaction with barium peroxide, for example:

$$BaO_2 + Cl_2 \rightarrow BaCl_2 + O_2 \quad (10)$$

Oxygen piles continue to remain an integral part of submarine atmospheric control, as usual, and for use in emergencies. Although the above measures dealt with respiratory gases, the overall air quality remained poor. After a day of patrolling, the smell was described as a combination of "the smell of unwashed corpses," the nauseating smell of past meals, cooking, fuel oil, and damp clothes. On the air composition problems, the crews of British submarines operating in tropical waters were severely affected by the high temperatures, which led to heat stroke, ankle swelling, and septic and fungal skin infections. It was estimated that this would reduce human efficiency to 60% after 13 hours of diving [14].

2.2. Air monitoring in World War II generation submarines

Efforts to introduce carbon dioxide monitors in Royal Navy submarines took place in the late stages of World War II, but such tools were considered to be highly sensitive instruments [1]. Several American oxygen measuring devices (Pauling and later model -2D Beckman) were evaluated. These devices were based on the paramagnetic properties of oxygen (as opposed to the diamagnetic properties of nitrogen) and had direct accuracy and readings, but were easily damaged. Additionally, the official view was that the presence of air monitoring equipment in submarines would negatively impact the team's morale. In a British report in 1945, 13 carbon dioxide monitors were evaluated, some of which were obtained from German submarines. These devices included instruments based on ultraviolet absorption and thermal conductivity. However, many carbon dioxide sensors at that time relied on the absorption of carbon dioxide by a test agent (for example, soda-lime) inside a small chamber and then measuring the resulting decrease in pressure with a manometer. This principle was a device tested in German submarines in 1942 [2]. When this device was evaluated by the British, it was recognized as a robust and precise instrument [1]. By the end of World War II, German and Italian submarines had tools for measuring carbon dioxide, oxygen, and humidity, and thus could prevent the harmful effects of high carbon dioxide concentration and low oxygen concentration. However, it appeared that they were not used regularly. The reason for this is not clear, but the complexity of the procedures likely made their use difficult. Although the instruments of that time may not have been suitable for operational war purposes, they were sufficiently robust for marine testing.

In 1947, a successful air quality experiment was conducted on a British submarine using tools to measure oxygen, carbon dioxide, and carbon monoxide. The concentrations of oxygen were measured with a Pauling paramagnetic oxygen analyzer. Carbon dioxide was measured by thermal conductivity using an instrument from Cambridge Instruments. This was a significant advancement compared to the tools available during the war. Carbon monoxide was measured using the type III carbon monoxide chemical indicator from the Royal Aircraft Establishment, Farnborough [3]. The principle of operation of this tool is not explained. The experiments were notable in that they indicated a change in the culture of indifference towards air quality in the Royal Navy submarines. By the end of World War II, submarines were more 'real' than ever at depth and began to evolve as 'the ultimate goal of self-reliance from atmospheric air for propulsion and life support was achieved in 1939 when the Germans evaluated a small developed test submarine that used hydrogen peroxide as an oxygen source to power a diesel fuel turbine [4]. Hydrogen peroxide was catalytically decomposed into oxygen, but was unstable and prone to unexpected explosions. Despite this problem, some operational boats were built, although none saw combat. After the war, two British submarines (Excalibur and Explorer) were built based on German design. They briefly achieved an underwater speed of 26 knots and could outpace many surface vessels [5].

3. Nuclear Submarines

The success of nuclear submarines ended the short-lived relationship with the hydrogen peroxide system, which played an important role in highlighting the strategic advantages of air-independent propulsion. The nuclear reactor provided the means for air independence and almost unlimited energy. This was a logical extension of the concept of AIP. Advances in air purification and air monitoring in diesel-electric submarines provided the early technology for nuclear submarines. However, it was inappropriate because it relied on non-regenerative methods of carbon dioxide removal and oxygen production. Since these submarines were supposed to spend months at sea and be submerged most of the time, the large amounts of soda lime (or lithium hydroxide) piles and oxygen (or compressed oxygen) required to make this approach impractical. These limitations became apparent when one of the first nuclear submarines, the USS Nautilus, went to sea in 1955. As a result of the poor air quality, more comprehensive air purification equipment was gradually installed to facilitate longer diving times. The introduction of rocket-carrying submarines in the 1960s accelerated the development of air purification [15]. The stealth requirements of these submarines were crucial to Cold War strategy.

