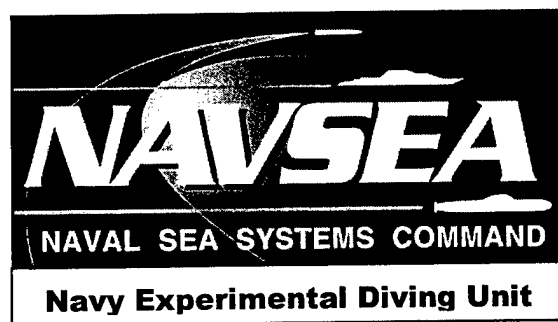


Navy Experimental Diving Unit
321 Bullfinch Road
Panama City, FL 32407-7015

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**REVIEW OF TWO METHODS TO REMOVE CO₂ USING SEAWATER
FROM SUBMARINES DURING EMERGENCY CONDITIONS**



**Authors: D.E. Warkander, Ph.D.
R.S. Lillo, Ph.D.**

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INTRODUCTION

During normal operations, U.S. Navy submarines use an electrically-powered regenerative scrubber system to remove CO₂ from the atmosphere¹. These scrubbers employ a water solution of monoethanolamine (MEA) to absorb CO₂ from submarine air that is forced through the system by an air blower. Subsequently, the CO₂-enriched MEA is heated under pressure to release the absorbed CO₂ gas, which is then passed out of the scrubber through a cooler, compressed, and discharged overboard. This is an efficient system with few problems, except it is bulky and requires significant power to repeatedly heat and cool the MEA. In addition, the MEA is quite toxic, so that, at a minimum, weekly monitoring of its levels is required. A non-regenerative method of CO₂ removal is also available onboard, using canisters of lithium hydroxide (LiOH), that can be used as a backup to, and in conjunction with, the regenerative scrubber to increase the capability to remove CO₂. Five canisters (each containing 6.3 pounds of LiOH) are arranged in parallel in a portable blower assembly (hopper) powered by 120 VAC and with a nominal rating of 60 cfm.

Under distress situations, where the submarine is disabled (DISSUB) and unable to surface, there is likely to be flooding due to a collision, grounding, or a weapon accident. Consequently, it is very probable that the nuclear reactor will have to be shut down with the resulting reduction in electrical capacity. If only the aft compartment is flooded, DC power from the ship's main batteries in the forward compartment should be operational. However, since the inverters and motor generators are located in the aft, there will be no AC power to run the non-regenerative hopper to circulate the air. Conversely, if the forward compartment is flooded, the batteries, the source of DC power, will probably be lost. In both cases, CO₂ removal by either the regenerative procedures with MEA or the hopper will be impossible. In this situation, the current guidance recommends that the lithium hydroxide canisters be opened and the pelletized material spread out on the floor and other flat surfaces. The crew is expected to stir the LiOH every 15 minutes and manually fan the air over the absorbent continuously.

There are significant problems related to the use of LiOH with or without electrical power:

1. Lithium hydroxide is expensive to purchase, very corrosive, and can be difficult to dispose of due to environmental concerns. Handling and fanning the LiOH releases significant amounts of highly caustic dust into the atmosphere that is likely to cause burns in the respiratory membranes, the eyes, and on the skin. A recent study by the Naval Submarine Medical Research Laboratory showed that the amount of LiOH dust generated by the non-regenerative procedures substantially exceeded the maximum exposure level recommended by the Naval Environmental and Health Center².
2. Covering the horizontal surfaces with LiOH granules reduces the area on which survivors would be able to lie down and rest or sleep. This would not only add

to the stress, but more importantly, increase the amount of CO₂ that they would produce, adding to the CO₂ load of the emergency scrubbing system.

3. The efficiency of any stirring and fanning would be expected to be considerably less than that of the hopper.
4. The supply of LiOH onboard is limited and is expected to last only for a three-day emergency, which is shorter than the most optimistic forecasts of time required to effect a rescue using the current Deep Submergence Rescue Vehicle (DSRV).
5. Despite limited stores, the LiOH supply still occupies significant space on submarines.

Consequently, there is a strong need to develop an alternative CO₂ scrubbing system for submarine use that uses either no power, limited human power, or the ship's main batteries. This report reviews two methods for such removal of CO₂ using seawater.

REQUIREMENT

Any system will need to solve at least four problems: 1) removing CO₂ from the submarine compartment air, 2) storing or removing the scrubbed CO₂ from the submarine, 3) circulating enough air through the scrubber to keep up with the CO₂ production rate by the crew, and 4) mixing the compartment atmosphere. Experience suggests that item #3, the need for adequate circulation of air through the scrubber, probably will be the most difficult problem to overcome.

SEAWATER USE

Because of the unlimited supply of seawater available, and the high solubility of CO₂ in seawater, the possibility exists to use seawater to remove CO₂ from the submarine atmosphere either by 1) direct water contact with the air or 2) indirect contact in conjunction with a membrane system.

