REMOVAL OF REFRIGERANT GASES FROM THE ATMOSPHERE OF NUCLEAR SUBMARINES

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ABSTRACT

This article examines the development of equipment designed to remove refrigerant gases from the atmosphere of nuclear submarines. It covers the requirement for such equipment and describes the chemical processes involved. The effect of new refrigerants developed as a result of the Montreal Protocol is also discussed.

Introduction

Recent articles[1,2] in naval engineering magazines have described the philosophy and equipment used for submarine air purification. BR 1326[3] covers this in depth. Refrigerant gases are widely used in submarine chilled water plant and fridge plants, and passive controls ensure that the type of refrigerant gas used in submarines is as safe as practicable. However there is a finite limit and once in the atmosphere the stability of refrigerants makes them awkward to remove. In theory refrigerant gases should stay in the equipments or bottles but leaks and failures cause them to escape. Once in the atmosphere they can cause significant damage to submarine equipments and operational interference. This article examines active means of removing the gases once they have escaped into the atmosphere.

Refrigerants Used in Submarines

Traditionally the main factors considered when choosing refrigerant gases are:

(*a*) Cost.
(*b*) Toxicity.
(*c*) Thermal Stability.
(*d*) Thermodynamic performance.

Other factors taken into account include flammability, corrosion, miscibility with lubricants, and operating pressure. In the past the Navy has used a variety of refrigerants and, before the advent of Chlorofluorocarbons (CFCs), gases such as ammonia, carbon dioxide and even steam were used. The widespread introduction of CFCs in industry in the 1930s had many potential advantages for the Navy. The excellent thermodynamic performance of CFCs combined with their low toxicity meant that small, safe and efficient refrigeration plant could be developed. In addition they were cheap and, unlike steam vacuum plants, did not require a constant supply of steam. R12 and R114 are the two refrigerant gases currently used in submarine chilled water and fridge plants. In the submarine world they are commonly referred to as 'freon'. 'Freon' is in fact the proprietary trade name for Du Pont's refrigerant gases. (ICI call their refrigerants 'Arcton' and Rhone Poulenc use the term 'Isceon'). R22, although widely used in the surface flotilla, is not used in submarines as it is more toxic than R12 and R114.

Problems caused by High Atmospheric Levels of Refrigerant

All gases found in submarines are given a Maximum Permitted Concentration (MPC) and this figure takes into account the toxicity of the gas to humans over a period of time. CFCs such as R114 and R12 have a relatively high 90 day MPC (MPC 90) of 500 ppm, as they are of low toxicity.

High Temperature Burners

It has been known for many years[4] that CFCs decompose when passed over catalysts at high temperature. In the 1970s and 80s severe corrosion was found in the Keith Blackman high temperature CO/H_2 burners. Investigations[5] revealed that the freon was being decomposed by the hopcalite catalyst into hydrochloric (HCl) and hydrofluoric (HF) acids. These highly acidic gases were then attacking the copper of the cooling coils and back end of the burners. This is part of the reason why the Atlantic Research and Wellman burners use Hastalloy components which are more corrosion resistant but much more expensive. These are fitted to TSSBN and SSN 17 onwards and will be back fitted at refit to all SSNs.

DC Machines

Freons decompose at high temperature and sparking DC equipment will break down the CFC into HCl and HF. This might be part of the mechanism that causes excessive brushwear on some DC machines, e.g. TG exciters. The Defence Research Agency is investigating this phenomenon.

Removal of Refrigerant

Upon diving, the atmosphere of a submarine is continuously monitored. As CFCs are stable they do not naturally break down and any leaks of refrigerant will cause the concentration of refrigerant in the atmosphere to rise. The medical staff plot a graph of freon concentration versus time which is usually linear; the slope being determined by the leak rate. Good refrigeration plant maintenance combined with regular freon leak searches normally allow the rate of rise of freon to be 'acceptable'. 'Acceptable' is a subjective term but, providing the level of freon is extrapolated to be below 500 vpm when the submarine is next due to surface, the regulations of BR 1326 are being maintained. It is only when dived that small leaks will be noticed but rigorous leak searching at the end of maintenance periods can significantly reduce leakage. However, even small oil leaks from freon plant compressors will cause noticeable rises in freon levels. At sea, most leaks can be fixed by judicious use of Henleys Compound and by taking proper engineering precautions. Condoms on the top of spare freon bottles are an excellent method of preventing/detecting unwanted leaks. Over-enthusiastic leak searching can make matters worse, e.g. over tightening of valves leading to shearing of spindles or even pipework.