3.1. Air Purification in Nuclear Submarines

3.1. 1. Carbon dioxide removal

Nuclear submarines have used regenerative carbon dioxide removal systems based on molecular sieve zeolites and amines. Carbon dioxide capture/removal from molecular sieve can be achieved by changing the pressure (pressure fluctuation) or changing the temperature (temperature fluctuation), and removing moisture from the air. The second problem is solved by passing air over the pre-drying beds and then absorbing water and returning the water vapor to the submarine's atmosphere. The French have continued to use molecular sieves, while both the Royal Navy and the United States Navy have abandoned the system and have switched to amines (in aqueous solution) instead [10]. Carbon dioxide absorption occurs at ambient temperature, and desorption occurs at a temperature of approximately 135 °C. In amine plants, carbon dioxide-laden air passes through a packed adsorbent tower where carbon dioxide reacts with amine. The reaction mixture is then transferred to a boiler where the pure carbon dioxide is removed, compressed, and discharged into the sea, in a state of flux, while the amine is returned to the adsorbent tower in a continuous process. Monoethanolamine in water and relatively low fluctuations is the most commonly used amine. This process requires monitoring of amine concentrations by acid-base titration under non-ideal conditions of the submarine environment. In some cases, there is a leakage of an amine solution that requires attention and is complicated by the toxic nature of MEA. To reduce the release of runaway amine from the scrubber, the discharged air passes through an ion exchange resin filter bag before entering the ventilation system. The atmospheric concentration of 0.5% carbon dioxide can be achieved with this type of scrubber, and unlike the molecular sieve system, there is no nitrogen or water damage in the waste carbon dioxide stream. The solid amino acid potassium salt, methylalanine, has also been evaluated and considered as a substitute for MEA. It has the advantage of low salt fluctuations, but in some conditions, it tends to precipitate as bicarbonate [15].

3.1. 2. Oxygen production

Initially, nuclear submarines used compressed oxygen to revive the air and oxygen supplies for emergencies. This system was quickly replaced (1953) by electrolytic oxygen generators based on industrial equipment [15]. This is an energy-intensive process that can only be accomplished through the availability of a power source, such as a nuclear reactor. The by-product, hydrogen, is discharged into the sea. There are two types of electrolyzers, low-pressure and high-pressure (200 atmospheres) at sea. Low-pressure electrolyzers are newer and have fewer components, and are easier to operate [16].

Figure 2 shows a low-pressure electrolyzer sample.

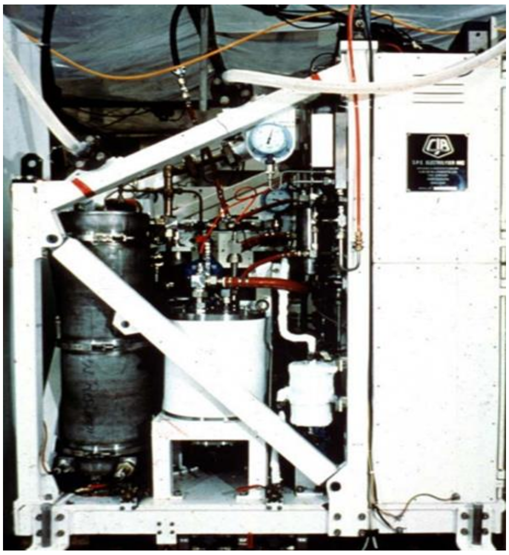

Figure 2. Wellman Defense Ltd Low Pressure [11].