DIRECT WATER CONTACT

To implement this method, the air is bubbled into seawater or seawater is sprayed into the air, in both cases using a tower to maximize the time for gas exchange to occur. CO₂, being approximately 30 times more soluble in seawater than other gases in the air such as oxygen (O₂) and nitrogen (N₂), would be differentially reduced. After the CO₂ exchange, the water and air would have to be separated and the air dried since the air will likely be saturated with water vapor. In a submarine scenario, two possible pressure configurations (assuming that the CO₂ exchanger is inside the submarine) are:

1. The seawater is brought into the submarine, depressurized to inside submarine pressure, CO₂ transferred by air bubbling or seawater spraying, and the seawater re-pressurized and pumped back out.
2. The seawater is brought into the submarine, but maintained at outside pressure. The air is compressed to outside pressure, bubbled through the seawater, and then depressurized before returning to the submarine atmosphere.

An alternative to pumping the seawater back out of the submarine would be to divert the CO₂-enriched seawater into the bilge or other holding area inside the submarine.

Issues related to a direct seawater system include: 1) scaling up of any water tower or bubbler, 2) handling the seawater after it is saturated with CO₂, and 3) finding ways to increase the affinity of CO₂ for seawater or to precipitate out the dissolved CO₂ (e.g., CaCO₃) by using additives to the water.

MEMBRANE SYSTEM

Indirect contact between the air and water can be achieved by using a semi-permeable membrane which can either be a single sheet of material or a series of gas-permeable hollow fibers. The gas is circulated on one side of the membrane or within the hollow fibers with seawater on the other side. With the appropriate membrane, CO₂ would pass from the air into the water at a higher rate than the other gases (i.e., N₂ and O₂) and a significant amount of CO₂ removed from the air. An added benefit may be that O₂ could also be concentrated in the gas with the proper membrane, although this may not be desirable due to pulmonary oxygen toxicity concerns. In a submarine scenario, there are three possible ways to design the membrane gas-exchange system depending on pressure configurations (assuming that the CO₂ exchanger is inside the submarine):

1. The submarine air is compressed to outside seawater pressure, requiring a pressure housing for the exchanger. This would increase the pressure gradient for CO₂ transfer. After gas exchange, the remaining air is depressurized. A diagram of how such a system might be configured with a compressor, and a turbine that uses some of the energy released during the decompression of the air to aid in compression is presented in **Fig. 1**.
2. The seawater is depressurized to inside submarine pressure, not requiring a pressure housing for the gas exchanger. However, the water must be pressurized after the gas exchange if it is to be pumped out of the submarine.
3. Gas exchange takes place at existing pressures: air at inside pressure and water at outside pressure. In this case, the membrane sheet or hollow fibers need to handle the full pressure differential between outside and inside. Fortunately, the current fibers being studied (see below) can tolerate quite large internal and external pressures, up to 80 atmospheres absolute (ATA.) The

advantage of this approach is that power requirements for pressurization and depressurization of water and gas would be eliminated.

DIRECT WATER CONTACT – AQUARIUS TEST

The feasibility of a system based on direct contact of air with seawater was evaluated by Nuckols³ from the U.S. Naval Academy, in May 1999, at the Aquarius underwater habitat offshore of Key Largo, FL. Using the known solubility of CO₂ in seawater and a measured value of the CO₂ production, an unpressurized seawater tower was designed. Water was sprayed at a rate of 1.75 gallons/min into air circulating at 14 actual cubic foot/min through the tower. The design goal was to hold the atmosphere at 0.5% sev CO₂ with six crew members at a 45 fsw storage depth.

During the test, CO₂ was observed to rise over 1% sev over a one-hour period. Based on his results, Nuckols concluded the gas flow through the tower would have been inadequate even if absorption efficiency had been 100% vs. the observed 30-40%. In addition, CO₂ production rates exceeded design expectations by over 25%. However, the testing proved the principle that seawater could be used to remove CO₂ from a human habitat. Nuckols concluded that by increasing the air ventilation rate to 30 actual cubic foot/min and by increasing efficiency to approximately 80% (by raising tower pressure, reducing tower temperature, or improving the mixing of water and gas), the goal of holding the CO₂ level at 0.5% sev could be achieved.

MEMBRANE SYSTEM TESTING

Dr. Stern started this project at Syracuse University, and showed that it was possible to reduce the CO₂ to acceptable levels during diving using a seawater/membrane system⁴. In 1996, at Dr. Stern's initiative, the project was transferred to the University of Buffalo where Drs. Lundgren and Warkander have explored the possibility of using gas-permeable hollow fibers for CO₂ removal, primarily for use in diver's breathing apparatus⁵. Fibers of this type have been used extensively by the gas-separation industry with the selectivity of the fiber material chosen in terms of which gases are desired to permeate through it most easily. Fibers can be made with or without pores and can also have a very thin coating that is either hydrophobic or hydrophilic. The fibers are rugged and difficult to tear, thus well suited for the harsh environment of diving.

METHODS

Membrane gas-exchange modules were designed and manufactured in-house as shown in **Fig. 2**. These acrylic rectangular modules were approximately 24 cm by 19 cm, with a single layer of hollow fibers oriented length-wise in the modules. The modules held approximately 400 fibers, each less than 0.5 mm in diameter, for a total external surface area of approximately 1,000 cm². The performance of the following

three different types of fibers were studied: 1) microporous polypropylene (Mitsubishi Rayon America, New York, NY), 2) coated polysulfone (Innovative Membrane Systems, Inc., Norwood, MA), and 3) uncoated polysulfone (Innovative Membrane Systems).