There have been numerous cases when the linear graph has taken a step change upwards. This is indicative of a major freon excursion. Possible causes include fractured TEV piping, major failure of refrigeration plant or accidental opening of spare freon bottles. In particular the action taken some years ago to remove isolating valves and thereby remove potential leak sources has proven to be an 'own goal'. This action means that it is practically impossible to break into the plant for defect rectification without initiating a major freon excursion.

Ventilating

In the past the only way of reducing the levels of freon in the atmosphere was to bring the submarine to periscope depth and ventilate the boat. For operational reasons this is often impossible or highly undesirable. If MPC levels are exceeded then smoking is banned and the crew go on to the Emergency Breathing System (EBS). Running of air compressors is prohibited as this would charge the bottle groups with foul air. This condition can only be maintained for a short period of time before ventilation becomes essential.

Smoking

The positive effects of smoking are often ignored and smoking is often deemed an antisocial habit. However, smokers have a beneficial effect on freon levels in submarines although unfortunately not enough to make a significant difference. The high temperature of the ash acts as a high temperature burner and decomposes freon into HF, HCl and phosgene. This social behaviour is unfortunately harmful to the smoker's lungs which is why smoking is banned when freon levels breech the MPC 90 level.

Freon Removal Unit

For the SSBNs a Freon Removal Unit (FRU) was developed. It works by oxidizing the freon over a catalytic bed at high temperatures and then absorbing the acid gases evolved in standard soda lime canisters. The catalyst bed is maintained at a temperature of $400 \pm 10°C$ by means of heaters and recuperative heat exchanger. CJB Developments Ltd (CJB), the manufacturers of the electrolyser and TSMA, carried out this work and developed the Mk.1 FRU subsequently fitted to SSBNs. It is designed to remove 9.1 kg/week of R12 from the atmosphere at a background level of 500 ppm.

Temperature Swing Molecular absorber

The design of the Temperature Swing Molecular absorber (TSMA) developed for TRAFALGAR Class took into account freon removal. A Zeolite bed was used to extract R12 from the atmosphere and it was then pumped overboard along with other contaminants. TSMA fitted boats usually have the lowest levels of freon in their atmospheres. However for a number of reasons later TRAFALGAR Class and TSSBN do not have the TSMA and so have no method of reducing freon levels when dived.

Refrigerant Removal Unit

TSSBN has a US-designed chilled water plant which uses R114. The plant is of excellent design and operates at low pressure. It incorporates a built-in purge and pump out unit as well as a foul gas receiver. It is expected that TSSBN will have much lower levels of freons in her atmosphere than previous submarines. Nevertheless it was deemed prudent to incorporate some method of freon removal into the suite of air purification equipment. A number of methods were considered, including molecular sieves and catalytic decomposition.

Work done under the submarine Secondary Improvement Programme (SIP) indicated that the catalytic process used in the FRU could be improved to remove R114. CJB was awarded the contract to design the unit. It was called the Refrigerant Removal Unit (RRU) and was designed to remove primarily R114 and also a small amount of R12 (R12 is used in the cold and cool room plants due to the lower temperatures required). FIG. 1 is an overall view of the RRU. It will remove 14 kg of R114 and 1 kg of R12 per week from a background of 500 ppm.

Technical Description

FIG. 2 is a cutaway view of the plant and FIG. 3 shows the process loop of the RRU plant. Contaminated air is sucked in via a filter and silencer and heated in a recuperative heat exchanger as well as by electrical heaters before passing to