3.1.3.Carbon Monoxide and Hydrogen Removal

Nuclear submarines have fewer batteries than diesel-electric submarines and only have a small diesel engine for emergency propulsion. Nevertheless, enough carbon monoxide and hydrogen are produced to ensure a high-temperature catalytic oxidizer to remove these gases from the atmosphere [17]. Hapcalite catalyst, a mixture of copper oxide and manganese dioxide, has been used in coal mines for some time to remove carbon monoxide in the air. The air passes through a heat exchanger and then through the catalyst substrate, which operates at 315°C. The system is also effective in removing many organic air pollutants by oxidation to carbon dioxide and water [18], and there is anecdotal evidence that this process eliminates biological pathogens in submarines.

3.1.4.Volatile organic compounds

The submarine environment is contaminated by volatile organic compounds emitted by machinery, electronics, building materials, paints, lubricating oils, hydraulic fluids, and human habitation activities. In addition to removing VOCs by a catalytic burner, a large activated charcoal filter is used in the air conditioning system. Charcoal can absorb up to 20 to 25 percent of its weight in VOCs [19] and is effective at reducing odor and eliminating all but the most volatile compounds.

3.1.5.Aerosols

There are many sources of aerosols in submarines. The main source of conventional diesel-electric submarines is the exhaust of the diesel engine. Analysis of aerosols collected on filter papers in the Royal Navy Nuclear Submarines Machinery Area showed that the average concentrations were approximately 0.2 mg/m3, of which approximately 65% were probable aliphatic organic compounds from lubricating oils [19]. To reduce aerosol emissions, valve precipitators are used to remove oil fog from the valves of oil tanks, while atmospheric particulate matter is removed by two-stage electrostatic precipitators. Some of these are modular and can be removed for easy cleaning, while others are self-cleaning [18]. The latter uses a cleaning solution that is sprayed automatically and periodically on the electrodes to remove deposits.

3.2. Air Monitoring in Nuclear Submarines

In 1954, an analyzer was installed aboard the USS Nautilus to monitor the atmosphere, but it never functioned. The next working version (Version II) measured the concentrations of carbon dioxide, carbon monoxide, oxygen, hydrogen, and hydrocarbons, and was about the size of a closet. Air samples were taken from eight different locations throughout the submarine [6]. The concentrations of carbon dioxide, carbon monoxide, and hydrocarbons were measured using infrared absorption technology developed in Germany before the war. As expected, sensitivity to hydrocarbons was relatively low, with a full-scale range of 6500 ppm. Oxygen was measured using a paramagnetic sensor and hydrogen using a thermal conductivity sensor. Later versions (IV-III) were equipped with infrared Freon sensors. These sensors were not sensitive to small leaks of refrigerant. The cells were pressurized (6 atmospheres) to improve sensitivity, but both the cells and the infrared sensors were not reliable. Pressurized cells were replaced with atmospheric pressure cells that were 1.2 meters long to provide the necessary sensitivity. To further improve sensitivity, Version V used an automatic gas chromatograph to analyze all gases. Although these instruments worked well in the laboratory, they were not suitable for submarines. The analyzer was very complex for the crew and faced reliability issues.

In the 1980s, the hydrocarbon monitor was replaced by a simpler and portable optical ionization sensor [16]. Eventually, the entire analyzer was replaced with a central atmospheric monitoring system using mass spectrometry (magnetic analyzer), which achieved the reliability it sought in the next 25 years. This system did not include any prior concentration or separation of air pollutants. Air samples were directly introduced to the mass spectrometer, and air pollutants were separated in the magnetic analyzer according to the mass/charge ratio using a fixed collector set for each mass. Thus, the selection of target compounds was incorporated into the instrument's hardware. Carbon monoxide was measured using a separate infrared absorption device. By the mid-1980s, an advanced version of I-CAMS became available, II-CAMS, capable of scanning within the desired mass range (300-2 amu), determined by software. This led to a greater degree of flexibility resulting from the use of microprocessors that were not previously available. The early nuclear submarines of the Royal Navy were equipped with a system for air monitoring that included a gas chromatograph with four separate packed columns to monitor hydrogen, oxygen, carbon dioxide, and carbon monoxide [7]. Like the early monitors in U.S. submarines, this system also faced reliability issues and was replaced in 1980 by the British version of the U.S. Navy CAMS. However, the British CAMS used a quadrupole analyzer instead of a magnetic analyzer. Quadrupole analyzers were more sensitive to calibration drift. The reliability issues associated with these air monitoring systems are not necessarily related to technology. Often, it is the installation and maintenance procedures that can lead to these problems[20]. The complex and often hostile environment poses a challenge for any air monitoring technology. There is also a requirement for continuous operation for 90 days without factory support or calibration. In addition, real-time monitoring has been addressed by both the U.S. Navy and the Royal Navy with past airborne monitoring for gases and particulate matter [7]. In the Royal Navy, over 30 organic compounds are quantitatively determined using gas chromatography-mass spectrometry.

