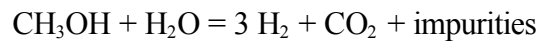


## CHAPTER 4 - FUEL CELLS WITH REFORMER

We have seen that the storage of hydrogen has some difficulties associated with it. The question therefore arises as to whether we can do in a submarine what we do on land, and that is to make the hydrogen from some easily storable feedstock. Since the hydrogen is probably going to be fed to a PEM fuel cell some considerable purification will have to be applied to the product.

Although there are various ways of making hydrogen from different feedstocks, the only one that seems reasonably practical is a process called steam reforming. This is one of the earliest industrial processes and in its modern guise involves reacting a fuel with steam over a catalyst at a few hundred degrees to get a mixture of carbon dioxide and hydrogen plus a small amount of impurities of which carbon monoxide is usually the most plentiful.

At the moment only three fuels are under active consideration : methanol, ethanol and diesel fuel. In the case of the methanol the overall reaction is



Operators of submarines would like to have a really convincing reformer of diesel fuel, but it seems as though this will be much more difficult to achieve than a methanol reformer. In the first place the reaction temperature to reform diesel fuel seems to be quite high, certainly over 500 °C and the presence of sulphur in the fuel causes difficulties down stream.

Even if submarines don't normally carry methanol, it is nevertheless widely available and easily transportable to the dock side. It has the disadvantage of being rather toxic and we are told that the French engineers preferred to move to the less poisonous ethanol to fire their MESMA combustion chamber. On the other hand industrial methanol is usually very pure and is free of sulphur. The burden of thought then, is to see if a methanol reformer could be constructed which might work in a submarine.

I think there was some idea in the early stages that you could just go along to a contractor and buy a reformer more or less off the shelf. This idea revealed a rather basic difference between what is needed for submarine chemistry and what happens behind the wire fence of an industrial complex. Chemical manufacturers sometimes make a lot of fuss about how highly automated their projects are, and a bystander is left with the impression that chemicals are somehow made without human intervention on automatic machines.

I worked in chemical plants for a long time, and what is meant by automation in my experience is that the plant will be able to get through the night shift. After this an instrument artificer will go round and put right the instruments that failed since last evening. The idea that a naval officer should be able to press a button and switch on a completely autonomous plant that will then operate without attention, and produce a chemical, for three weeks has little realistic precedent in industrial chemistry.

Land based chemical plants have several generic faults when seen from the point of view of installation in a submarine. (1) Firstly the pipes and joints leak. Of course, they only leak a bit,

and they often only leak innocuous things like steam or dirty water or fairly non toxic chemicals. Some of these chemicals are metabolised by bugs of one type or another. The plants are on vast sites and a bit of a leak is never going to harm anyone. Leaks in an enclosed space like a submarine cannot be tolerated; even if the re-circulating atmosphere is not made toxic, traces of chemicals can easily overwhelm the scrubbing systems. (2) Chemical plants use pneumatically operated valves often without feedback. These valves have a high rate of malfunction on a lowish sort of level. Mostly they can be restored to some sort of function by cleaning bits of them or simply giving them a kick, but this is not on the script for a submarine. (3) Chemical plants have unwanted by-products. Sometimes these can be sent along a pipe to some other process entirely but often they are either burned or thrown on to a tip. Mostly you can't do either of these things in a boat. (4) Chemical plants can give out lots of low grade heat. On land this just goes into the environment. In a submarine, you have to get rid of it.

Essentially, for submarine purposes, we have to make a chemical plant that is completely enclosed and is highly controlled. Only a few years ago I would have been doubtful that the matter could be managed without a large expenditure. The technology does exist to control chemical plants, and leaving aside the control systems in aeroplanes, the sort of gear you want is seen to its best effect in Formula One racing cars which are highly controlled and highly monitored and are highly reliable. What must be done is to study how the chemists do reformation, and then to go away and do it properly.

#### *The basic reformer process*

I have based this discussion on the operation of a methanol reformer, since I have hands on experience of these units. I have also added some of the calculations in an appendix to the chapter.

In a methanol reformer, you start with a tank of methanol water mixture which is prepared before hand. The precise mixture is quite important to the operation of the reformer and it is as well to take time in its preparation. Certainly in a submarine, we will not be talking about mixing pumps and the like.

Fuel mixture is pumped towards the vaporizer, where enough heat is applied both to vaporize the mixture and raise it to the temperature needed in the reaction chamber, which is likely to be around 400 °C.

The vapor then enters the reactor chamber where it is brought into contact with a catalyst. The detailed means by which this is done is one of those things that is always "under review". You have to balance the need to provide as many catalyst sites as possible ( which means having a powdered catalyst) with the need to let heats of reaction enter or leave the reaction chamber. Heat transfer is usually not good in powder so there are compromises to be made.

