

CHAPTER 8 - DISPOSAL OF CARBON DIOXIDE

In a submarine with a fuel cell, and obtaining its hydrogen from a metal hydride source, the only exhaust product is water which may be retained in the boat or put overboard as required. In all other forms of AIP propulsion, there are by-products of combustion which have to be dealt with. The by-products are mostly carbon monoxide, and the problem is to see what can be done with a stream of wet, impure carbon dioxide.

So far as is possible, designers like to keep the submarine at a constant weight, because this not only simplifies the design but it makes it easier for the crew to manage the trim. It seems clear from reading earlier papers that earlier workers looked around to see whether they could hold the carbon dioxide of combustion on board the submarine. They tried to liquefy or solidify the carbon dioxide.

Difficulties soon become clear. If you can manage somehow to get the carbon dioxide into a condensed state (itself a task which turns out to have notable difficulties) then either you are forced into providing a very large new storage tank, or you must find a way of hiding the newly formed carbon dioxide in the increasing ullage of the LOX tank.

No matter what the detail of the heat engine, the reaction scheme is always close to



so that 48 grams of oxygen produces 44 grams of carbon dioxide. The density of liquid oxygen at 20 Bara is 0.920 gm/cc and for liquid carbon dioxide it is about 1.068 at 15 Bara. (See an appendix for the properties of saturated CO₂). So therefore you need a second tank roughly the same size as the LOX tank into which you can collect the carbon dioxide.

Unless the carbon dioxide tank is to be refrigerated the carbon dioxide will be in the tank at temperatures roughly corresponding to those in the storage spaces of the submarine, usually a few degrees Celsius, and if the gas is to be liquid it is going to be at a considerable pressure. This is best seen from the P-T diagram CO₂PT and the data table in the appendix to this chapter.

Furthermore the pressure in the tank will change sharply with small changes in temperature. At the temperatures of the submarine the gas is near its critical point of 31 °C, the point at which everything will turn to a vapour. It appears already that we going to be operating this tank in rather difficult working conditions.

Although the idea of having a separate tank, comparable in size with the LOX tank, in the submarine seems to be quite unacceptable, we might yet be able somehow to unify the two tanks if we can think out how to handle the condensation of the carbon dioxide. For such a commonly used gas, you might think that the liquefaction or solidification would be a simple matter and you would not be wholly wrong. It *is* easy to liquefy or solidify carbon dioxide. You just can't do it in a small enclosed space like a submarine. As a matter of fact you more or less can't do *any* chemistry in a submarine.

A typical early scheme might have been that described by Kerros (See Ref 1 Chapter on MESMA). They intended to hold the entire combustion process, right through from the LOX tank to CO₂ storage, at 60 Bara. Once the fuel had been burned, the gases would be cooled down, the water vapour condensed out and the CO₂ would then start to condense into a holding tank. Kerros and his co-authors have indicated that they abandoned this scheme for safety reasons, but I think they have chosen not to mention that the whole scheme would soon have started to creak with engineering difficulties.

In a land based chemical plant you have a lot of space, and you can afford to purify the chemicals at any point of a process to any desired degree. The first thing you have to remember about carbon dioxide from a burner is that it is accompanied by water vapour, and therefore if you allow any part of the equipment to fall below 0 ° Celsius then this water vapour will condense as ice on the walls of the pipes and block them up. In a chemical plant on land you just put in drying towers until the gas is dry enough that the rate of ice formation is so low that the rest of the plant will run for some known long time until a planned de-icing procedure can be activated. There is no space for such towers in a submarine.

Even if you could dry the gas somehow then you are still faced with installing quite a large heat exchanger. In a 200 kW boat you will be producing something like 1 mole of CO₂/sec depending on the prime mover. This gas must be compressed enough to liquefy it, or maintained at a high pressure, and have about 8 kW of energy taken out as heat of vaporisation. Up to now no-one has published a really convincing scheme to liquefy the carbon dioxide from a burner working inside a submarine.

