

CHAPTER 7 - SOURCES OF OXYGEN IN A SUBMARINE

In order to have any believable sort of Air Independent Propulsion system in a submarine, you have to have to be able to supply oxygen from a store inside the submarine. There are only a few ways of generating oxygen and the most common ones are shown in the tables which are in an Appendix to the Chapter.

Many of the reactions which I have listed in the tables are used to produce oxygen *in situ* for various reasons, but they are mostly not of engineering interest because they involve solid reactants. For industrial chemistry you want liquid reactants so that you can move them about. Failing a liquid a gas is next best. Solids are bad news : You can't get the reactants to mix properly, hot spots often form, and the by-products are sometimes difficult to handle.

An honourable exception to this general rule is a device called an oxygen candle which is a proprietary mixture of barium oxide, a chlorate, some iron filings and possibly some manganese oxide. A certain candle supplied by Molecular Products, Millend, Thaxted Essex CN6 2LT in the UK will weigh 3.456 kg and occupy 1.95 litres if it is to supply 1.0 kg of oxygen. (This will supply one man for one day, but a 200 kW diesel will need about 151 Kg/day and there will be heat problems to deal with). Candles are not only used in submarines but find use in space. The Mir space station certainly used a Russian version of the candle.

There are only a few realistic engineered possibilities for supplying a large prime mover with oxygen, and these are compressed air, high test hydrogen peroxide, and liquid oxygen. The best thing to do is to characterise the storage capacity in terms of the weight and volume of the system to deliver 1 kg of oxygen. These numbers should include everything, such as tanks, auxiliary pipes, taps gauges and so on. The answers are as follows :

Storage of oxygen as a compressed gas

In Europe we have something called the K-type cylinder. This is a forged steel cylinder outside diameter 0.23 m length=1.46 m giving an external volume of 0.071 cu m and internal volume of about 0.04 cu m. Such a cylinder contains 9.5 kg of oxygen at 175 Bara and has a tare weight of 64 kg.. If you pack the cylinders together you have to multiply by about 1.25 to allow for the empty interstices so that you have 0.088 cu m per 9.5 Kg of oxygen.

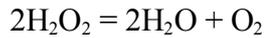
Thus you can deduce the “storage factors” :

For 1 kg of oxygen you need either 7.7 kg of cylinder
or 9.34 litres of cylinder

Storage of oxygen as HTP

HTP is shorthand for “High Test Peroxide” and is a mixture of water H₂O and hydrogen peroxide H₂O₂. HTP is pretty nearly pure hydrogen peroxide.

Hydrogen peroxide gives off oxygen when it is either heated or passed over certain materials like lead shot which act as catalysts.



One mole of HTP (MW=30 grams density=1360 kg/m³) will yield 0.425 moles of oxygen. From this allowing an extra 5 % for tank weight you get the storage factors :

For 1 Kg of oxygen you need either 2.32 kg of tanks containing HTP
or 1.61 litres

So straight away you can see that HTP holds much more usable oxygen than cylinders. For the cylinder to compete the gas pressure would have to be raised by about four times, and I don't think we have the materials for this.

Storage of oxygen as liquid oxygen

A certain commercial 20 te tank has length 7400 mm od=2600 mm external volume 39.2 cu m Tare wt 13.5 tes and holds 18500 litres of LOX whose density at 20 Bara will be about 0.87 grams/cc. (See the appendices to this chapter) So the tank holds 16.1 tes of oxygen.

The storage factors are then

For 1 Kg of oxygen you need either 1.83 kg of tankage
or 1.62 litres

In fact for a military tank we have to allow a bit more than this

For 1 Kg of oxygen you need 2.0 kg of tank or
1.8 litres

Now it would appear from this that we must try to make a rational choice between HTP and LOX. Both materials have been used in submarines, but as we shall see, LOX has got the upper hand in the second wave of AIP development.

Advantages and disadvantages of HTP

Hydrogen peroxide has been a commercial product since about 1880, and is usually sold as a solution diluted with water. One of its earlier uses was in bleaching straw hats. It was widely used as a household bleaching agent. It used to be used in laundries and in recipes for creating blonde hair from various less fashionable starting points. It is used for disinfecting cuts, and as a

bactericide. These applications, use dilute solutions (less than 8 %) which are innocuous, given a modicum of common sense.