These compounds include aromatic hydrocarbons, low molecular weight alcohols, and ketones[8]. Additionally, 30 other compounds are determined semi-quantitatively. Particulate matter in the air is collected on glass fiber filters for 24 hours and is analyzed retrospectively for metals using inductively coupled plasma spectrometry. Filter samples are also extracted with carbon dioxide (supercritical fluid) and are analyzed for polycyclic aromatic hydrocarbons (PAHs) and water-soluble ions: fluoride, chloride, chlorate, nitrate, nitrite, bromide, sulfate, and phosphate using ion chromatography[8].

4. Conventional submarines

After the war, diesel-electric submarines were designed and built in the 1950s and into the 1970s, which were mainly based on World War II concepts. In the period that followed, for the first time, operational submarines were built without a keel. However, progress in the air purification system has been slow to match the capabilities of nuclear submarines.

4.1. Air Purification in Conventional Submarines

The French submarines were equipped with charcoal filters with a total of 80 kg (minimum) distributed throughout the submarine, which were replaced every 90 days. UV (for airborne pathogens) is also included in each of the units [10]. The air purification system 1 of the Australian Collins-class submarines, which were launched between 1996 and 2003, is more advanced than other conventional submarines. In addition to lime and oxygen candles, these submarines have a wet carbon dioxide scrubber, similar to nuclear submarines. The air conditioning system is installed in the front compartment of the submarine [21]. A low-temperature 2H/CO catalytic burner is installed in the engine room. The catalyst is composed of platinum and palladium-coated tin oxide, which is more active and can operate at lower temperatures than alumina, with the 2 palladium-coated coatings used in Calles Oberon submarines [22]. Unlike the high-temperature hoplite catalytic burner used in nuclear submarines, the system has little effect on hydrocarbons and minimal impact on 3 4 CFCs, although some of the more reactive VOCs are partially oxidized by the catalyst. For example, ethanol and trichloroethylene are oxidized to acetaldehyde and vinylidene chloride, respectively [10], which are more toxic than the main compounds. To meet the growing demand for atmospheric control in conventional submarines, a small-scale modular air purification system with particulate filtering, a hydrogen/carbon monoxide oxidation catalyst that operates at ambient temperature, and a high-temperature catalyst for methane removal has been produced. An activated charcoal filter is used to remove higher molecular weight VOCs, and carbon dioxide is removed with lime soda. The system is designed for a crew of 12 to 30 people and a relatively short dive time typical of diesel-electric submarines [10].

4.2. Air monitoring in Conventional Submarines

In general, the diesel-electric submarines that have received more attention in terms of air quality are those operated by naval forces equipped with nuclear submarines. This is based on the assumption that there cannot be two standards of air quality in their submarines. Currently, only France has both conventional and nuclear submarines, while the Royal Navy relatively recently retired the Upholder class of diesel-electric submarines in the 1990s. Other navies have paid more attention to submarine air quality due to increasingly stringent health and occupational safety regulations regarding air pollution. The navies of Canada and Australia have largely adopted air quality standards from the United States and the United Kingdom for nuclear submarines [23]. Air quality surveys in conventional submarines, such as the British Oberon class, have shown that the main source of air pollution in submarines is hydrocarbon vapors and aerosols [14]. VOC concentrations in the engine room, which mainly consist of diesel fuel (hydrocarbons), range from 50-2 ppm. The highest concentrations are obtained immediately after shutting down the engines. Under these conditions, the engine room is poorly ventilated and, due to the heat of the engines, it is at a high temperature, leading to fuel evaporation from various sources. These fuel vapor concentrations are also present in modern diesel-electric submarines, although diesel vapors may primarily be limited to the engine room. Submarines equipped with charcoal filters, such as the Australian Collins-class submarines, typically include the engine room in their air purification system. Maintaining good air quality in the living areas of submarines is important as it allows the body to eliminate some of the pollutants that may have been absorbed in more polluted areas, such as the engine and machinery rooms.

