

# THE USE OF SCRUBBERS IN SUBMARINES

## REMOVAL OF CO<sub>2</sub> BY MEA

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### ABSTRACT

Monoethanolamine (MEA) has been used as a medium for continuous removal of CO<sub>2</sub> from the atmosphere of nuclear submarines in the Royal Navy since H.M.S/M. *Dreadnought*. Surprisingly, the process by which such plants operate has not been fully appreciated or exploited. A new MEA scrubber of American design and much improved performance will come into service in the near future. Spurred by this improvement, a design review of the older plant has revealed certain process changes by which its performance could be uprated.

### Introduction

For a nuclear submarine to operate with complete freedom, it must not be constrained by having to return periodically to the surface to ventilate. To achieve this, effective atmosphere control must be performed on board. The two main requirements for such control are to produce oxygen and remove carbon dioxide, the two gases involved in respiration. One method by which carbon dioxide can be removed as a continuous process is by harnessing the properties of a member of the amine family, such as monoethanolamine (MEA), which will absorb CO<sub>2</sub> when cool and release it when hot. Using this property a plant can be constructed whereby CO<sub>2</sub> is absorbed from the atmosphere by cool MEA which when subsequently heated will release its charge of CO<sub>2</sub> for disposal in some way. This article is concerned with the use of such plant in the Royal Navy.

In all nuclear submarines from H.M.S. *Dreadnought* to the last of the *Swiftsure* Class, CO<sub>2</sub> removal has been performed by an MEA-based CO<sub>2</sub> scrubber. Following a short departure with the use of alternative techniques for removal, SSN17 onwards will yet again be fitted with an MEA scrubber, this time of an improved U.S.N. design built under licence in Britain. Despite the obvious importance of this plant, its operation remains something of a black art. To anyone who has operated the amine scrubber certain recurrent defects will be all too familiar. Typical process problems associated with the degradation of MEA are ammonia production, darkening of the solution, and foaming of the absorbant, frequently resulting in loss of CO<sub>2</sub> removal capacity and carry over of MEA into the submarine atmosphere. Mechanically, failure of the CO<sub>2</sub> compressor used for disposal of the gas remains top of the S2022 charts.

Surprisingly, in many cases where degradation reports have been supported with an amine sample for full chemical analysis, the presence of extensive degradation has not been confirmed. A concentrated solution of amine can exhibit the properties commonly associated with degradation. In one case an extremely black viscous sample of amine returned from an operational submarine, when restored to its correct strength by simple dilution with distilled water, was shown to be a perfectly serviceable solution. Further, the process by which the scrubber operates is not widely understood and in particular the sensitivities of that process are not appreciated.

Spurred by the superior performance of the U.S.N. plant, a review of the older Royal Naval plant has been completed. Certain simple process changes have been highlighted by which the performance of these plants could be improved and it is hoped in the near future to perform land-based trials to prove these potential improvements and develop subsequent modifications for in-service plant.

This article focuses on the operating principles of the amine scrubber to show what improvements may be possible and it highlights areas which require vigilance by operators in order to achieve optimum performance from the plant. Unfortunately there is little the operator can do once at sea to change the process parameters of the plant and often he must watch rather frustratingly as the Command complains about high CO<sub>2</sub> levels in the submarine.

### **Sources of Carbon Dioxide and Atmospheric Limits**

Carbon dioxide is present in fresh air at volumetric concentrations of around 0.03%. An alternative way of expressing this concentration is in terms of partial pressure. The partial pressure is that pressure which a constituent gas of a gas mixture would exert on a vessel if it occupied that vessel in isolation. The partial pressure can be simply calculated as it is the product of the absolute pressure and volumetric concentration. Hence a volumetric concentration of 0.03% carbon dioxide at an absolute pressure of 760 mm Hg exerts a partial pressure of 0.228 mm Hg.

Partial pressure is important since it is this property of a gas which provides the driving force for certain important reactions. In respiration, for example, it is the partial pressure of oxygen which provides the driving force for oxygen to pass through the membrane wall of the lung into the blood stream and it is the difference in partial pressure which allows carbon dioxide to pass out of the bloodstream into exhaled air. As will be described later, it is the partial pressure of carbon dioxide which provides the driving force for its removal from a submarine atmosphere by chemical means as employed in the MEA scrubber.

TABLE I—*Physiological Effects of CO<sub>2</sub>*

<i>Partial Pressure Carbon Dioxide (mm Hg)</i>	<i>Effect on Man</i>
<7.6	No observed effects
7.6 to 15.2	Slight increase in depth of respiration with headache and fatigue.
22.8	Severe headache with diffuse sweating and dyspepsia. There is a marked loss of efficiency
30.4	Flushing of face. Palpitations
45.6	Hard work impossible. Visual disturbances
60.8	Tremors, convulsions, coma and death

Returning to the concentration of carbon dioxide in air, fresh air, and hence inhaled air, contains CO<sub>2</sub> at a partial pressure of 0.228 mm Hg. Exhaled air contains carbon dioxide at a partial pressure of 23 mm Hg (3.03% at 760 mm Hg). Under normal conditions this exhaled gas disperses throughout the atmosphere to be removed by various natural processes.

On board a submarine however, in a closed environment, the volume into which the gas can disperse is limited and there is no natural process for its removal. Unless action is taken, carbon dioxide levels will rise continuously.