The test modules were placed in a testing tower (**Fig. 3**) where the flow of water on the outside of the fibers could be varied independently of the flow of gas through the fibers, with the temperature of the water controlled. The tower was located inside a hyperbaric chamber that allowed the ambient test pressure to be increased. In this experimental design, the inlet gas simulates the exhaled air in a diver's breathing apparatus. As the CO₂-rich gas (4% CO₂, 18% O₂ in N₂) enters the module and travels through the fibers, CO₂ moves across the fiber membrane and dissolves in the water on the outside. The water enters the module at the bottom of the tower, travels between the fibers, and leaves at the top after being enriched with CO₂. A mass spectrometer was used to analyze the composition of the effluent gas to determine the amount of loss of CO₂. Readings were taken until a stable value was reached. Thus, in the data presented below, each data point represents one reading. Testing consisted of determining the effect on CO₂ removal by a number of variables, including water and gas flow, water temperature, type of fiber, fresh vs. salt water, and elevated pressure.

RESULTS AND DISCUSSION

1. Water and gas flow

This test evaluated the effect of the flow rates of water and gas on the removal of CO₂ using the microporous polypropylene fibers (**Fig. 4**). At all four gas flow rates, the CO₂ in the effluent gas began to level out with increasing flow of water, suggesting that gas flow was becoming the limiting factor at this point. However, the leveling out occurred at higher CO₂ concentrations with the increased gas flows, reflecting the shorter time that was available for CO₂ transfer. Conversely, effluent gas CO₂ began to climb as the water flow decreased for all gas flows tested, as the water flow now became the limiting factor in CO₂ removal. These measurements suggest that the minimal ratio of water-to-gas flows needs to be in the range of 10 to 20 for effective operation at atmospheric pressure, although it is clear that both gas and water flows must be matched for optimal performance of the gas exchange module.

2. Water temperature

As can be seen in **Fig. 5**, there is only small, if any, influence of water temperature on CO₂ removal under a wide range of water and gas flows when using the uncoated polysulfone fibers. This should make any final system easier to design as temperature control may not be necessary. In addition, there may be fewer temperature restrictions on its use. This small dependence on temperature contrasts sharply with conventional chemical absorption (e.g., LiOH) where temperature can make a very large difference in terms of absorbent capacity.

3. Different fiber types

The performance of different types of fibers was studied by holding gas flow constant at 20 mL/min as water flow was varied. As is shown in **Fig. 6**, there were very large differences among the three fibers, apparently reflecting differences in the rate of CO₂ transfer across their membranes. The best performing fiber under these test conditions was the uncoated polysulfone, although it is unknown whether this would be the best fiber under all experimental conditions. These results suggest that selection of fiber type will be a very important factor in any future work relating to CO₂ removal. Recently, another fiber manufacturer (CELGARD LLC, Charlotte, NC) has provided polypropylene fibers that are manufactured as a cloth instead of as a single fiber wound up on a spool. Preliminary data from a single layer module show that this fiber has better performance than any of the other three types that we tested.

4. Fresh vs. salt water

The effect of salinity was investigated using the uncoated polysulfone fibers (**Fig. 7**). There was a large performance improvement with the salt water (about 3% NaCl) as seen in the much lower CO₂ of the effluent gas CO₂.

5. Elevated pressure

Tests were performed at pressures up to 4 ATA while the input gas partial pressure of CO₂ was held constant to simulate a diver's exhaled gas. Results showed that there were minimal, if any, effects of pressure *per se* on CO₂ elimination, thus allowing this factor to be ignored in any final design considerations (**Fig. 8**).

ISSUES CONCERNING SEAWATER SCRUBBING

Gases other than CO₂ will be absorbed by the water although their absorption should be much less than that for CO₂. In the case of a membrane system, the loss of other gases can be reduced by choosing an appropriate membrane or fiber in terms of its selective gas permeability. However, the loss of other gases could actually be an advantage if the disabled submarine experienced flooding that increased the inside pressure. The ability to eliminate gas would help reduce the pressure, potentially avoiding decompression problems after rescue.

Materials and hardware of any absorption system should be made from materials that are resistant to corrosion and marine fouling. However, contaminants in the water are also a concern. For the direct seawater method, such contaminants may be introduced into the air that would be breathed; for the indirect method, the contaminants may coat the membrane affecting gas transfer or produce partial or full blockage of the gas flow through the fibers. These problems should be avoidable by using appropriate filters in the gas-exchange system. The best performing fiber (uncoated polysulfone) was tested with different substances for breakthrough, which would result in water entering the fiber

or gas escaping through the pores. In separate tests, the outside of the fibers in gas-exchange modules was coated with natural seawater surfactant, sorbitan-mono-oleate, stearic acid, and fibrinogen. Modules were also dipped in gasoline and fuel oil. In addition, the inside of the fibers was coated with pulmonary surfactant to simulate possible effects of a diver coughing. Each exchange module was tested with positive and negative pressures of 50 cm H₂O. No detectable leaks of water into the hollow fiber or of air out from the fiber were found.

The pressure at which CO₂ absorption occurs should be maximized to produce the highest pressure gradient for CO₂ transfer. If the efficiency of CO₂ transfer remains constant, the amount of water required for both the direct and indirect methods would go down with the ratio of inside submarine pressure to the gas-exchange pressure. For instance, if the pressure inside the submarine is 1 ATA and the CO₂ exchange is performed at 10 ATA, the water flow and required surface area of any gas-exchange system would be reduced by 90%.