The schemes by Brighenti (Ref 1) and by Rathson (Ref 2) attracted some interest. In both cases the idea was to use the reservoir of low temperature in the LOX tank to bring about the condensation of the carbon dioxide which would then be stored in the Brighenti case as liquid carbon dioxide in a toroidal tank incorporated into the hull of the submarine. In the Rathson case it was hoped to solidify the gas and store it near to the LOX tank. No matter what is written by the authors, I suspect that the inability to free the incoming gas of water vapour scuppered these schemes.

As the AIP submarine continues its mission, the LOX tank gradually becomes empty. Surely, reasoned the designers, there must be a way of filling this space with the unwanted carbon dioxide. Perhaps the carbon dioxide could be solidified into the LOX tank ? Or perhaps it could be solidified in a completely separate operation and then dumped into the LOX tank ?

This very attractive idea seems to fail. The LOX tank is very cold say -183 °C or 90 °K, so before you can allow the carbon dioxide anywhere near the LOX tank you must thoroughly dry it otherwise water will simply freeze on the inside of the feed pipes and block them. Let us suppose that we *could* dry the carbon dioxide stream, and let it proceed in the direction of the LOX tank. Then the CO₂ itself will freeze in the pipes because the LOX is at 90 °K and the CO₂ goes solid at 216.6 °K. In fact you can't have liquid carbon dioxide at LOX temperature, and this means in turn that you can't, in practical terms, put the carbon dioxide in the LOX tank.

Could we perhaps solidify the CO₂ into dry ice blocks and keep them in a cold enough atmosphere moderated by the LOX tank ? In a land based plant blocks of dry ice are nearly always made by expanding a stream of carbon dioxide gas through a nozzle which is then cooled by the Joule Thomson effect and falls to the ground as a sort of snow. This is then picked up and compacted into a block using something that looks like a baling machine. I don't think you can do this in a submarine, mainly because solid handling processes in chemistry nearly always need men standing around to debug them. As I said in an earlier chapter, to be convincing at industrial chemistry you need to stick to liquids or gases.

Frustrating and unlikely as it seems, it has proved completely beyond our skills to get the carbon dioxide inside the LOX tank and some other scheme must be adopted for getting rid of the gas.

In principle, you might be able to react the carbon dioxide with some other chemical to stabilise it into some storable form. In practice, no one has come up with a suitable scheme. Even if they did, it still seems as though it must be scheme that enables the carbon dioxide containing compound to be put into the LOX tank or the scheme will be demanding 40-50 m³ of valuable submarine space. Really, we have to throw the carbon dioxide overboard, there seems to be no other choice.

I think both the MESMA system and the Stirling system push 60 Bar carbon dioxide overboard. I don't know what happens in this case. It's quite possible that the carbon dioxide might be liquid when it leaves the boat. Even if it is, it will quickly turn back to gas unless the submarine is below about 300 metres depth.

If anyone makes a submarine with a fuel cell that gets its hydrogen from a reformer, it too will blow gaseous bubbly CO₂ overboard. The Closed Cycle Diesel system has a different system in which the carbon dioxide is dissolved in water in a rotating absorber so that a bubble free CO₂-in-water solution is put overboard. There seems to be opportunities for attaching the CCD gas dissolution system to the back end of other systems.

A vexed question is whether carbon dioxide can pumped in a gaseous form from a submarine without making the submarine suicidally visible to attackers. The gas leaves the submarine as bubbles, so potentially a volume of bubbly water will be attached to the rear of the submarine. Bubbly water is exceptionally visible to active sonars (See note (2)) and the net effect is to make the submarine look bigger as a whole and to add a nice shiny-sonar bit to the main submarine image which might have been dimmed by anechoic tiles and the like.

The submarine will remain low visibility to other submarines, which naturally can't use active sonar, but will be highly visible to a frigate. As described below, it seems to me that the bubble plume behind the submarine is quite large.