Stronger solutions of hydrogen peroxide become progressively more active and have to be treated accordingly. Perhaps the extreme case of such activity is the use of hydrogen peroxide, at about 98 % strength, as a rocket propellant. This is what we call HTP. The HTP is shown a silver catalyst and decomposes to steam and oxygen, the heat given out speeding up the subsequent reaction. The hot gases are used to provide driving force for the rocket. One moral is clear at once : Wherever you have HTP you have to keep it away from anything that can catalyse decomposition.

A second use of hydrogen peroxide, usually at about 85% strength, is again in rockets and other prime movers. In this case the peroxide is used to provide oxygen to burn a carbon based fuel. This was used by the German submarine engineer Walter to make the Walter turbine, which was in turn developed by the Russians into the *Whale* class submarines used in the 1950's and by the British company Vickers Shipbuilding and Engineering in *HMS Explorer* and *HMS Excalibur*.

The turbine is based on the observation that if you place a hydrocarbon in a stream of oxygen rich gas, then the greater the proportion of oxygen, the lower the ignition temperature. In pure oxygen any slight friction will cause the hydrocarbon to go on fire. So in the Walter turbine, HTP and kerosene are mixed together in a combustion chamber where they ignite to burn very fiercely. The hot gases are fed into a turbine based propulsion system. This system was a highly energy dense system and submerged speeds of more than 30 kts for a 1000 te submarine could be obtained, in a *milieu* where a 25 kts sprint was thought of as being creditable. I am briefly repeating here material from an earlier chapter.

Gradually however peroxide fell from grace. There were continual doubts as to whether HTP could spontaneously detonate. The loss of the *HMS Sidon* was thought to be due to peroxide fuels in the torpedoes exploding. Since the torpedos in the moored submarine were not fitted with warheads, there does seem to be a good case for this supposition. The Walter turbines in *HMS Explorer* gained a reputation for being more trouble than they were worth; it is said that the crew referred to the boat as *HMS Exploder*, although what precisely caused the problem is not clear at this distance in time.

I am not aware of any explosions taking place in even 100% HTP under controlled conditions. I asked my chemical industry friends whether they could devise a method to make HTP explode, but I could not get them to come up with a method. I think it is a perfectly respectable industrial chemical if it is treated properly. However, hydrogen peroxide is a material which is dangerous to spill. As we've said it tends to ignite oily materials. It can also react with various organic materials to give products which, while harmless when wet, explode if allowed to dry out and then be subjected to friction. Even professional chemists are wary of peroxide solutions that might have become contaminated. A visiting American colleague of ours lost a hand while cleaning small glass flasks containing peroxide residues. He had all reasonable safety gear including a steel glove. (A tough guy this, he was back doing chemistry in a few weeks). So I think that while hydrogen peroxide itself is safe, when it's put into an industrial environment, it becomes difficult to manage.

In recent years a considerable amount of data on detailed experiments of hydrogen peroxide engines have become available. Much of this material refers to aircraft systems and rockets and does not appear in a published form. The information is in company reports that have been de-restricted because of their age. Gradually some of this material has come into my possession through various means. A different impression is given of the problems of handling HTP. The aircraft companies also had their problems with explosions in high pressure feed lines, but they took a much more enlightened attitude in dealing with it. They eventually got the problem under control by rigorously excluding anything that could rust. They used good quality stainless steels in both the motors and the storage systems, and they paid a lot of attention to cleanliness and good working.

There seems to me to have been a certain amount of mental weakness amongst the naval approach to HTP. It seems very surprising that organisations that routinely load up their vessels with tons of explosive and then transport it around the world in appalling conditions without any apparent trouble, cannot manage tin-pot stuff like HTP.

A further problem with HTP is that it is not widely available. For running submarines you have to use fuels that can be brought to the dockside in road tankers. Even in European countries you would have difficulty in arranging supplies and the situation would be more difficult in deep sea export markets. HTP is expensive mainly because it isn't widely used.

HTP is, I think, a fuel much better suited to unmanned submarines. It becomes progressively more difficult to put LOX tanks in small boats. The insulation round the LOX tank for example takes up a relatively higher proportion of the total available space. Small quantities of oxygen can easily be derived from HTP using some mild catalyst or heat.

Considerations in the use of LOX

LOX remains as the main candidate for the oxidant in manned submarines. It is widely accepted now that AIP systems will have a LOX tank holding 20-40 tes of liquefied gas at about 30 Bara. LOX itself is quite cheap, something like \$140/te in 1999. Certainly, it is cheaper than even tax free diesel fuel.