CONCLUSIONS

1. The concept of direct and indirect (membrane) use of seawater for CO₂ removal from a closed-space atmosphere has been proven.
2. Both direct and indirect methods offer the potential for greatly extending survivability during a DISSUB scenario.
3. The feasibility of these techniques using seawater for CO₂ removal in the DISSUB, and the best way to design the system remain to be investigated.

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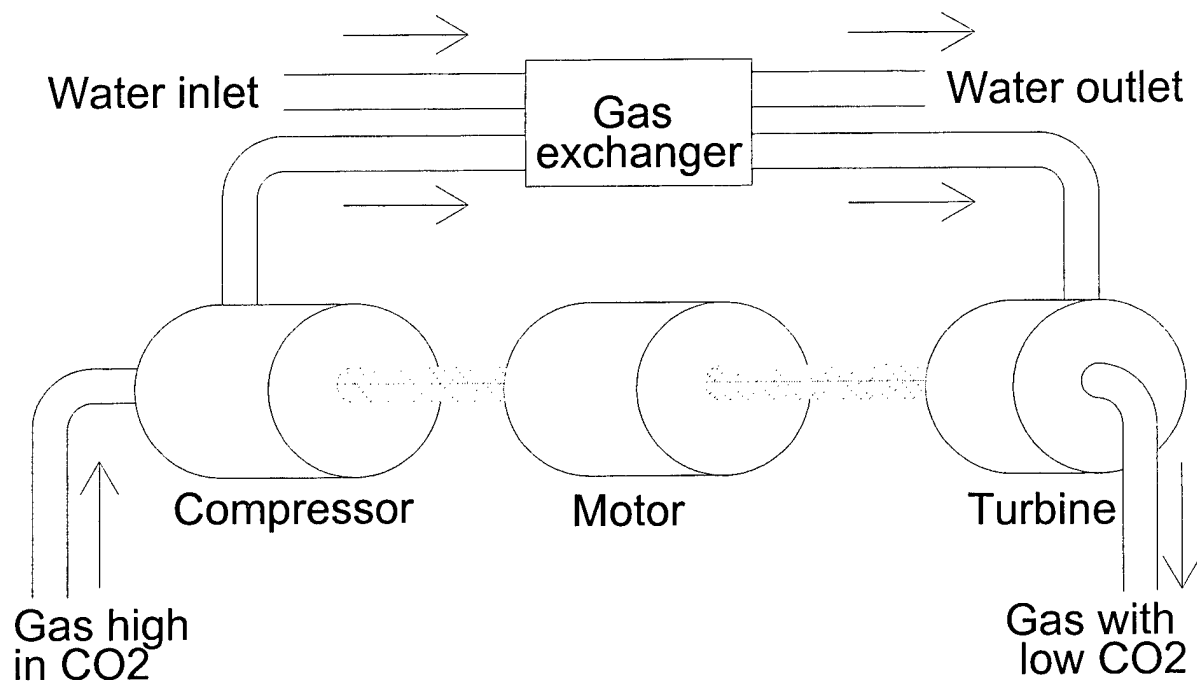


Figure 1. One possible configuration for CO₂ elimination on a submarine using a membrane gas-exchange system. Seawater is brought into the submarine and maintained at outside pressure. Submarine air is compressed to outside pressure and CO₂ exchange takes place at this pressure in the gas exchanger. A turbine uses some of the energy released during decompression of the air (following the CO₂ removal) to aid in initial air compression. The power for the motor could be from batteries or human power.