What you would like to do arithmetically, is to put the bubbles out through a device, and knowing that the bubbles were a certain diameter, and then calculate how long the bubbles persisted before they were finally absorbed in the water. Then you could work out how long the crocodile's tail was. When you try to do this you get a bit stuck. There are too many uncertainties in how the gas moves inside the bubble and particularly in how the water moves just outside the bubble. Remember that if there were no water movement at all, the gas could

only leave the bubble and get into the water by monstrously slow diffusional processes. If this were the case the boat would have a bubble tail extending right the way to the surface. The only thing that is very clear from calculation is that if the carbon dioxide inside the bubble is contaminated with a much less soluble gas like nitrogen or hydrogen or oxygen, then the bubble will persist for much longer than a bubble of pure carbon dioxide. What happens is that the CO₂ near the bubble wall gets dissolved into the water first and a hydrogen rich layer of gas sits against the water. You would think that inside the bubble there were no active gas mixing processes, so the carbon dioxide can only get to the water by diffusional mixing with the hydrogen. But even gas diffusion is slow. The net effect is to give the bubble a much longer life.

After a lot of rather experimental arithmetic I thought that a 5 mm diameter bubble of pure carbon dioxide emitted into a free sea, might ascend for about a metre and for about 20 seconds before it was absorbed. In a boat travelling at four kts, this might mean a plume about one boat's length would be following the submarine. I also thought that a bubble contaminated with nitrogen might last for at least ten times that distance. It seems that the depth at which the bubble is injected into the sea was of secondary importance. If you allow several small bubbles to coalesce into one larger one, then the lifetime of the bubble is very much extended. However, these numbers are merely indicative. Large pinch of cautionary salt must be taken.

Having noted that it is rather tricky to work out the life of a bubble *ab initio*, the next thing to do is to see if you can look the answer up somewhere in the literature. Unfortunately this also proves to be somewhat of a failure. People who do experiments on ascending bubbles seem to have hedged their experiments around with so many secondary conditions so as to try and achieve repeatability that the whole study is meaningless from our point of view. The paucity of this basic data is reflected in engineering handbooks such as Perry and Chilton "Chemical Engineers' Handbook".

It occurred to me that I could get the answer pretty well by employing a scuba diver and arming him with suitable gas bottles fitted with nozzles, and with a strong torch and a ruler. Let the gas escape and after some perseverance doubtless you could get an idea of the life time of various sorts of bubbles ascending in free water.

I mentioned this idea to an acquaintance of mine who worked for a department of the British Ministry of Defence. He said he could probably arrange to do this in a submarine escape training tower. After about a year I asked him if he'd managed to do this work. He said he had, but as he'd had to take out a job number to get enough cash to do it, the results were classified "secret" and he could not give them to me !

Next I went to talk to some friend at a German submarine factory where they had had some incidental experience in watching carbon dioxide bubbles. They said that their general impression was that a bubble of a few millimetres size would rise for one or two metres. Not as much as five metres they thought.

Recently a book by a man called Basilyevski about the development of Russian submarines in the period 1917 - 1977 has appeared.(Ref 3) This book, which is of quite breathtaking candour, describes Russian experiments in how to get rid of bubbles being put overboard by an early form of closed cycle diesel. The work was carried out just prior to and just after World War 2.

(Further comments about this will be found in a separate chapter)

The main conclusions of their work was that coalescent of bubbles from neighbouring orifices had to be avoided at all costs. The bubbles had to leave the boat as single entities and remain as these single units. Because of the quantity of gas this proved to be far from a trivial problem. Eventually the Russians developed a workable solution in that they placed a pipe along the whole length of the boat's keel. They found also that the bubbles affected the boundary layer to some extent so that frictional forces impeding the boat's motion through the water were somewhat lessened. The author does not say how big this effect was, but I hear an echo of this some fifty years later in the action of the Russian *Skval* torpedo, which by forcing air into the boundary layer of the device, so lessens the drag forces that the torpedo could travel in excess of 300 km/hour. (Ref 4)