5. New Generation of Conventional Submarines (AIP)

The most significant recent development in submarine technology has been the development of air-independent propulsion (AIP). Several AIP propulsion systems have been developed, and both the Sterling engine (Sweden) and the fuel cells (Germany) are currently used in operational submarines. Both technologies require liquid oxygen. The Sterling engine is a vibration-free external combustion engine and can be used on almost any fuel. The main source of energy is the hydrogen fuel cell, although it does not contain hydrocarbon or alcohol fuels. It can be modified to produce hydrogen.

5.1. Air Purification in the New Generation of Conventional Submarines

The modern AIP can allow a submarine to operate underwater for 2 weeks or more. Due to the availability of liquid oxygen, oxygen replenishment can be easily achieved; however, the problem of carbon dioxide removal is similar to that of nuclear submarines. The currently producing AIP submarines, such as the German Type 212 and the Swedish Gotland class 19A, use a non-regenerative system (lime soda or lithium hydroxide). Ironically, the same problem was encountered in the early years of nuclear submarines. To take full advantage of the potential benefits of AIP, a regenerative carbon dioxide removal system is also required, in addition to other air purification and air quality control measures. However, unlike nuclear submarines, AIP submarines have limited power and limited space, and therefore, it is not appropriate to directly transfer air purification technology from nuclear submarines. The current technology for regenerative carbon dioxide removal is a liquid amine scrubber. A system that has recently been developed [24]. The main advantage of this system is that it is free of liquid amine leakage and potentially has a lower emission of amine vapors. Although tests have been conducted on AIP submarines (Swedish and Canadian) so far, the system has not been installed in an operational submarine. The MEA scrubber is the adsorbent tower that is replaced by a hollow fiber hydrophilic membrane that separates the carbon dioxide-filled air from the liquid amine stream (or amino acid)[10]. A system on a 4.1 kW Dutch submarine that eliminates 2.5 kg of CO2 per hour. This has to do with slightly lower energy efficiency than existing MEA scrubbers, although a full-scale unit has not yet been built. Carbonic anhydrase is immobilized on polymethyl methacrylate granules in a packed column. Carbon dioxide-rich air passes through the immobile enzyme in an aqueous medium to form soluble bicarbonate. Rinsing the system with water removes the bicarbonate while leaving the enzyme motionless [25]. The variation of this process involves the use of a liquid membrane containing an aqueous solution of carbonic anhydrase to facilitate the removal of carbon dioxide from the airstream that passes through a hollow fiber membrane [17]. A completely different approach to carbon dioxide removal has been proposed, in which gas removal is integrated with a liquid oxygen heat exchanger in the MESMA system involving the use of a closed-cycle Rankine turbine powered by ethanol. Moisture is first expelled from the airstream by condensation, then carbon dioxide (along with air pollutants) condenses at -150 °C.

It is estimated that a concentration of carbon dioxide less than 0.7% can be achieved by this process. With the liquid oxygen heat exchanger, the power consumption can be limited to 1 kW. It is unclear if the system is planned to be installed on the new French AIP submarines. In the case of a decommissioned submarine, where there may be minimal electrical energy, lime soda, and lithium hydroxide will undoubtedly be retained as the main absorbers of carbon dioxide. In recent years, the use of absorbent-filled permeable fabric curtains has been accepted for the static removal of carbon dioxide, which relies on the natural convection of air in the submarine and the diffusion of air through the fabric and the absorber. Curtains are crimped bags approximately 0.5 meters wide and 1.5 meters long with a capacity of 5-6 liters [10].