The main properties of liquid oxygen are shown in an appendix to this chapter. LOX is made in very large quantities by the fractionation of air and usually contains some argon. It can cause problems simply because it is cold. For example it can cause embrittlement of containers and tanks. Storage tanks have the inner holding tank made of austenitic stainless steel. Carbon steel becomes pretty useless at LOX temperatures.

In LOX storage tanks the inner holding tank is surrounded by an outer shell which is filled with a material called Pearlite and then evacuated. Pearlite is a rock found near volcanoes. It has gas trapped inside. What the manufacturer does is to grind the basic rock up to a standard size and then heat it to 800 °C when the granule swells up like pop corn.

LOX by itself cannot be made to explode. In a nice little South American war a few years ago a missile was seen to penetrate a LOX storage tank and fly out of the other side without the

warhead detonating.. This scenario is usually fatal for frigates which catch fire from the rocket exhaust, but in this case the LOX fell boringly to the floor. However LOX in combination with a few substances, notably carbon, LOX forms an explosive material that can be detonated by knocks. (This has always seemed rather strange to me; a good way to lessen the activity of explosives is supposed to be to cool them thoroughly).

The main practical hazard with LOX is that it can get out, form an oxygen enriched atmosphere, and so cause fires. The fires occur because as the proportion of oxygen in the atmosphere goes up, the energy to cause ignition, particularly with hydrocarbons, goes down. Going from the normal 21 % O₂ to 100 % O₂ lowers the ignition energy by a factor of about 100. Increases pressure makes this effect worse. Going from 1 Bar to about 20 Bars reduces the ignition temperature by about half. Higher pressures seem to have no more effect. What happens in practice is that in an O₂ rich environment, bits of grease lying on the floor will go on fire if you stand on them. Nevertheless, the problems with by-products are vanishingly small when seen against the backdrop of HTP.

Some metals will burn in oxygen where they won't burn in air. Gold and silver can't be ignited. Copper and nickel alloys are very difficult to ignite so that bronzes are used for pumps and valves. Although stainless steels are used for tanks, they are not suitable for valves as they can be ignited.

Some of the physical properties of saturated oxygen are shown in Appendix B, and from the figures it can be seen that the LOX is probably going to be held in the range 20 to 40 Bara. The higher the pressure you are dealing with the less the density of the liquid and so the tank tends to be slightly bigger. French engineers, developing MESMA, reported that a tank designed to hold LOX at 60 Bara would hold about 20% less LOX than one designed to hold the liquid at 20 Bara. In the absence of other considerations you would expect a pressure like 30 Bara to be specified.

Design of LOX tanks, especially for submarines

Some designers favour having horizontal LOX tanks, others favour a vertical arrangement. In both cases there are usually two heat exchangers. One is used in a circuit close to the tank to keep up the pressure in the ullage by evaporating small quantities of liquid. Gas is normally supplied to the prime mover from the liquid phase, the liquid passing over an evaporator which both vapourises the LOX and raises its temperature.

Two matters have led one to consider higher pressures. Firstly there has been a suggestion (not from a liquid oxygen manufacturer, I should add) to store the oxygen as "supercritical oxygen". This means that the oxygen is held in a small region which I have sketched, just above, but near to, the critical point at about 55 Bara. The material is quite dense here, but as it isn't quite a liquid there is no surface and sloshing of the liquid with boat movements can be avoided. At least that is the theory. In practice it would be very difficult to hold the oxygen in this state. Examination of the P-V-T diagram soon shows you that small changes in the conditions of storage lead to large changes in pressure. So far as I know, no-one at the moment is trying to carry out this unwise idea.

A second consideration which is militating for higher pressures in LOX tanks, is the supposed need to be able to vent the oxygen overboard in the case of an emergency such as a fire. There appear to be two ways you might do this. One is to pump the LOX straight overboard with a centrifugal pump. In this case the LOX tank need never be at sea pressure. A second way of venting is to blow boat's compressed air into the ullage and blow the tank this way. In this case you would have to have the tank stressed to sea pressure which for most non-nuclear submarines means no more than 35 Bara. This form of venting is becoming progressively less attractive as submarines are designed to approach a 500 m diving depth.