The author goes on to say that when the boat's underwater diesel was run with the boat tied to the dock and on the surface, bubbles "were barely visible even from a distance of only several metres". But the submarine's diameter was about six metres and the fact that they were visible at all means that they travelled at least six metres and were probably in the water for tens of seconds. Since a typical patrol speed is about 4 kts and 1 kt is close to 2 m/sec, if the bubbles were in the water for 30 secs they would persist for a distance of about 60 metres which is about the length of your average submarine.

The Russians went on to make various modifications to their preferred arrangements, and one of these variants is illustrative of the problems. Instead of dispersing the bubbles along the keel, an engineer fed them into the region of the propeller, thinking no doubt that the increased local agitation would somehow make the gas dissolve more quickly. In fact, this idea was a failure, not only did the bubbles become much more visible but the propeller lost efficiency.

I have had a lot to do with the design of high speed carbon dioxide absorbers for use in submarines and several things are clear. Firstly, there is virtually no data available on *rates* of dissolution of a gas into a liquid. This is almost certainly due to the fact that there is no way of specifying "degree of turbulence", Reynolds number not being sufficiently precise for the purpose, and so you can't relate rate of dissolution to a measurable state of the water. Secondly, the rate of dissolution seems to be increased by making the water pass over a large rough surface at increasing velocities. Being unable to categorise the detail, I think of the carbon dioxide being "folded" into a plethora of tiny Karman vortices, where they are trapped long enough for the gas to pass into the body of the water. I have explained this a bit further in the chapter on Closed Cycle diesels.

Equally, what does *not* seem to be effective in hastening the dissolution of a gas bubble into water is to hit with a table tennis bat. This is essentially what the Russian engineer was trying with his modified propeller driven dissolution system. It is not enough in dissolving things to apply energy. It must be applied in a suitable system which has "high mixing" in some sense.

At the moment I think that a fuel cell system deriving its hydrogen from an onboard storage will produce no external bubbles, as will the Argo Closed Cycle Diesel. The MESMA and Stirling

systems seem likely to produce a bubble plume. These devices may now have some technological invention attached, but there is no clue what it might be.

There is one final matter to do with disposal of carbon dioxide and this is to do with cleaning up the breathable atmosphere inside the boat. I have considered this separately in the chapter on Integration.

APPENDIX – PROPERTIES OF SATURATED CARBON DIOXIDE

By saturated I mean both liquid and gaseous CO₂ being present together

Molecular weight =44.01 grams

Triple temperature=216.6 Solid, liquid and gaseous phases all simultaneously present

Critical temperature=304.2 No liquid above this temperature

Critical pressure = 73.83 Bara

Critical volume=92.4 ccs/mole

T °K	P Bara	Liquid density kg/litre or gms/cc	Heat of vaporisation kJ/mole
216.6	5.18	1.179	15.188
220	5.996	1.166	14.982
225	7.357	1.148	14.665
230	8.935	1.129	14.295
235	10.75	1.109	13.965
240	12.83	1.089	13.582
245	15.19	1.068	13.169
250	17.86	1.046	12.729
255	20.85	1.023	12.258
260	24.19	1.00	11.752
270	32.03	0.946	10.612
275	36.59	0.916	9.957
280	41.6	0.880	9.236
290	53.15	0.805	7.449
300	67.1	0.680	4.611
304.2	73.83	0.466	0

These figures are shown as one of the lines in the Figure CO₂PT. The meaning is that, for example, at 275 °K (a very typical sea temperature) a portion of carbon dioxide would have to be at a pressure greater than 36.59 Bara to be liquid. There are roughly 10 metres of sea water column to a Bar, so the boat has to be below this depth to be sure that liquid carbon pushed overboard will stay liquid. Actually, this is pretty deep for a military submarine, most of which manoeuvre in the top 5% of the water column.