In terms of carbon monoxide and hydrogen removal, low-temperature catalysts, such as platinum and zinc palladium, currently used in submarines, perform adequately with little or no electricity requirement. If the range of these catalysts is to be expanded to include the complete oxidation of hydrocarbons (e.g., nuclear submarines), photocatalysis may be required [26]. The problem of dealing with the decomposition of HCFCs arises again, and therefore, it may be expedient to use activated charcoal filters to remove VOCs. Ozone, which leads to problems such as yellow powder. High-efficiency air particle filters have significant resistance to airflow and require a higher energy investment than electrostatic precipitators. A large portion of aerosols appear to be semi-volatile liquids that cannot be permanently trapped in HEPA filters, while they can be adequately removed by self-cleaning electrostatic precipitators.

5.2. Air Monitoring in the New Generation of Conventional Submarines

Currently, there are two main approaches for real-time air monitoring in submarines. The United States Navy has CAMS, which has a proven track record of 30 years of service in submarines. A smaller version called CAMS-Mini, designed based on CAMS, specifically for conventional submarines, was developed in the early 1990s and was tested by the navies of Italy, Sweden, and the UK. Like CAMS, the main drawbacks of this system are the initial cost, the need for long tubes for air sampling at various locations within the submarine (which may lead to some damage in reactive gases), and dependence on a single analyzer for all gases. An analyzer (ANITA) has been proposed for use in submarines. This tool is derived from the European space program, where there is a need to monitor trace gases in long-duration spacecraft. This device is capable of simultaneously identifying and measuring 32 pollutants in real time. It is expected that this device will take over the role of CAMS. A more conservative approach is to use dedicated sensors distributed throughout the submarine. This requires infrared sensors, which may be used for carbon dioxide, carbon monoxide, volatile organic compounds, freons, and halons, as well as electrochemical sensors for most other air pollutants. The main advantages of this system are redundancy and relatively low initial costs. The biggest problem with using electrochemical sensors is cross-sensitivity, especially to hydrogen, which can exist at concentrations above 500 ppm and in severe cases up to 20,000 ppm. Other disadvantages include the need for regular calibration and the short lifespan (> 2 years) of electrochemical sensors. As with nuclear submarines, the long immersion times of air-independent submarines (AIP) require sampling of the entire air and a return monitoring for comprehensive air analysis, and as insurance against unexpected spikes in air pollutants or unexpected species. This will include further investment in scientific resources to support this increased operational capability.

6. Modern air purification methods

6.1. Ionic liquid-based filters

Advantages:

.1 Ionic liquid-based filters have recently gained attention as an innovative and efficient method for air purification. These filters, utilizing the unique properties of ionic liquids, such as high thermal stability, negligible vapor pressure, and chemical tunability, are capable of removing a wide range of pollutants. Types of pollutants that can be absorbed by ionic liquids include a wide range of air pollutants, such as:

.2 Volatile Organic Compounds (VOCs) like benzene, toluene, and formaldehyde

.3 Heavy metals: such as mercury, lead, and cadmium

.4 Suspended particles: like dust and soot

.5 Acidic gases: such as sulfur dioxide and nitrogen dioxide

A filter containing ionic liquid typically consists of a porous substrate (such as foam or fabric) coated with a thin layer of ionic liquid. Contaminated air passes through this substrate, and the pollutants are absorbed by the ionic liquid [27].

6.2. Deep-eutectic-solvents

Advantages:

1. Reusability (easy reproduction with heat or pressure).
2. High safety due to low vapor pressure and lack of evaporation.
3. Chemical adaptability by adding suitable functional groups.

Disadvantages:

1. High production costs.
2. Sensitivity to moisture in some types.
3. Environmental challenges in disposing of used ionic liquids.