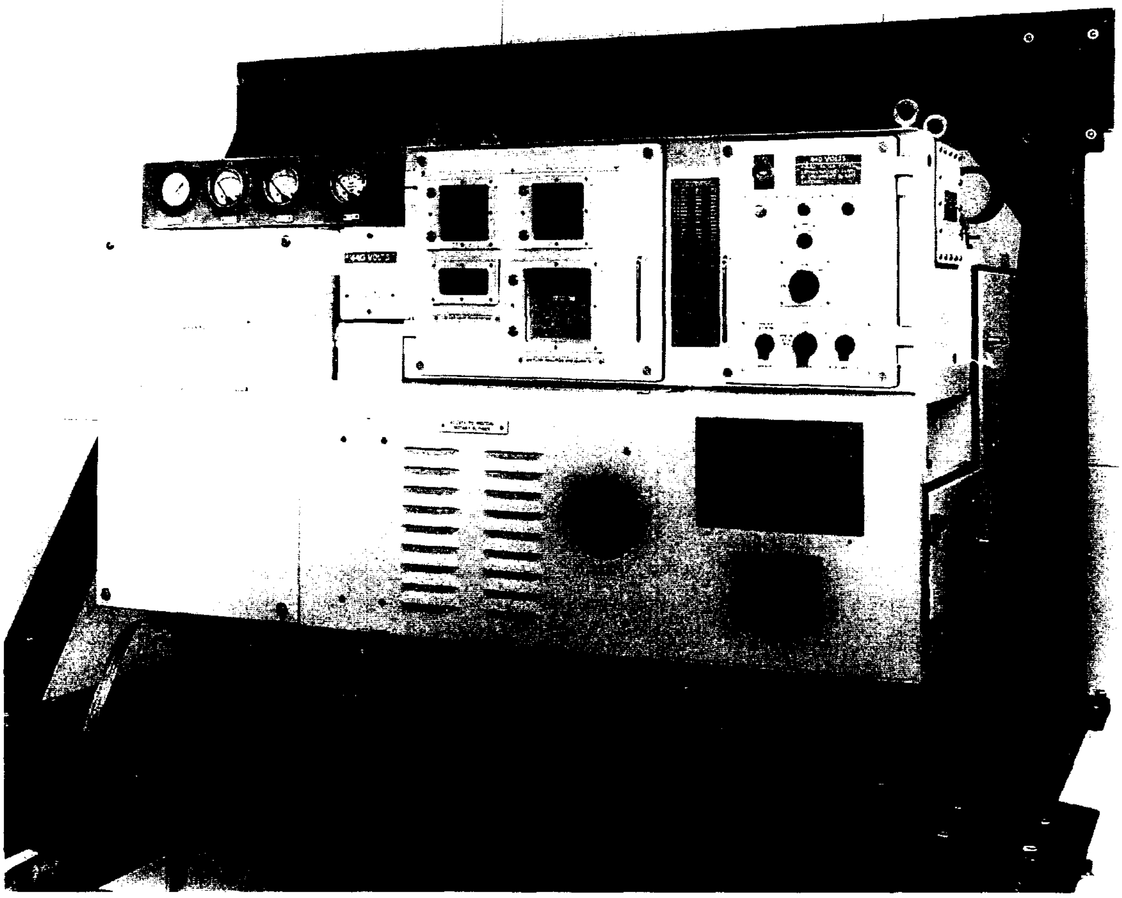

FIG. 1—THE MK. 1 REFRIGERANT REMOVAL UNIT (RRU)