Increasing the partial pressure of carbon dioxide affects the body physiology. Clearly as the partial pressure rises, the driving force for CO<sub>2</sub> removal from the bloodstream falls. The body compensates for this by automatically increasing the respiration rate. The body cannot however compensate indefinitely. Breathing increased concentrations has been observed to have the effects listed in TABLE I.

Clearly there is a requirement to set a limit for concentration of CO<sub>2</sub> in manned spaces. In submarines where personnel are expected to conduct extended patrols, a limit known as the Maximum Permissible Concentration for continuous operation for 90 days, or MPC<sub>90</sub> is set. This limit takes into account long-term effects in addition to those effects described in TABLE I and is currently set at 7.6 mm Hg or 1% at 760 mm Hg.

For short periods higher concentrations can be withstood and in an emergency, for example following a fire, an emergency exposure limit is set at 22.8 mm Hg or 3% at 760 mm Hg.

### **Evolution of CO<sub>2</sub> Removal Equipment**

In 1778, during the American war of independence, David Bushnell planned to sink the British blockading fleet with his new invention, the *Turtle* (FIG. 1). This was a small submersible about the size of a large barrel, propelled by means of a horizontal and a vertical propeller and powered by its single occupant. Its weapon was an explosive charge attached to a screw.

The pilot was to manoeuvre underneath his target and attach the charge to the hull. The mine would then be primed and the *Turtle* would retreat.

Sergeant Ezra Lee was the willing volunteer for the first mission. It was not a success and on his return he reported that he was unable to attach the charge due to the copper sheathing on the Royal Naval ships. However, records indicate that the vessels blockading North America at that time were not copper sheathed.

Upon going to closed boat conditions, the CO<sub>2</sub> level in the *Turtle* would rise. It is estimated that Sergeant Lee would have reached our current MPC<sub>90</sub> after only five minutes. He would have reached our current Emergency Exposure Limit after fifteen minutes and would have been incapable of operation after forty minutes. It is far more likely that the first submarine attack failed and had to be aborted due to lack of atmosphere control.

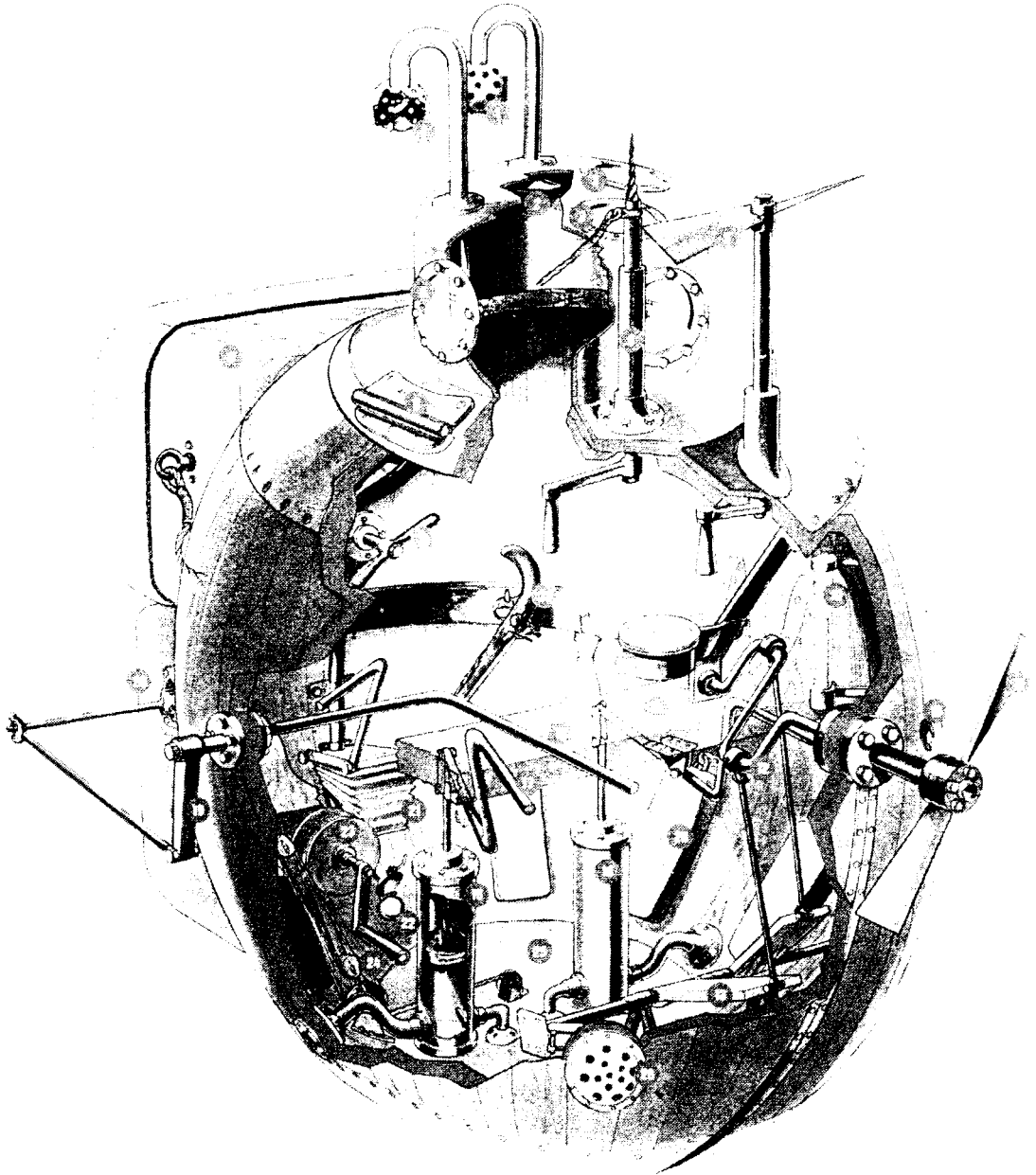


FIG. 1—THE AMERICAN 'TURTLE', 1778: A RECONSTRUCTION BASED ON CONTEMPORARY INFORMATION

Key to relevant items:

1. Ventilation pipes with self-sealing valves to prevent water entering
2. Ventilation pump to force fresh air in and hence foul air out at 2.

Up to World War Two, submarines were really only submersibles. They carried relatively small crews and their dived times were limited. There was also little regard for the long-term effects of exposure to high levels of CO<sub>2</sub>. For the dived times required, the CO<sub>2</sub> level in submarines would not rise to levels where crews were incapacitated and so there was no requirement for a CO<sub>2</sub> removal system.

During World War Two, Royal Naval submarine operations extended into waters off northern Norway<sup>1</sup>. To avoid detection submarines would charge their batteries at night on the surface and dive during the day to avoid air attack. During summer months, submarines were required to operate in nearly 24 hour daylight and hence were threatened with continual air attack. Often submarines missed the opportunity to charge their batteries and had

to remain dived for periods of sixty hours or more. In addition to the obvious requirement for battery capacity, there was also a need for some form of air purification including carbon dioxide removal. The solution was the carbon dioxide absorption unit. This device consists of a small fan which can be mounted with canisters containing soda lime. Soda lime is a mixture of calcium hydroxide, sodium hydroxide and calcium carbonate, which when exposed to carbon dioxide react irreversibly to remove the gas. Hence air drawn over soda lime is scrubbed of carbon dioxide. By the use of this simple system, a small amount of soda lime could be used to give vital extra hours to a submarine's dived time.

Following World War Two, the conventional submarine was largely superseded by the nuclear submarine. There was now the potential to operate for extended periods remote from the surface. The dived time was increased from tens of hours to tens of days. To support an SSN for a two month patrol would have required approaching 20 tons of soda lime. This would clearly have been a severe constraint on operations had the soda lime system simply been scaled up.

The need was recognized for a regenerative CO<sub>2</sub> removal system, which could operate continuously. In this way carbon dioxide from the submarine atmosphere could be removed at the same rate as it was produced, collected and disposed of in some way. Such equipment had been used in commercial gas treatment facilities since the early 20th century. Typically these processes employed a liquid reagent from the amine family. One method of manufacturing bulk carbon dioxide is to burn a hydrocarbon fuel to produce CO<sub>2</sub>-rich air. The CO<sub>2</sub> is then separated from the air by the amine process. CO<sub>2</sub> is still produced in this way for certain parts of the brewing industry.

The CO<sub>2</sub> removal equipment of the large scale industrial plant was scaled down and fitted in submarines. The details of this plant and a discussion of the problems associated with it is the subject of the remainder of this article.

Before leaving this historical survey, the use of molecular sieves to remove CO<sub>2</sub> should be mentioned. In the early 1970s, it appeared that the MPC<sub>9</sub> would be reduced to 3.8 mm Hg. The amine plant then in service could not achieve this. The U.S. Navy proceeded to upgrade their amine plant. The Royal Navy, however, opted for the use of an alternative process based upon a family of materials called Zeolites which act as molecular sieves. The basic molecular structure of a Zeolite is a cube. The molecular dimensions of the void in the central area of this cube can be controlled by means of the actual molecular build up of the Zeolite. It is possible to produce a zeolite which has a central void of similar dimensions to a CO<sub>2</sub> molecule and which can trap such a molecule. The capacity of the zeolite to hold or adsorb CO<sub>2</sub> is dependent on temperature and pressure. Hence by cycling these two parameters a process can be developed which will adsorb and desorb CO<sub>2</sub>, so producing a continuous CO<sub>2</sub> removal process. This process was used in the temperature swing molecular adsorber or TSMA as fitted in the early TRAFALGAR Class vessels.

By comparison with its U.S. counterpart, known as the MEA Packed Tower or MPT, the TSMA plant did not perform well. The capacity of a TSMA was only just over half that of the U.S. amine plant. Moreover, the TSMA occupied over three times the volume, consumed nearly four times the power and twice the chilled water and also cost considerably more. Since the U.S. amine plant appears to have considerable advantages over the TSMA, a licence to build it in Britain has been obtained and derivative plant will be fitted in SSN 17 onwards.

Hence amine-based plants remain the basic equipment for CO<sub>2</sub> removal in the Royal Navy.