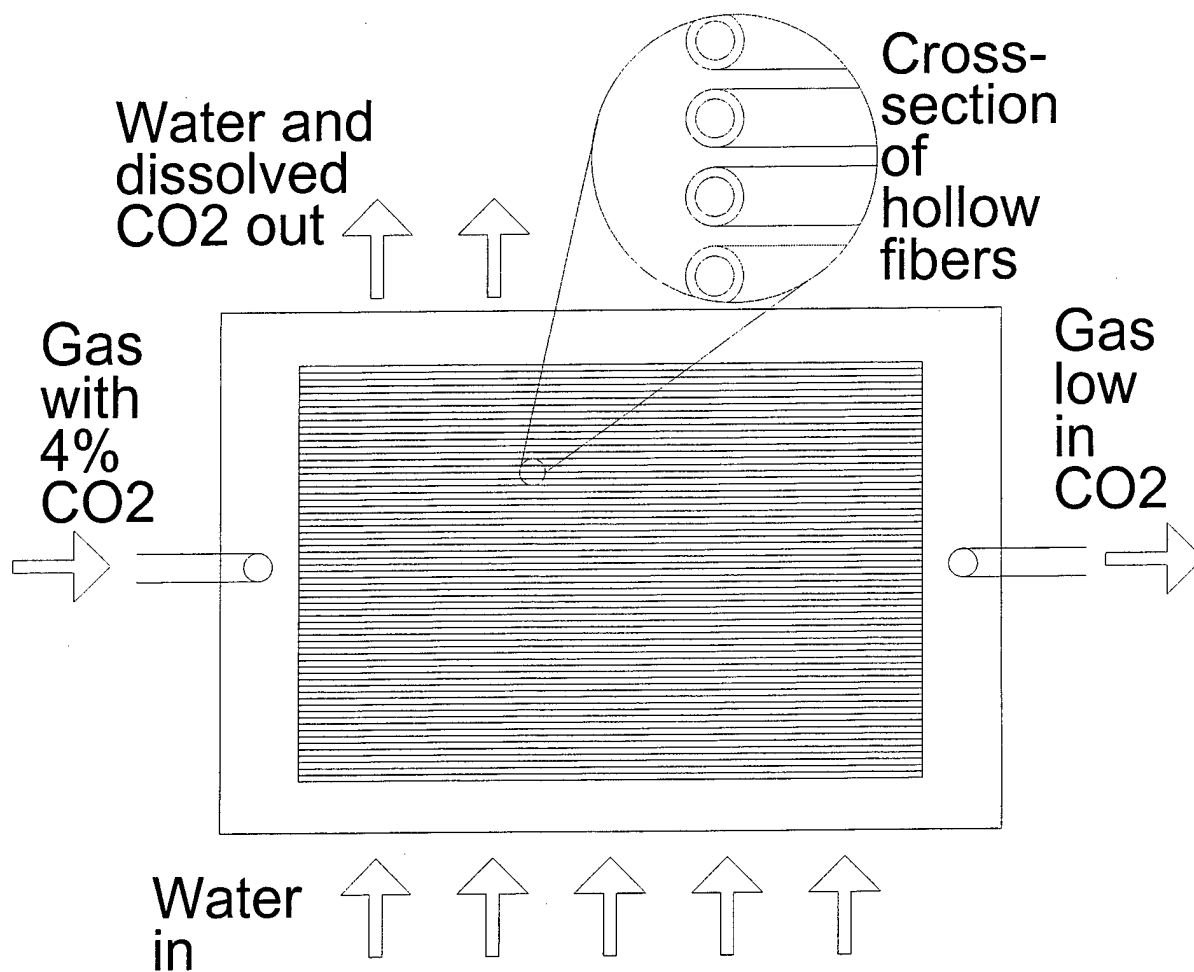


Figure 2. Schematic diagram of a membrane gas-exchange module using gas-permeable hollow fibers. As CO₂-rich gas enters on the left and travels through the fibers, CO₂ moves across the fiber membranes and dissolves in the water on the outside. The water enters the module at the bottom, travels between the fibers, and leaves at the top after being enriched with CO₂.

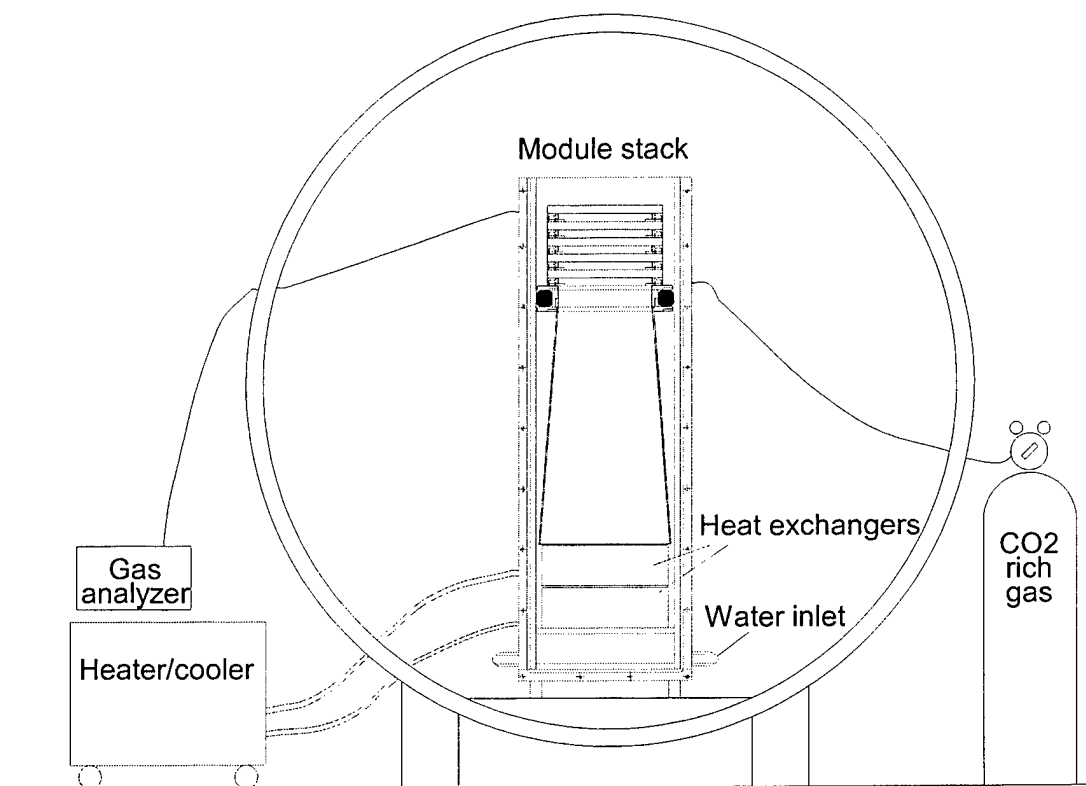


Figure 3. Tower setup allowing testing of the membrane gas-exchange module (Fig. 2) inside a hyperbaric chamber at atmospheric and elevated pressures. The gas enters from the right and leaves at the left. The water travels upwards past the module stack. The water pump and the delivery system are not shown.