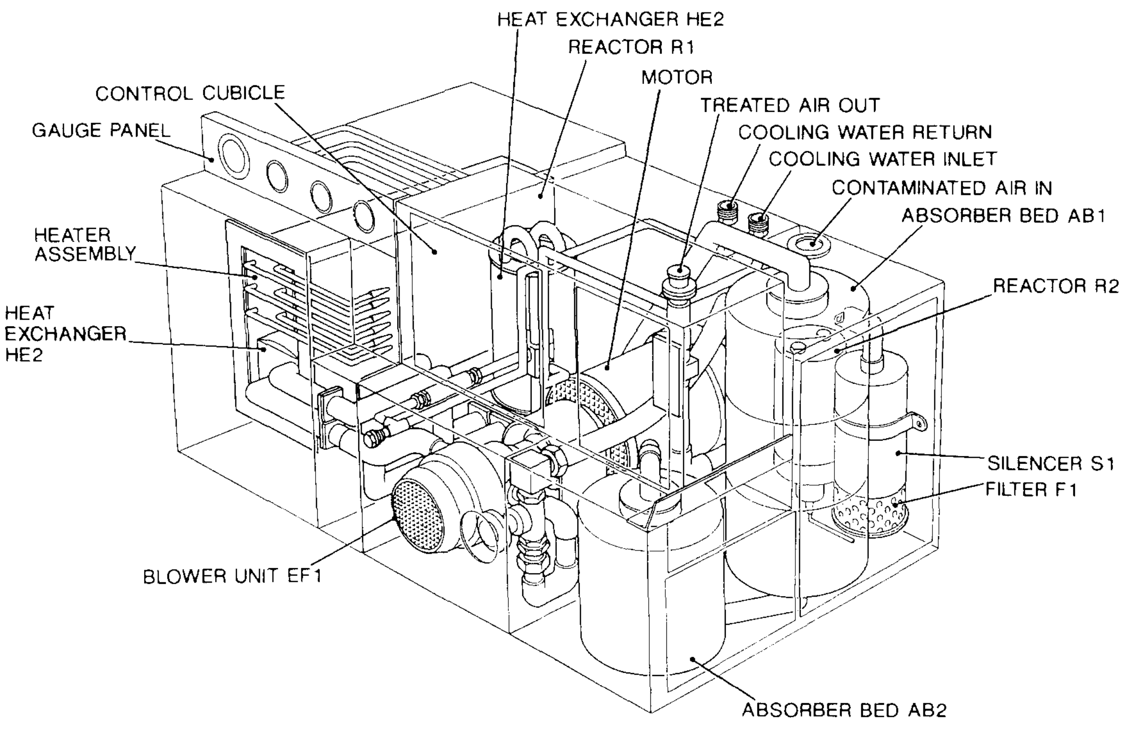

FIG. 2—REFRIGERANT REMOVAL UNIT

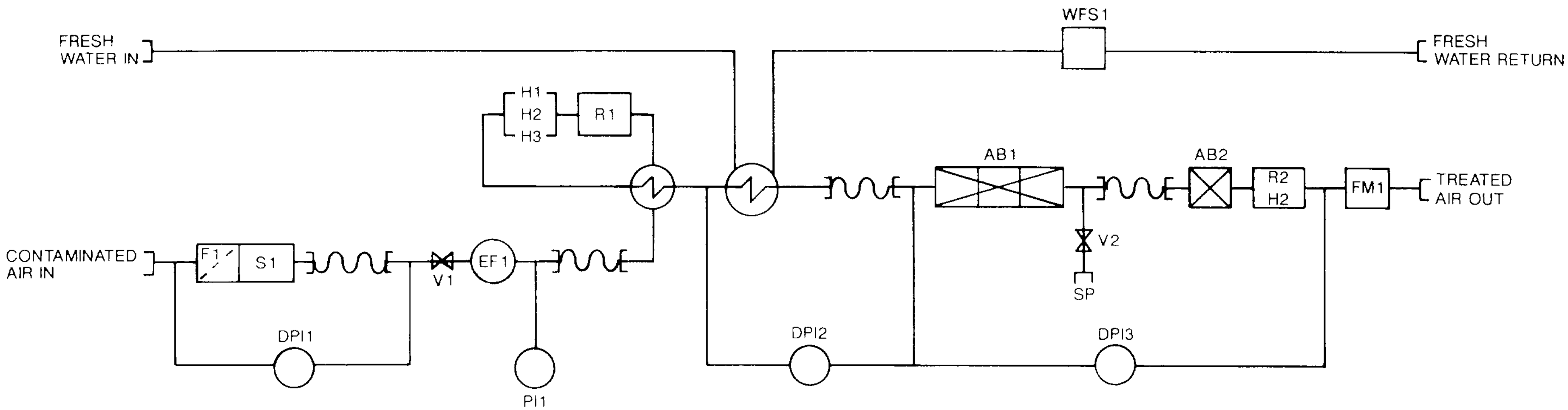

FIG. 3—PROCESS LOOP OF RRU MK. 1

AB: Absorber
DPI: Differential Pressure Indicator
EF: Blower
F: Filter
H: Heater
PI: Pressure Indicator
R: Rector (catalyst bed)
S: Silencer
WFS: Water Flow Switch

the first catalyst bed. This contains the catalyst (the identity of this catalyst is commercial-in-confidence information and so is not divulged in this article). Here the R114 and R12 are broken down and react with water vapour to form hydrofluoric and hydrochloric acid. The hot gases are cooled by the heat exchanger and by a fresh water cooled heat exchanger. The acid gases are then absorbed by soda lime canisters. The gas flow then passes through another catalyst bed containing palladized tin oxide. This oxidizes any carbon monoxide that might be present before returning the air into the submarine.

Problems During Development

At the outset the project was perceived as being of low technical risk as it was simply an improved version of the FRU. However, it was found that R114 broke down at a higher temperature than R12 and this caused a number of problems.

Gasket material

The high temperatures combined with acidic gases proved too much for graphite-based gasket materials used in the hot section. After a number of trials, exceptional approval was given to use Klingerite, an asbestos based material.