APPENDIX – SIZES OF DIFFUSER PLATES

Consider a submarine at 300 metres depth, being propelled along at a few knots by a 200 kW heat engine.

Approximately 0.75 moles/sec of carbon dioxide will be produced (depending on the type of prime mover, its efficiency and all that). This is a gas flow of about 17 L/sec at one Bara or 0.6 L/sec at 30 Bara sea pressure. Suppose the gas is forced into the sea through a number of orifices each with diameter D metres, with the flow through a single orifice as Q_1 m³/sec.

The diameter of the bubble (D_b metres) just before it detaches itself from the orifice can be found in Perry and Chilton “ Chemical Engineers Handbbok” in section 18 as

$$D_b = D * \left\{ \frac{6 * T}{(\rho_{hol} - \rho_{hog}) * D^2} \right\}^{1/3}$$

where ρ_{hog} and ρ_{hol} are the liquid and gas densities T is the surface tension of the water, which for pure fresh water is 80.10^{-3} N/m.

The number of bubbles formed per sec is

$$f = [Q_1 * g * (\rho_{hol} - \rho_{hog})] / (\pi * D * T)$$

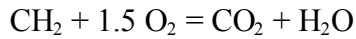
f should be less than 1 otherwise bubbles will be running together and coalescing.

From this we can get an idea of what might be wanted for our submarine. If the gas was voided through a plate with 1 mm holes, the bubbles would be about 8 mm diameter when they left the orifice. If they were to leave at rate of ten bubbles per second then you would need 5,000 orifices. The orifices would need to be separated by about 10 bubble diameters to prevent re-agglomeration and so you come up with an orifice plate with an area of about 36 sq m.

Calculations along these lines let you design an orifice plate that will put the gas into the water in bubbles of the most advantageous form. It would nevertheless be best if there were no bubbles at all.

Note (1) REACTION SCHEMES

I have written in this book, the reaction scheme of burning fuel by the equation :



and a few engineers have indicated that they find this confusing, “fuel” really being something like C_8H_{18} .

Notwithstanding the fact that various additives are added to commercial fuels to modify such matters as ignition delay time and so on, the vast majority of the contents of a tank of fuel are hydrocarbon molecules of a type known as saturated alkanes. They have the general formula $\text{C}_n\text{H}_{2n+2}$ and if we write this out a bit they consist of a string of CH_2 units capped at each end by a CH_3 block. Thus octane is thought of by a chemist as being $\text{CH}_3(\text{CH}_2)_6\text{CH}_3$.

By extension you can think of the fuel tank as being full of CH_2 groups. Sure, there are few foreigners, but this is not going to affect the accuracy of any calculations we might perform on the burning of the fuel. We just pretend that the tank is full of CH_2 groups burning according to the scheme above.

As an aside, I should mention the following : In the development of the argo closed cycle diesel we had a problem which persisted for about five years in that the measured oxygen consumption was always one or two percent less than what was calculated from the reaction scheme above. We could never account for this, but we assumed that our measurements were somehow wrong. In 1996 a colleague explicitly measured the oxygen consumption of a closed cycle diesel by hiring a large number of oxygen cylinders and weighing them before and after an extended period of running. This experiment, while difficult to carry out, revealed that the correct amount of oxygen was burned to within at least one tenth part of one percent.

Note (2) VISIBILITY OF BUBBLY WATER TO SONAR

In sonar detection a sound wave is propagated into the water. It is a property of waves that if the refractive index or velocity of sound in the water changes, then some of the energy is reflected back towards the source. Thus if the waves come across a solid lump like a submarine, the velocity of sound is different in the submarine to that in the water and sound energy goes back to a detector.

The velocity of sound in water is related to the quantity (bulk density/density). If you have gassy water with bubbles, the bulk density becomes very small and the velocity of sound can fall from a typical value of 1500 m/sec to only a few tens of metres/sec.

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