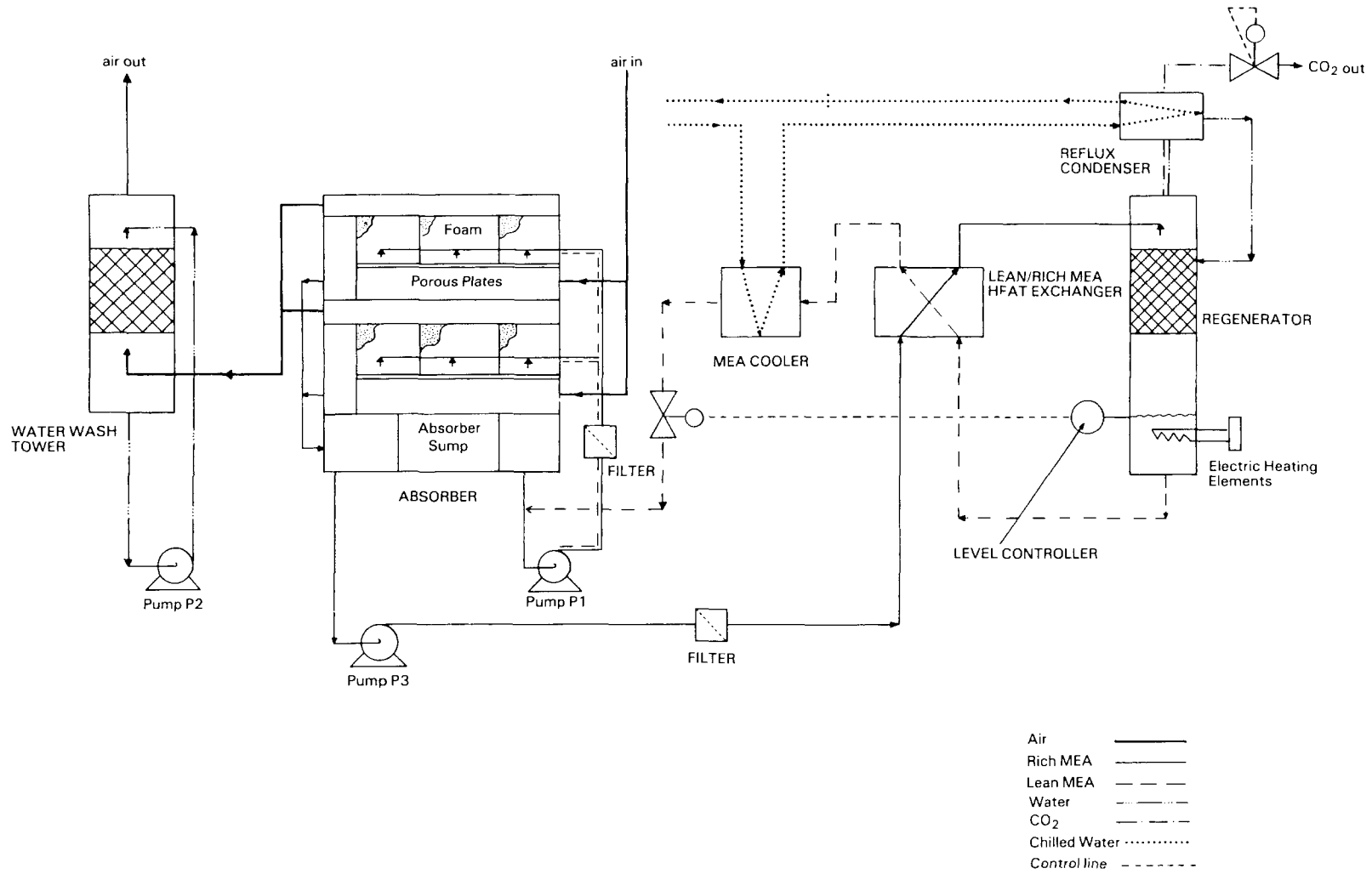


FIG. 2—FOAM BED SCRUBBER SYSTEM

### Plant Description

The solubility of  $\text{CO}_2$  in a cool solution of MEA is much higher than the solubility of  $\text{CO}_2$  in a hot solution of it. Hence if a cool solution is allowed to absorb  $\text{CO}_2$ , then by subsequent heating the solution will become supersaturated and will release  $\text{CO}_2$ . If the hot solution is then cooled again it is capable of absorbing more  $\text{CO}_2$  to enable the cycle to be repeated. This in effect is the basic operating principle of all R.N. MEA scrubber plants.

The scrubber designed in Britain for the Royal Navy in the 1960s is known as the foam bed scrubber. This name arises from the foam bed used to achieve intimate contact between air and amine which results in  $\text{CO}_2$  being scrubbed from the submarine's atmosphere.

The design of the latest foam bed  $\text{CO}_2$  scrubber as installed in SWIFTSURE Class submarines has changed very little from the original designs installed in VALIANT Class. The plant comprises four basic elements:

- (a) An absorber column where the contaminated air is contacted with the cool amine solution.
- (b) A regenerator column where the  $\text{CO}_2$ -rich amine solution is heated and stripped of its  $\text{CO}_2$ .
- (c) An amine solution circulation and conditioning system to transfer amine continuously between absorber and regenerator columns.
- (d) A water wash tower to ensure that MEA carry-over in the outlet air stream is removed before the clean air is fed to the ventilation system.

Lean and rich MEA solutions refer to the relative concentrations of  $\text{CO}_2$  in solution. A lean MEA solution (low in dissolved  $\text{CO}_2$ ) is produced in the regenerator. A rich MEA solution (high in dissolved  $\text{CO}_2$ ) is produced in the absorber.