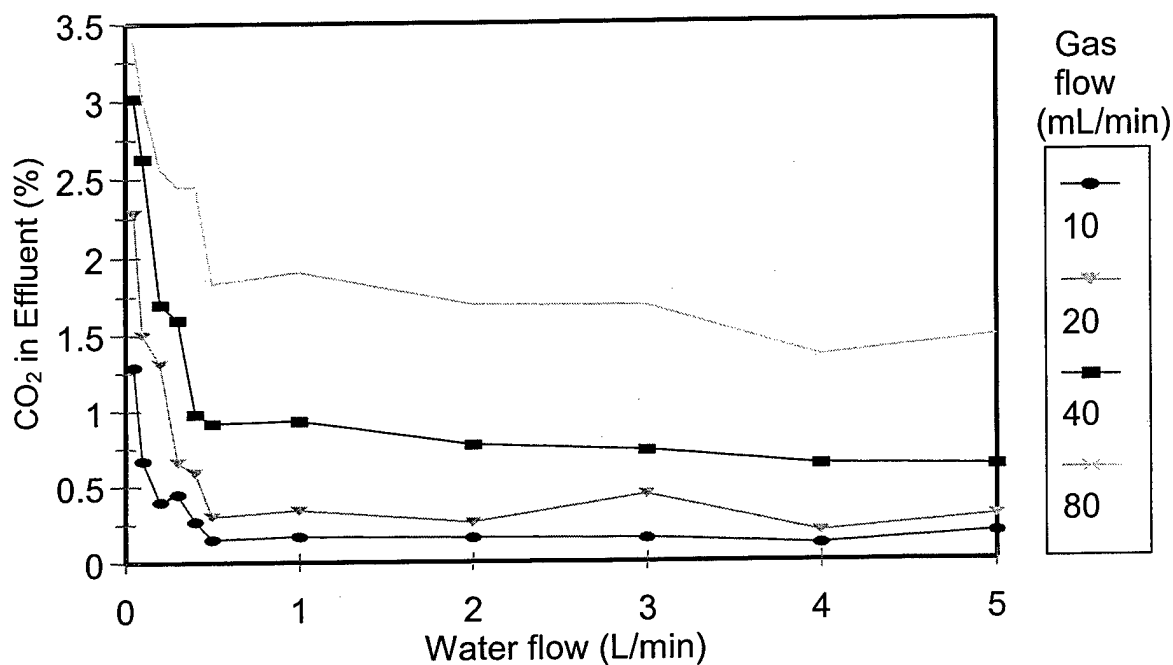


Figure 4. Both water and gas flow rates have large effects on CO₂ removal using the membrane gas-exchange module (Fig. 2). The reduction in the effluent gas CO₂ is relative to the input gas concentration of 4% CO₂. Water temperature was 21 °C; fiber was microporous polypropylene. Results suggest that water and gas flows must be matched for optimal performance.