Deep Eutectic Solvents (DES) are recognized as a novel technology in air and environmental purification. These solvents are a combination of two or more substances that react through a hydrogen bond and have a lower melting point than their components. These features make DESs attractive as green and safe solvents compared to conventional organic solvents, which are usually toxic and volatile [28].

Table 4. Comparison of DES-based, IL-based, and sodalime filter[11, 27, 28].

Criterion	Soda lime	Ionic Liquid (IL)	Deep Eutectic Solvent (DES)
Cost	Very cheap	Very expensive	Relatively cheap
Absorption rate	Very fast	Medium to slow	Medium
Recyclability	Almost none	Good recyclability	Good recyclability
Biocompatibility	Caustic dust harmful	Sometimes toxic	Generally eco-friendly
Thermal stability	Moderate	Very high	Moderate
Ease of use	Very simple	Requires special setup	Relatively simple
Advantages	Cheap, fast, high efficiency, well-established	Very low vapor pressure, high thermal stability	Cheaper and simpler than ILs, more biocompatible, greener
Disadvantages	Limited lifetime, heat generation, only effective for CO_2	Expensive, potentially toxic, high viscosity	Lower absorption capacity

6.3. koala method

The KOALA system was created to provide a clean air source to operating rooms in hospitals. Considering the specific restricted environment, this system has been experimentally selected to improve air quality in submarines, which is divided into the following components:

1. Mechanical filter
2. Special activated carbon filter
3. Ion filter
4. Microbial sterilization element
5. Ionizer

Description of the filtration stages: The mechanical filter is a fabric mesh filter capable of trapping particles up to 200 microns. The special activated carbon filter is made from 800 grams of a special mixture of activated carbons that have been deliberately enriched to selectively enhance their adsorption properties against toxic gases of indoor pollution. Similarly, it is effective against 'external' pollutants (for example, incoming diving gases) as well as 'internal' pollutants. The ion filter is a very specific filter based on the principle of bombarding air with electrons, which alters the electrical properties of the molecules exposed to it. Tests conducted confirm the filter's efficiency, and it blocks impurities down to one-thousandth of a micron**.** Figure 3 shows an example of a Koala filter.

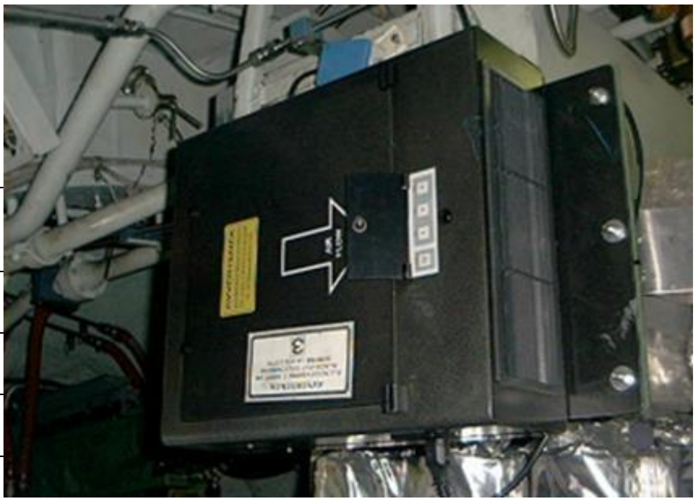

Figure 3. The KOALA device installed on the Pelosi.S SSK is shown in the image[29].

Advantages:
1. It does not require pre-polarization of dust to attract them.
2. It does not use high tensions in the air and therefore does not produce ozone.
3. It does not use stacked interception plates, thus eliminating the need for control and maintenance to prevent electrical discharge from shorts due to the accumulation of stopped materials.
4. It also does not emit dust and bacterial loads without maintenance, even if used intermittently.
5. Air ionization occurs cleanly and prevents dust from settling on environmental surfaces. - It can be used in the presence of other heating and/or environmental air conditioning systems because the type of airflow and air discharge velocity does not create interference or turbulence. In the absence of such devices, it still respects the convective movement of the environment, blending the air near the ceiling with the air near the floor. To prevent resuspension in the air of particle and bacterial loads is of crucial importance.
Z6. Quick and maintenance-free replacement allows recovery from gases even for specific work needs, using special kit filters aimed at specific pollutants[29].