The operation of the foam bed scrubber is shown in FIG. 2. Background air, with a  $\text{CO}_2$  content of 1% or less, is blown through the absorber section of the plant where it is scrubbed by lean MEA to reduce its  $\text{CO}_2$  content. A water wash on the air outlet eliminates any MEA contamination before the air is returned to the ventilation system. The design of the absorber is shown in FIG. 3. Two foam beds are fitted per plant, mounted one above the other and operated in parallel. Foul air enters a plenum chamber beneath each porous plate, while lean MEA is sprayed on top. The air rises through the plate causing a foam to be produced in the MEA where the transfer of  $\text{CO}_2$  occurs. Rich MEA subsequently overflows a weir into the sump at the bottom of the tower, to be recirculated back to the absorber sprays. The air outlets from the two absorber beds then combine and discharge through a common water wash tower which removes any solution carry-over from the air. A proportion of the rich MEA solution (about 25%) is taken from the absorber sump and pumped to the regenerator where the absorbed  $\text{CO}_2$  is stripped from the solution.

The rich MEA solution is heated in a heat exchanger before entering the regenerator (FIG. 4). Upon entering, the solution is sprayed over a pall ring packing where the  $\text{CO}_2$  dissociates from the solution to be swept away for disposal. The MEA percolates down to the liquid sump where it is boiled by electric resistance heater elements to produce steam which rises through the packing to sweep away the dissociated  $\text{CO}_2$ . The hot MEA is then returned to the absorber, passing firstly through the MEA/MEA heat exchanger, where it heats the incoming MEA, and then through a chilled water cooler to cool it to the absorber operating temperature. The temperature in the regenerator is set by controlling the operating pressure of the column via a pressure regulating valve on the  $\text{CO}_2$  outlet line from the column. The uncondensed  $\text{CO}_2$  is collected and disposed of via the  $\text{CO}_2$  compressor.

The absorption process is carried out at around 30°C and the stripping process at around 130°C (corresponding to a saturated steam pressure of 30 lb/in<sup>2</sup>, gauge).