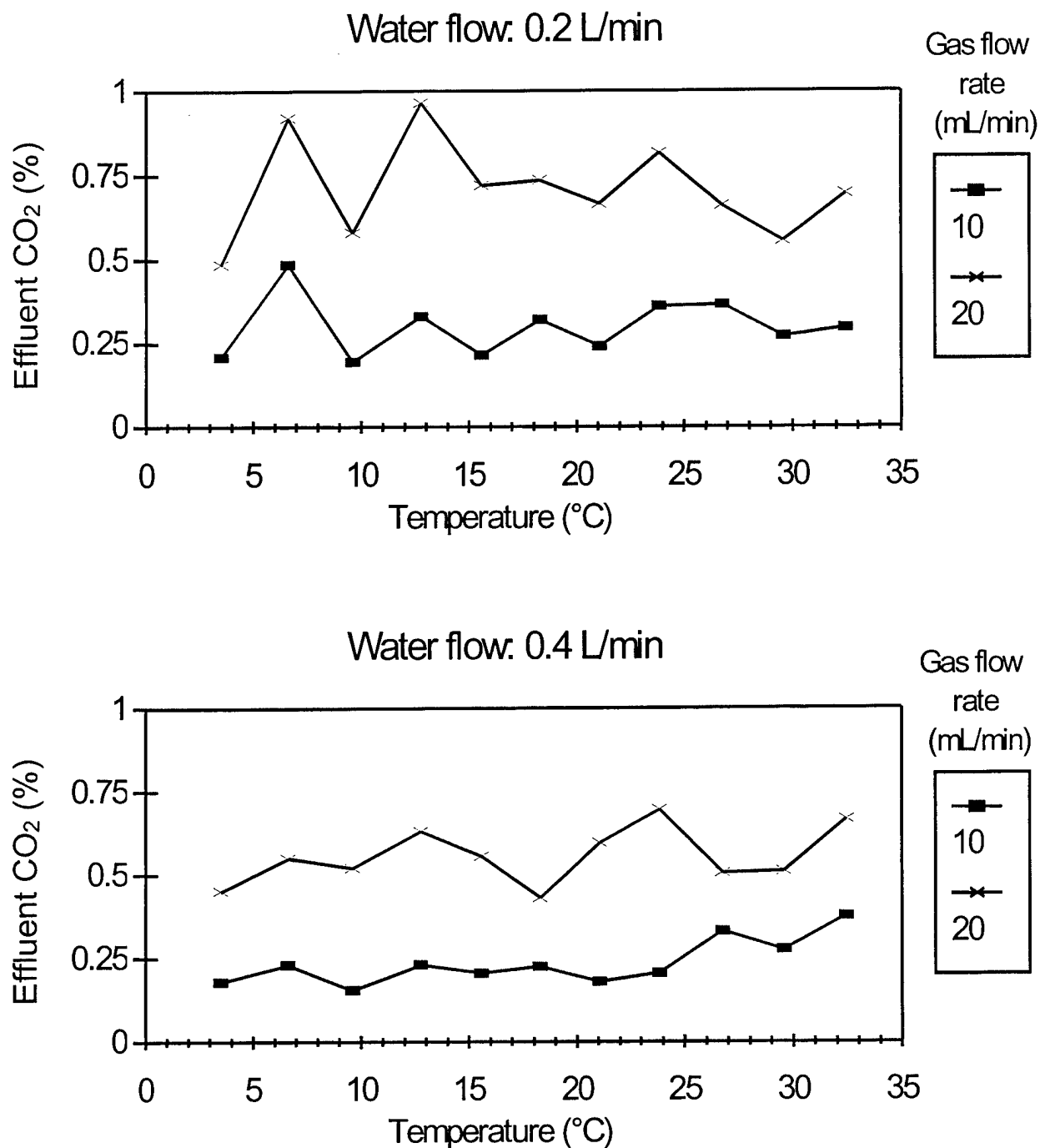


Figure 5. Water temperature has only a small, if any, effect on CO₂ removal using the membrane gas-exchange module (Fig. 2). The reduction in the effluent gas CO₂ is relative to the input gas concentration of 4% CO₂. The fiber was made from uncoated polysulfone.

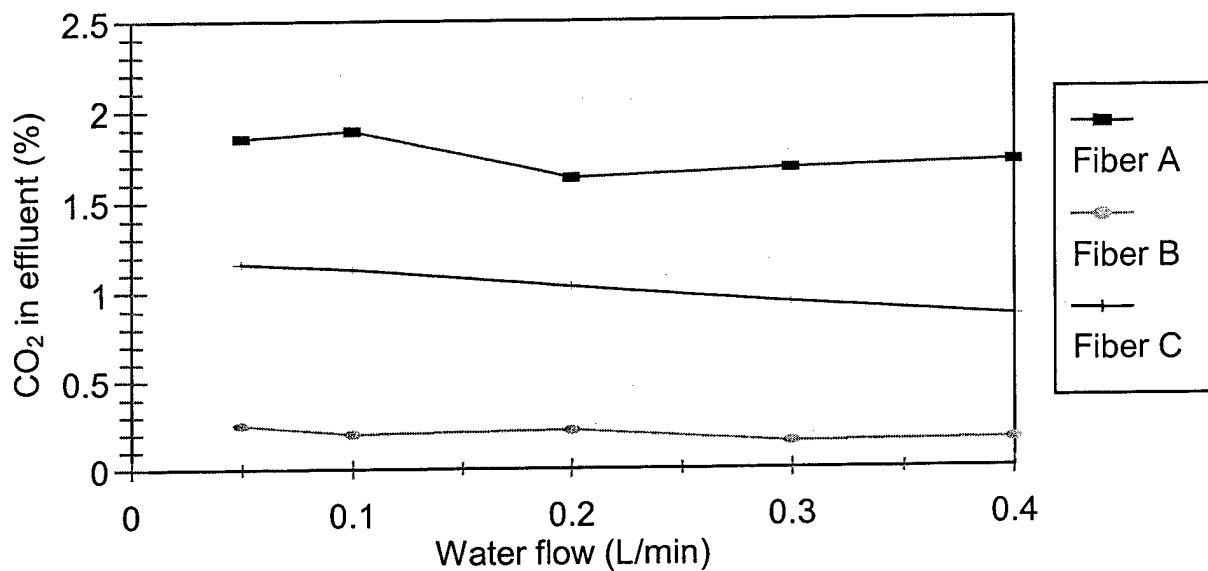


Figure 6. Different fiber types can have a large effect on CO₂ removal using the membrane gas-exchange module (Fig. 2). The reduction in the effluent gas CO₂ is relative to the input gas concentration of 4% CO₂. Gas flow was held constant at 20 mL/min; water temperature was 21 °C. Fiber A was microporous polypropylene, B was coated polysulfone, and C was uncoated polysulfone.