Carbon Monoxide

Another problem that was not detected until late in the development was the formation of carbon monoxide. The chemists had not predicted CO as being a breakdown product and it was not detected in the mass spectrometer analysis equipment due to masking by nitrogen present in the air. It was only found when investigating the cause of a blockage in the high temperature heat exchanger. Acid gases from refrigerant breakdown had attacked the heat exchanger due to the incorrect use of materials during construction and the occlusions due to the corrosion products had been compounded by carbon formed by the disproportionation of CO. The carbon monoxide is transferred to carbon dioxide and carbon in the reaction.

$$2CO \rightarrow CO_2 + C$$

The correctly constructed heat exchangers now in use do not suffer this problem.

Mounting

The final problem involved the fitting of the noise-reduced X-mounts. Despite following the guidance of the shock BR, the machine had an alarming list and it was necessary to add two more mounts. The shock BR has since been amended.

Testing

The prototype unit was subjected to an intensive trials programme. This included a 500 hour endurance trial as well as a standard package of environmental testing at West Drayton. These proved most useful as they highlighted some technical problems including EMC susceptibility and wiring deficiencies, as well as a number of material problems.

Status

The RRU has now been fitted in HMS *Vanguard* and two other production units have been delivered. It has yet to be used at sea.

Development Work

The prototype RRU has proven most useful in the last year and has been used in several developmental trials.

Freon Removal in SSNs

The Submarine Air Purification Committee (SAPC) perceived that the RRU may be of use to non-TSMA-fitted SSNs. As a result of this requirement trials were arranged using the prototype unit still held at CJBD. By optimizing the operating temperature, it was shown that the RRU was highly effective at removing R12 and that carbon monoxide was not produced. However, it appears unlikely that in-service SSNs will receive this equipment due to its size.

Montreal Protocol

There has been much work associated with the Montreal Protocol and in particular trying to find replacements for R12 and R114, both of which have to be phased out within the next four years. As the replacements are by their very nature less stable than existing CFCs there was concern that their breakdown products may be produced at lower temperatures and may be more toxic than those of existing refrigerants. In addition they may be damaging to equipments such as the high temperature burner. It was decided to investigate these breakdown products and the prototype RRU provided the ideal vehicle. By replacing the catalyst with hopcalite (the burner catalyst) it was possible to simulate the effect of these gases on the burner. Several replacement refrigerants were used in trials and the results were most interesting. They are still being analysed but, as predicted, the replacement refrigerants appear to break down at much lower temperatures. This means that they are likely to corrode the burner even more than R12 and that they may break down in other equipments as well. Further trials will be done to investigate this phenomenon. In addition, the RRU has been run to assess its effectiveness at removing these new refrigerants. These trends have shown that the RRU is highly proficient at removing them.

The Future

The obvious solution to the problem of atmospheric refrigerant removal is to prevent refrigerants leaking into the atmosphere in the first place and this is being tackled in a number of ways. Firstly, equipment mods and pump out units will be introduced to enable plants to be evacuated ('vacced down') effectively for defect rectification. Secondly, new designs of equipment will be introduced into service which have been designed from the outset not to leak. It is of note that US submarines rarely see high freon levels and perceive little need for dedicated removal equipment. However, it seems likely that small amounts of refrigerant will always be present in the submarine atmosphere and that it would be prudent to include equipment capable of removing them.

As part of the work associated with the Montreal Protocol alternative refrigeration cycles and cooling techniques have been considered. In many ways carbon dioxide would be an ideal refrigerant as the scrubbers would cope with any leaks and can provide a constant supply of pure gas. Unfortunately, its thermodynamic properties mean that it has a very high pressure cycle and that the plant condenser would require a supply of very cold water. This cannot be supplied when operating in the tropics. Steam vacuum cycles have also been reconsidered but discounted on the account of their size. Thermoelectric devices provide an elegant solution and work is proceeding on these. However, they are extremely inefficient at low temperatures, are large and have significant EMC drawbacks.

Conclusions

The RRU was designed to remove refrigerants that had leaked into the atmosphere as these have detrimental effects on equipment and personnel. The advent of new refrigerants is likely to make the problem worse. Dedicated equipment exists for removing them from the atmosphere but the best solution is to prevent them from getting there in the first place. This can be achieved by good refrigeration plant design and thorough maintenance.

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