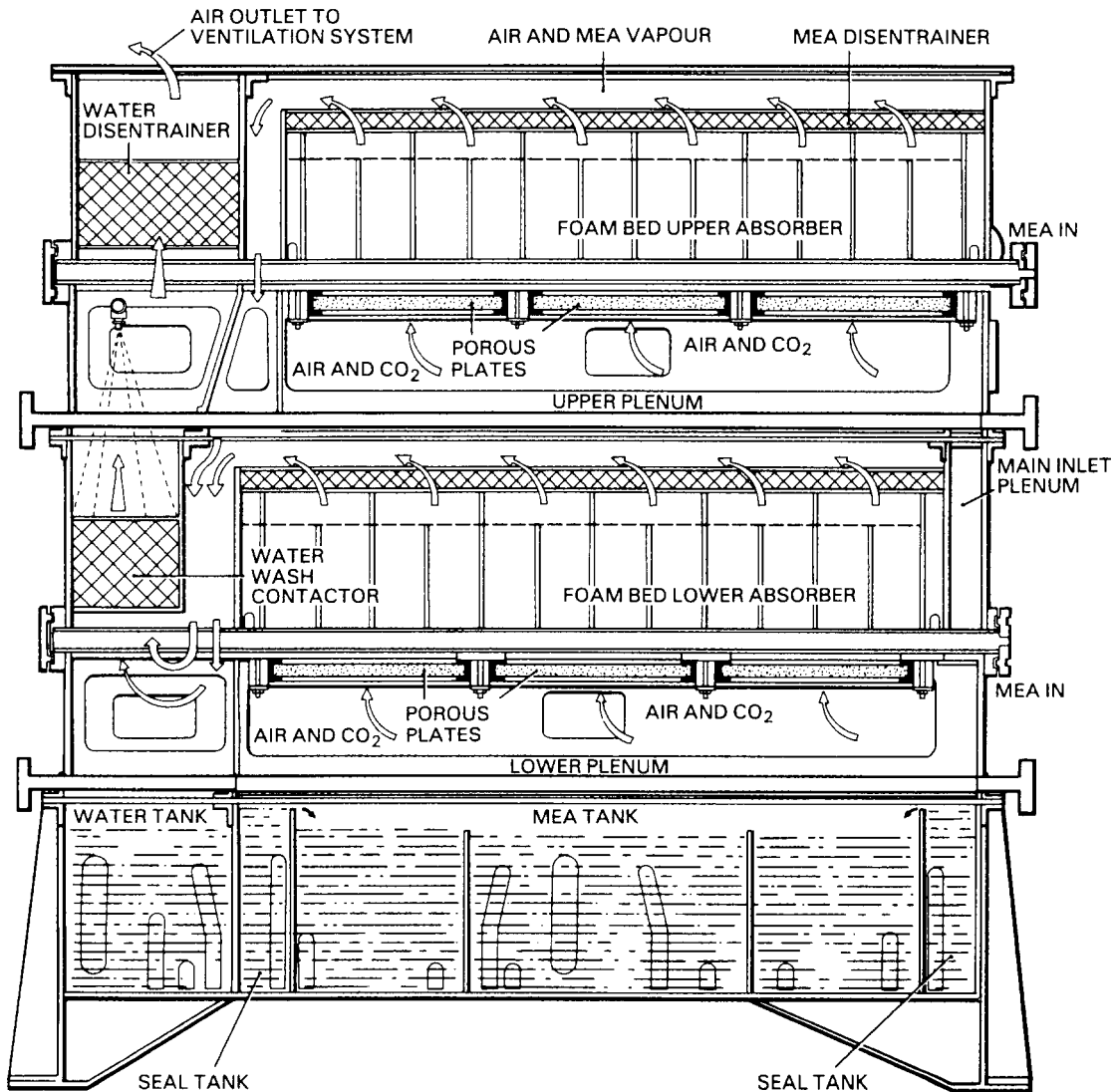


FIG. 3—ABSORBER OF FOAM BED SCRUBBER PLANT

### Operating Principles

The operation of an MEA scrubber depends on interphase mass transfer. CO<sub>2</sub> is first transferred from the gas to the liquid phase in the absorber and then back again to the gas phase in the regenerator. The equation describing the rate of CO<sub>2</sub> transfer in either the regenerator or absorber is:

$$N_s = K_g \times A \times (C_2 - C_1)$$

where  $N_s$  = mass of solute transferred/unit time  
 $K_g$  = overall mass transfer coefficient (on a gas phase basis)  
 $A$  = surface area over which mass transfer occurs  
 $(C_2 - C_1)$  = difference in CO<sub>2</sub> concentration between gas and liquid phases.



In any given installation the internals of the absorber and stripping columns cannot be changed and so the surface area is fixed. Similarly if flow rates remain constant then, within certain limits of concentration range,  $K_g$  remains constant. Hence the transfer rate of  $\text{CO}_2$  is dependent only on the concentration difference or concentration driving force.

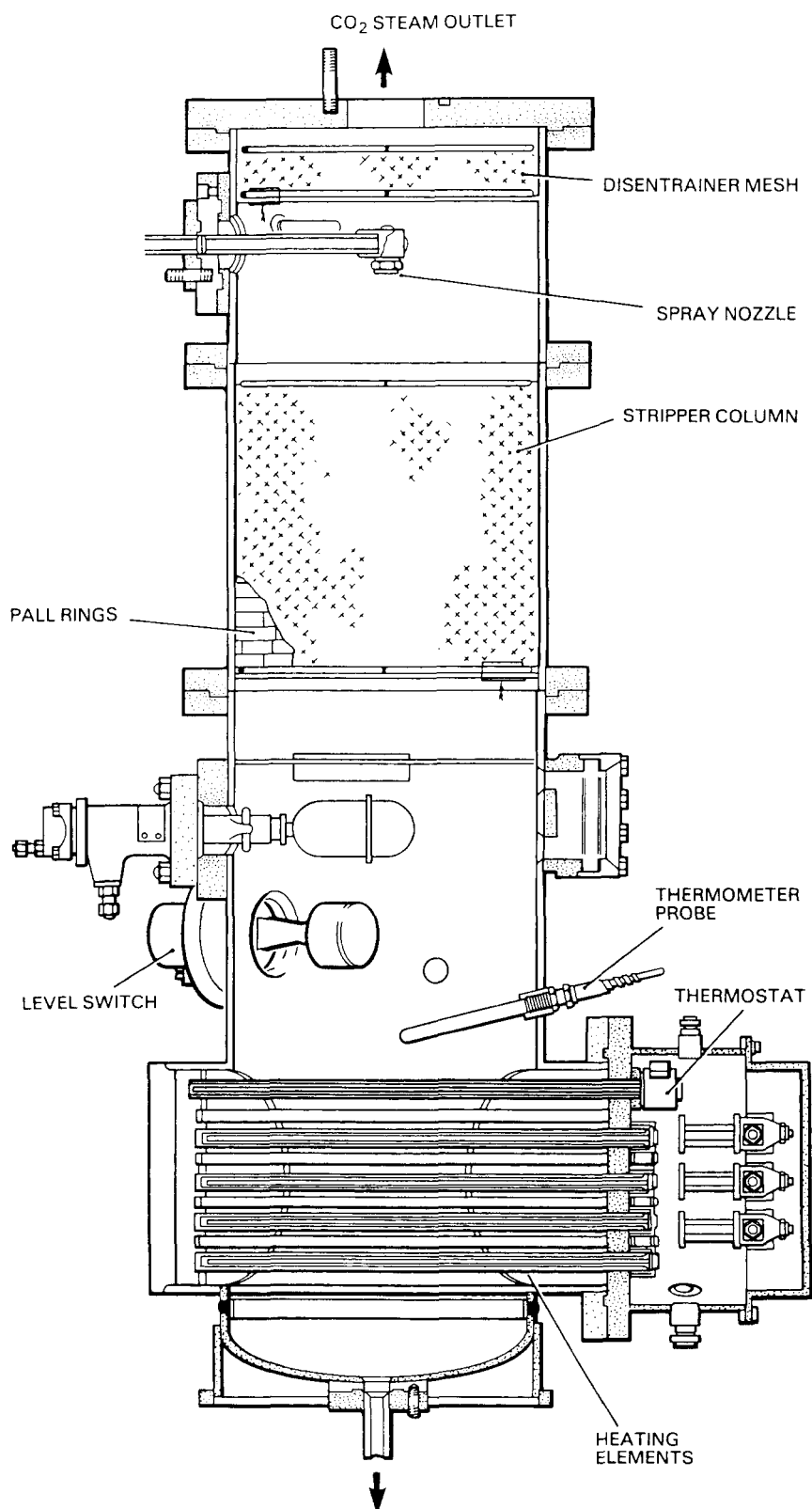


FIG. 4—REGENERATOR OF FOAM BED SCRUBBER PLANT

Both lean and rich MEA solutions contain dissolved  $\text{CO}_2$  to a lesser or greater extent and hence both solutions produce a partial pressure (vapour pressure) of  $\text{CO}_2$  above the solution. The driving force in the absorber is the difference between the partial pressure of the  $\text{CO}_2$  contained in the air and the  $\text{CO}_2$  vapour pressure of the MEA solution.