A submarine model is shown in Figure 4, showing its various components. It should be noted that the location of the filters can change depending on the internal architecture of the submarine, but these filters are usually installed in the crew cabin, which has adequate space for this.

7. Future works

Given that submarines today perform longer operations, they need to spend more time in the water, and given the military nature of submarines, proper stealth and maneuverability are essential. Therefore, soda-lime filters, due to their bulkiness, and deep-eutectic-solvent filters, due to their lack of proper and economical maintenance, may pose problems for military operations.

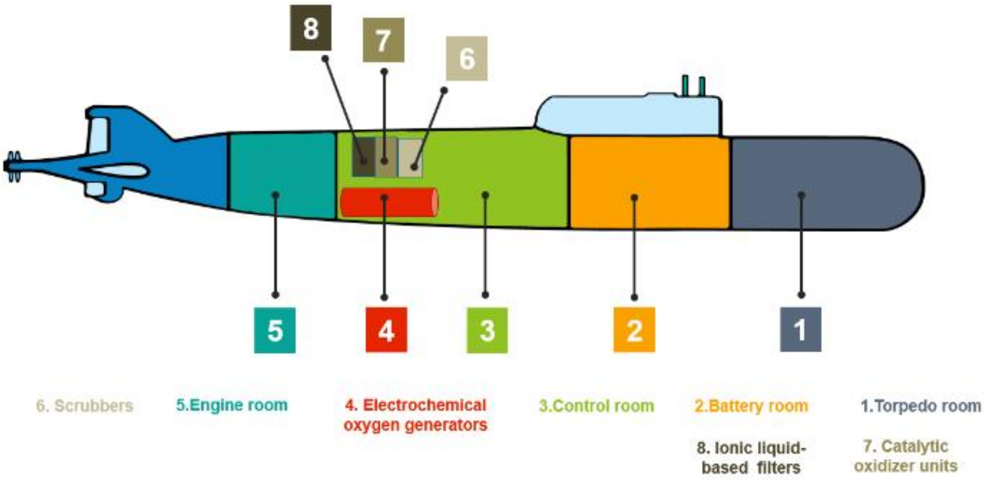

Figure 4. A submarine model showing the location of the filters and generators.

In the future, it is recommended that studies be conducted to reduce the volume and weight of the filters, as well as increase their durability in combat conditions.
Study and research on the following filters is also recommended.
1. Photosynthesis – Algal photosynthesis has the potential to remove CO2 and generate oxygen without generating unwanted by-products. Initial laboratory work to determine the feasibility of a submarine life support system is underway.
2. Biofiltration – extensive laboratory testing has been Conducted by DERA for the UK MOD. Results have indicated that the inoculum tested was capable of removing Volatile Organic Compounds, but required a significant increase in volume compared to Charcoal filters.
3. Molecular Sieves – long-term aim to examine improvements in molecular absorber technology as a potential for: CO_2, VOC, and refrigerant removal.
4. Photocatalysis for organic contaminant removal – Laboratory testing of coatings that will break down VOCs when exposed to high-energy ultraviolet.
5. Advanced sensor networks and AI-driven real-time air quality monitoring systems should be explored to enable predictive maintenance and adaptive purification control.

8. Conclusion

This review has traced the development of air purification technologies in military submarines, highlighting the critical role these systems play in enabling prolonged submerged operations. Early challenges in atmospheric management spurred innovations that have culminated in highly efficient and reliable air revitalization systems. The transition from diesel-electric to nuclear propulsion, and more recently, the emergence of air-independent propulsion, has further accelerated the development of advanced.

Technologies for oxygen generation, carbon dioxide removal, and contaminant control. As submarine technology continues to advance, future research should focus on improving system efficiency and reducing.
Energy consumption and enhancing the resilience of air purification systems against potential threats.
Ultimately, the ongoing refinement of these technologies is essential for maintaining the strategic advantage and ensuring the safety of submarine crews.

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