You cannot insulate a liquid gas tank perfectly. There is always some leakage of heat into the interior of the tank. This in turn causes evaporation of the contents, which in turn causes the pressure to rise. The manufacturer of the tank will supply the heat leak figures to the customer for a given tank, but for approximate estimation purposes you can take the daily leak rate as being about 0.2 % of the tanks capacity up to 40 tes and 0.1 % for tanks over 100 tes. Better estimates can be made up into a little estimating program by study of the data in Barron's book (ref 1)

On a land based tank, you have a pressure relief valve which lets off some of the pressure from time to time and you can do this in a submarine if you want. Perhaps a better arrangement would be to have a relief valve set high say at 35 Bara, together with a control room operated bleed. The tank pressure would be shown in the control room, and the officers might have a policy to release excess gas if the pressure got above 28 Bara. Then the boat's officers would not be faced with a sudden gout of escaping gas at some critical point of a mission.

It must be remembered, in considering the LOX tanks, that once you have such a tank in the boat it is almost certain that the oxygen for the crew to breathe will come from the LOX tank. When you have worked out your leak rate then, the first thing to do is to see if the crew can breathe the gas. As a round figure one inactive man will consume about 1.0 Kg of oxygen per day and maybe 2.5 Kg if he's working hard all the time.

If the crew can't breath all the gas that is created by the heat leaks into the tank, you still don't need to have a vent if don't want. You can put a refrigerator on top of the LOX tank and re-liquefy the escaping gas. Such refrigerators are used a lot in the chemical industry and are usually called "Philips Head Refrigerators". They are essentially Stirling engines driven backwards. For the quantities we are talking about they are quite small and compact, but they tend to be expensive because they are custom built.

The Walter Turbine re-visited

The Walter turbine involved mixing oxygen and steam derived from HTP with a hydrocarbon fuel. The HTP caused problems then, and would not be considered nowadays except for use in an unmanned submarine.

I can't see why we can't think of a Walther system in which the oxygen is derived from a LOX tank. I haven't tried to work out the details, but perhaps a reader might like to send some arithmetic.

APPENDIX A - VARIOUS WAYS OF MAKING OXYGEN

Storage of compressed oxygen in cylinders	
Evaporation of liquid oxygen (LOX)	
Decomposition of hydrogen peroxide	Dangerous side products can form
Items below here involve some sort of chemical reaction	
$\text{KNO}_3 + \text{Heat} = \text{NaNO}_2 + \text{O}_2$	
Distillation of air	Obviously you can't do this in a closed vessel like a submarine
$\text{Na}_2\text{O}_2 + \text{CO}_2 = \text{Na}_2\text{CO}_3 + \text{O}_2$	
$\text{NaOH} + 1300 \text{ degC} = \text{Na} + \text{H}_2 + \text{O}_2$	
$\text{KO}_2 + \text{H}_2\text{O} = \text{KOH} + \text{O}_2$	Used in experimental unmanned vehicles and weapons
$\text{KIO}_3 + 560 \text{ degC} = \text{KI} + 3\text{O}_2$	
$\text{CaO} + \text{Cl}_2 + \text{red heat} = \text{CaCl}_2 + \text{O}_2$	
Bleaching powder + Co salt = $\text{CaCl}_2 + \text{Ca}(\text{OH})_2 + \text{O}_2$	Reaction in warm suspension
$\text{BaO}_2 = \text{BaO} + \text{O}_2$	Starting point for oxygen candles
$\text{ZnO} + \text{Cl}_2 = \text{ZnCl}_2 + \text{O}_2$	
$\text{ZnSO}_4 + 450 \text{ degC} = \text{ZnO} + \text{SO}_2 + \text{O}_2$	
$\text{HgO} = \text{Hg} + \text{O}_2$	
$\text{PbO}_2 + 300 \text{ degC} = \text{PbO} + \text{O}_2$	
$\text{F}_2 + \text{H}_2\text{O} = \text{HF} + \text{O}_2$	
$\text{Br}_2 + \text{H}_2\text{O} + \text{light} = \text{HBr} + \text{O}_2$	
$\text{Pb}(\text{NO}_3)_2 + \text{heat} = \text{PbO} + \text{NO}_2 + \text{O}_2$	
$\text{KClO}_3 + \text{MnO}_2 = \text{KCl} + 3\text{O}_2$	
$\text{NaClO}_3 + \text{MnO}_2 = \text{NaCl} + 3\text{O}_2$	
$\text{Ag}_2\text{O} = \text{Ag} + \text{O}_2$	
Liquid ozone	Explodes in presence of organics
"Salcomine" = bis-salicyl aldehyde ethylene diimine-cobalt	Absorbs 4.5 % of their own weight as oxygen
Oxygen dissolved in a perfluoro liquid	1 kg of O_2 needs 1750 L of PFL
Lithium perchlorate LiClO_4	Stated to contain more oxygen per unit volume than LOX. See http://www.arl.psu.edu/techareas/altenrgsrcs/altenrgsrcs.html