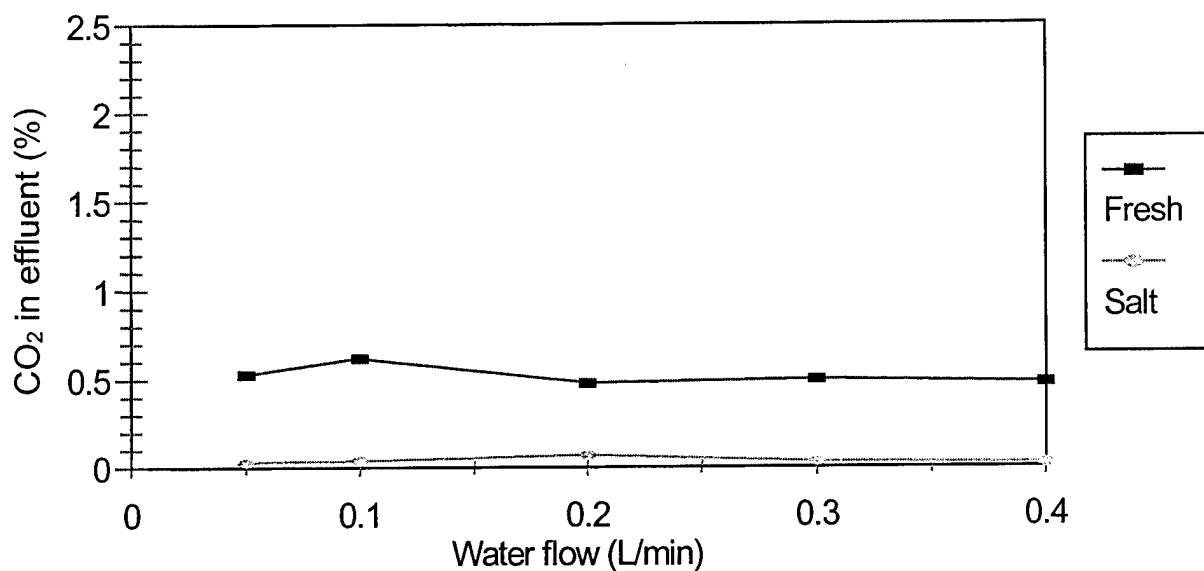


Figure 7. Salt water, compared to fresh water, greatly improves the ability to remove CO₂ using the membrane gas-exchange module (Fig. 2). The reduction in the effluent gas CO₂ is relative to the input gas concentration of 4% CO₂. Gas flow was held constant at 20 mL/min; water temperature was 32 °C; fiber was uncoated polysulfone.

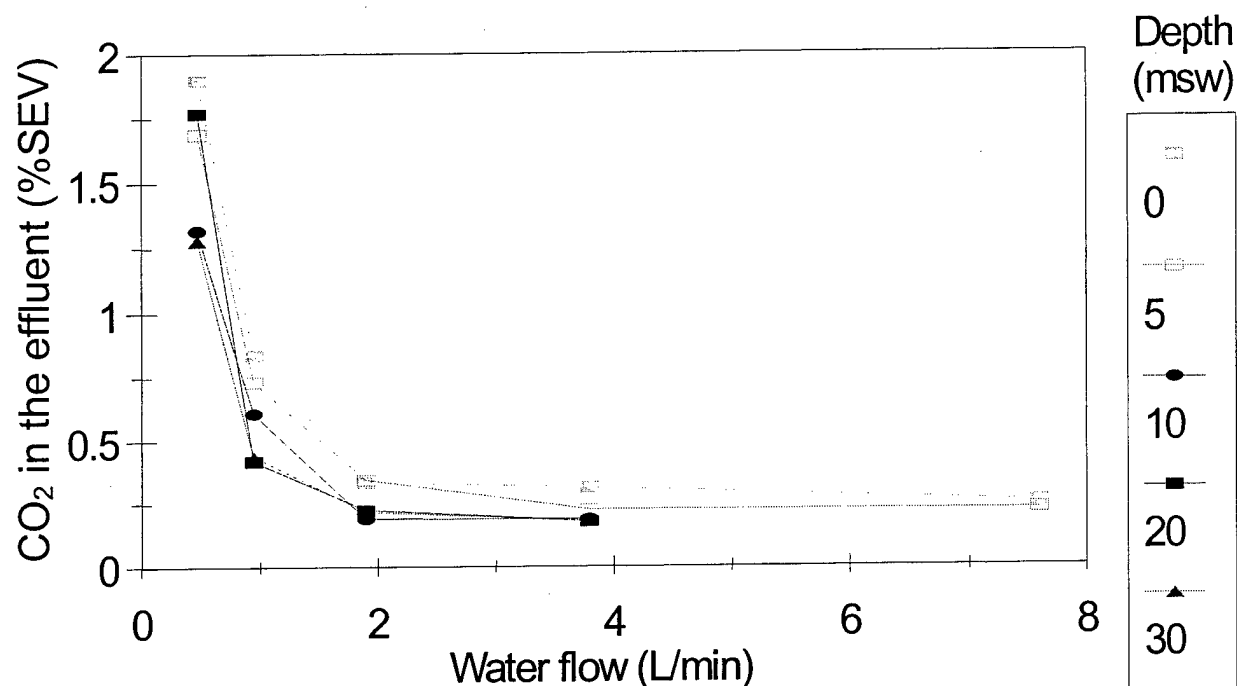


Figure 8. Increased ambient pressure has minimal, if any, effect on CO₂ removal using the membrane gas-exchange module (Fig. 2). The reduction in the effluent gas CO₂ is relative to the input gas concentration of 4% CO₂. Gas flow held constant at 20 mL/min; water temperature was room temperature; fiber was uncoated polysulfone.