As the background  $\text{CO}_2$  concentration and hence partial pressure increases, the driving force increases and so the mass transfer rate increases. The converse applies to low  $\text{CO}_2$  background levels. Hence the scrubber will remove a greater mass of  $\text{CO}_2$  (lb/hr) at high background  $\text{CO}_2$  levels than at lower background  $\text{CO}_2$  levels.

An analogous situation occurs in the regenerator column. In this case however, the transfer of  $\text{CO}_2$  occurs in the reverse direction, i.e. from solution to vapour. Again the rate is dependant on a  $\text{CO}_2$  partial pressure difference, only in this case the  $\text{CO}_2$  partial pressure from the rich MEA solution is higher than the  $\text{CO}_2$  partial pressure in the stripping steam and hence the  $\text{CO}_2$  is transferred from the rich solution to the steam. The richer the MEA solution the easier it is to remove  $\text{CO}_2$ , since a richer solution produces a higher partial pressure difference.

The mass transfer processes occurring in both the absorber and regenerator can be represented graphically on driving force diagrams (FIG. 5). On these diagrams the operating line represents the partial pressure of  $\text{CO}_2$  in the

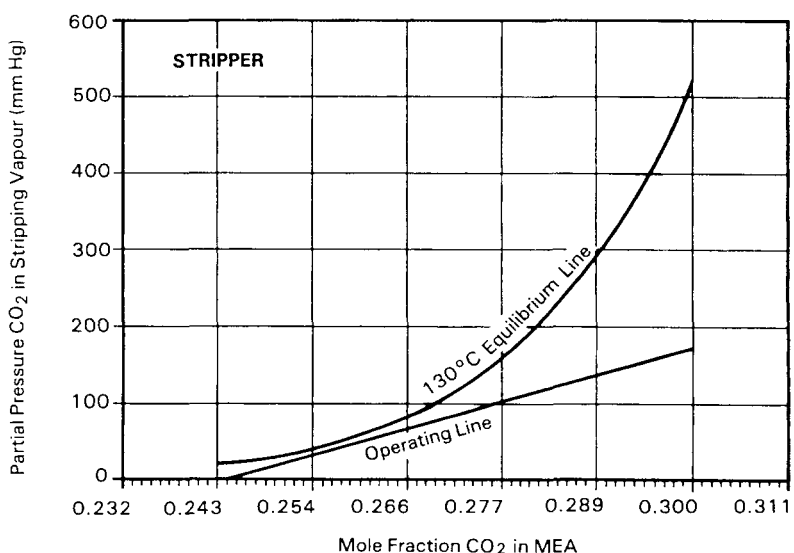
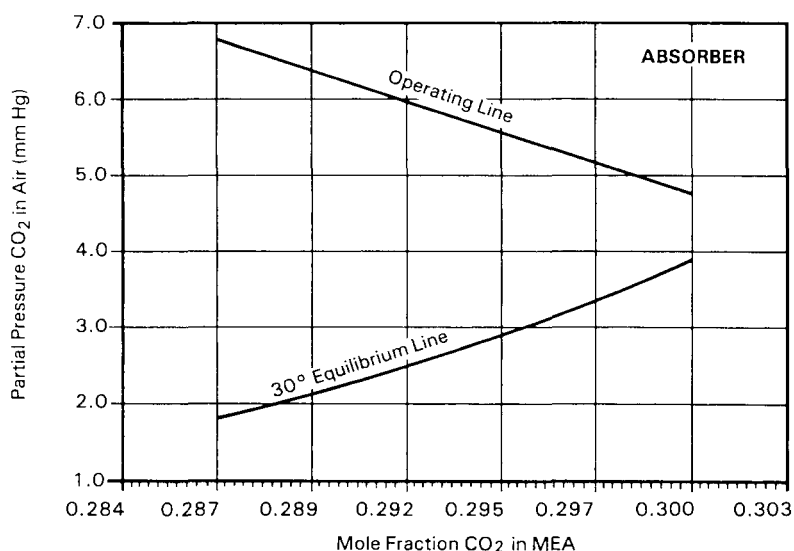


FIG. 5—DRIVING FORCE DIAGRAMS FOR FOAM BED SCRUBBER

MEA as it changes through the column. The equilibrium line represents the equilibrium or saturation  $\text{CO}_2$  concentration of the MEA. The vertical difference at any point represents the partial pressure driving force at that point in the column. Note that the absorber operating line lies above the equilibrium line representing mass transfer from the air to the MEA solution, whereas the regenerator operating line lies below the equilibrium line representing mass transfer from the MEA solution to the steam.