OXYGEN FROM SEA WATER

In addition to the various leads mentioned above, there is the question that never seems to go away “Can you get oxygen out of the sea water ?” . Leaving aside the weak minded brethren who think you might be able to decompose the water somehow, there is the question of the oxygen dissolved in the sea water or otherwise held there. Now, the short answer to the question is “No, because there is not enough dissolved oxygen”. This can be illustrated very well by the case of the Closed Cycle Diesel which not only breathes oxygen, but has water brought to it to dissolve away the waste carbon dioxide.. The diesel needs about 1.50 moles of oxygen per second. 50 litres/sec of water are brought to the engine (to dissolve the CO₂) and they bring with them about 0.016 moles of oxygen/sec.

Notwithstanding this typical arithmetic, there have been a number of proposals in recent years for artificial gills. The ones I have seen have all had the same error in the calculations : They have neglected to add in the power needed to pump the (vast amount) of water past the gills. The power needed is far more than could be supplied by an engine using all the oxygen that the gill supplied.

Nevertheless, every few years there is a paper on the idea. Use it for an exercise in arithmetical assassination.

APPENDIX B - PROPERTIES OF SATURATED OXYGEN

Molecular weight = 32 grams

Triple temperature= 54.35 °K

Critical temperature= 154.77 No liquid exists above this temperature

Critical pressure = 50.8 Bara

Critical volume=78.8 ccs/mole

By “saturated” we mean that there is both gas and liquid phases present.

T ° K	P Bara	Liquid density kg/litre or gm/cc	Heat of vapourisation kJ/mole
54.35	0.0015	1.288	7.638
55	0.0018	1.285	7.628
60	0.0073	1.265	7.561
65	0.0233	1.246	7.405
70	0.0624	1.225	7.293
75	0.1448	1.209	7.226
80	0.3003	1.183	7.050
85	0.5677	1.16	6.931
90	0.9943	1.136	6.800
90.18	1.0133	1.135	6.793
95	1.634	1.112	6.649
100	2.547	1.086	6.489
105	3.749	1.059	6.3072
110	5.443	1.030	6.102
115	7.559	1.002	5.843
120	10.21	0.969	5.600
125	13.28	0.934	5.302
130	17.44	0.899	4.953
135	22.19	0.854	4.55
140	27.82	0.808	4.07
145	34.45	0.750	3.48
150	42.23	0.672	2.685
154.77	50.87	0.406	0

These numbers are based on a table in “Chemical Engineers Handbook” Sixth edition Eds Perry and Chilton McGraw-Hill ISBN 0-07-Y66482-X but some factors of 1000 had to be added to their values.

APPENDIX C - TYPICAL SIZES OF LOX TANKS

(1) Tank used in the German submarine “Ex-U1” for sea trials of a Fuel Cell system and for a Closed Cycle Diesel

Length with all fittings	3700 mm
Length without fittings	3100 mm
Outer diameter	1300 mm
Inner diameter	950 mm
Inner volume	1560 litres
Max fill up percentage	95
Max pressure of inner tank	22 Bara
Wt including LOX	6.0 tes
Wt less LOX	4.5 tes

This is not a particularly good example. We are aiming to have about 50 % of the full weight as being liquid oxygen

(2) Storage tank supplied by British Oxygen Ltd

Length with all fittings	7400 mm
Outside diameter	2600 mm
Weight empty	13.5 tes
Weight full	29.0 tes

A better tank since 45 % of weight is LOX

(3) Barron gives the following dimensions for a larger tank than might appear in a submarine.

Length with all fittings	17.6 metres
Outside diameter	3636 mm
Volume of LOX	106 m3
Leakage per day	about 70 kg

HYDROGEN PEROXIDE

The density of pure hydrogen peroxide is 1414 Kg/m³.

REFS

R. F. Barron "Cryogenic Systems" OUP (1985) ISBN 0-19-503567-4

P. R. Stokes "Hydrogen Peroxide for Power and Propulsion" Read at the Science Museum, London 14 January 1998. Downloaded from w.ee.surrey.ac.uk/SSC/H2O2CONF/PStokes.htm

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