It should be remembered that for a given crew complement of a submarine, the production rate of  $\text{CO}_2$  is fixed within a certain range, depending upon crew activity. If stable atmospheric concentrations can be achieved with a scrubber operating, that plant must be transferring that rate of  $\text{CO}_2$ . The parameter of interest to the operator is the ambient concentration at which equilibrium is maintained, which is governed by the balance of transfer in the absorption tower and regenerator. Hence, a poorly run plant and a well run plant will always remove the same mass of  $\text{CO}_2$  from the submarine atmosphere. However it is the ability of the well run plant to achieve this at significantly lower  $\text{CO}_2$  concentrations that is the key point.

It is important to note that the MEA solution cannot be stripped of  $\text{CO}_2$  merely by heating the solution. The elevated temperature merely results in an increased  $\text{CO}_2$  vapour pressure. Unless a steam flow (or other  $\text{CO}_2$ -free stripping gas) is present to remove the dissociated  $\text{CO}_2$ , the solution will not be stripped.

### Scrubber Control

The operator of the scrubber has very little direct control over the performance of his plant. The emphasis is placed on good husbandry rather than direct control. He can alter the setting on the pressure regulator to increase or decrease the operating pressure (temperature) of the regenerators but, as will be seen, this is not always desirable. In the short term, improvement can be made as at the higher temperature  $\text{CO}_2$  will dissociate more freely from the solution so improving performance. In the long term however a high temperature will lead to degradation. Therefore, increasing the regeneration pressure cannot be considered as a long-term solution to poor plant performance.

Temperature, pressure and flow are measured at key points in the plant and the operator has to ensure that the scrubber is operated as close to optimum values as possible. Vital clues can often be obtained as to the cause of poor plant performance by close examination of the plant measurements. Even slight deviation from design values can indicate a possible problem. For example in the foam bed scrubber, pressure drop across the porous plates and visual inspection are the only ways of determining whether the foam bed is being generated correctly and hence if sufficient mass transfer area for  $\text{CO}_2$  removal is being generated. Small changes in absorber temperature can have a significant effect on  $\text{CO}_2$  absorption, since a high temperature solution will reduce the driving force for  $\text{CO}_2$  absorption by virtue of its high  $\text{CO}_2$  vapour pressure. Regenerator flow rates must also be kept steady to maintain adequate absorber performance, without which MEA will return to the absorber partly saturated, again reducing the driving force for absorption.

To avoid degradation, it is important that the temperature of the amine at any point in the process be kept as low as possible, commensurate with efficient operation of the plant. The operating temperature is highest in the regenerator where the bulk temperature is maintained at  $130^\circ\text{C}$ . To maintain this bulk temperature, the local surface temperature on the heater elements

must be significantly higher. In the foam bed scrubber, heating is provided by 27 heater elements wired in three delta groups of nine. Each group comprises three sets of heaters connected in series across each phase. Failure of one element will thus result in the loss of three heaters. The temptation to short out the failed elements must be avoided as such action would result in higher surface temperatures in the remaining two elements, so increasing the rate of degradation.

The most important operator duty, however, is to maintain the MEA solution strength, as measured by titration with sulphuric acid, at its optimum. The solution strength is constantly increasing since the treated air leaves the absorber tower with a higher water content than the inlet air. Although higher strength MEA solutions have an increased absorption capacity for CO<sub>2</sub> they are also more viscous. Increased viscosity reduces the mass transfer coefficient, reducing CO<sub>2</sub> absorption. The latter effect dominates, with the result that increased solution strength reduces CO<sub>2</sub> absorption. With weak MEA solutions the reduced absorption characteristic dominates over the viscosity effect, again resulting in reduced CO<sub>2</sub> absorption. The optimum solution strength is close to 4N (4×normal) which is the recommended operating strength.

### **Solution Degradation**

The U.S. Navy was the first to operate the amine scrubber at sea in the late 1950s. Early problems were encountered which became generally known as degradation. Although the plant would continue to remove the required mass of CO<sub>2</sub>, shown by the fact that stable CO<sub>2</sub> levels could be achieved from the atmosphere, it was unable to achieve it at low enough concentration levels. While the background CO<sub>2</sub> level was below the prescribed limit, degradation was of little concern. However, once the level was exceeded the submarine Command was placed in the position of either ventilating or continuing to operate outside prescribed limits.

Aside from the fall-off in scrubber performance, other symptoms of solution degradation were observed. The toxic irritant ammonia was generated as a product of the degradation reaction which caused discomfort to submarine crews. The solution became dark in colour, which interfered with its chemical analysis. Excessive amounts of amine make-up were required to replace degraded solution and excessive foam generation hindered control of the plant.

MEA degradation was a well-known phenomenon within the process industries from which the technology was obtained. The industrial solution to this problem is to simply tap-off a sidestream of the plant charge and replace it with fresh amine. When a sufficient amount of tap-off solution was collected it was batch distilled to separate the useful amine from the spent degradation products. The distilled amine was recycled back to the plant and the spent degradation products dumped as waste.

Such a solution was not a practical proposition for a submarine plant and an alternative solution to the problem was required. An extensive programme was initiated by the U.S. Navy in the 1960s aimed at eliminating or alleviating degradation problems. The American work<sup>2</sup> concluded that the MEA was being rapidly oxidized by the air, forming degradation products such as ammonia, non-basic nitrogen compounds and peroxides. The hypothesis advanced by research workers was that the oxidation reaction was proceeding mainly in the regenerator where the higher temperature increased the rate of reaction, the oxygen being provided by the MEA which was saturated with respect to oxygen upon leaving the absorber.