Finally, the reaction products leave the reformer and proceed in the direction of the fuel cell. These products cannot be allowed to enter the fuel cell directly at this stage because some purification is required. It is very rare that a chemical reaction will just produce the desired product and nothing else. For over a century chemists have, as a matter of course, quoted the

“yield” of the reactions they have developed. Yield is the weight of the desired product divided by the weight of all the products. You never have 100% yield.

Sometimes you can be lucky and have byproducts that are not harmful to the downstream processes. Often water and non toxic gases can be byproducts of processes and they can easily be got rid of. In our case the main byproduct is carbon monoxide which will damage and ultimately destroy a PEM fuel cell except in very small quantities indeed.

It would appear to be difficult, in the present state of knowledge, to make a reformer whose gaseous products can be directly fed to a fuel cell. Figure REFORMER 1 illustrates this.

There are several possible ways out of this dilemma. You can try to develop fuel cells so that they will work on the reformer gases, you can try to react the unwanted chemicals in a second, separate, reaction or you can try to remove the unwanted material by some other means.

It is by no means unreasonable to think that a suitable fuel cell with a catholic taste in gases might appear. So long as there is a commercial impetus behind the development of fuel cells, new ideas will gradually appear. However in fuel cell studies, there seems to be a long time interval between thought and saleable deed and we must look to other methods to achieve the end point.

There are many so called “oxidizing catalysts” which will enable CO to be reacted in the presence of oxygen to form CO<sub>2</sub>. Unfortunately, these oxidizing catalysts also oxidize the hydrogen product to water, and so this is not much good; it is throwing out the baby with the bath water. What we want is a selective oxidation. The chemists are quite hopeful about being able to convert CO to CO<sub>2</sub> without yet converting H<sub>2</sub> to H<sub>2</sub>O. I am less sanguine. I think it will be difficult to manage this in the context of a closed plant inside a submarine.

Furthermore, you have to think what will happen if the process goes wrong for a few seconds as it might do at start up or shut down, or when some power change was called for. Perhaps then an excess of CO would flow into the fuel cell. Since the CO is in most cases a cumulative poison, a small departure from the norm seems set fair to destroy the fuel cell.

You could try to absorb the carbon monoxide in an absorbent. For example you could pass the gases over iron filings. The devil is in the detail. It is actually rather difficult to find a workable system. Either the absorbent reacts with the hydrogen, or it has to be heated too much or the sheer volume is too large, or you can't absorb quite enough of the CO to get down to the (very low) level that the fuel cell will tolerate. Thus far a suitable system has not been devised.

If, for some reason, there is no choice but to try to purify the reformer stream and feed it directly to the fuel cell, then one needs to join the purification chemists and the fuel cell manufacturer into a single team. Otherwise, when things go wrong, each will blame the other.

You would really like to have a membrane that would prevent the CO passing but let everything else through. Once again there isn't a membrane with quite these properties, but there is something even better. There is a membrane that will let hydrogen *and only hydrogen* through.

Although the process has to be paid with by an energy input into the system, the hydrogen produced is one of the most astonishingly pure products that is found anywhere in chemistry.

The idea is based on the fact that the metal Palladium absorbs hydrogen selectively. It absorbs so much that you can actually see the sample expand. It took some long time before this basic observation could be converted into a workable membrane. The trouble was that the large strains caused by absorption of the hydrogen would cause cracks and holes to appear in pure palladium foils. Eventually a man called J B Hunter Ref (1) discovered that a 40 % silver 60 % Palladium alloy suffered much less in the way of strain cracking than did pure palladium. If, further, the material is fabricated into tubes about 1 mm diameter and impure hydrogen introduced on the inside, then the material will act as pretty near perfectly selective membrane and will have a long life before failure.

There is another good thing about these membranes. They do not fail catastrophically at the end of their fatigue life. Rather they start to slightly weep. Since there is nearly always water in the impure hydrogen source gases, the manufacturers of these membranes put a hygrometer down stream of the membrane. If everything is working properly no water will go through the membrane and the hygrometer will be hard against the left hand stop. If the hygrometer moves at all, damage to the membrane is taking place and you can switch off in good time and do something about it.

A downside of these membranes is that sulphur quickly damages them, because sulphur reacts with silver. This means in practice that you can not use such membranes to purify a hydrogen stream derived from reformed diesel fuel. Diesel fuel always contains sulphur. "Low sulphur", which the diesel fuel manufacturers are always boasting about, does not imply a low enough level to protect Pd-Ag membranes.

More hydrogen passes at higher input pressures, so in practice you have to arrange matters so that the reformer gases are both hot and at high pressure. You are typically working the membrane at about 20 Bara and 400 °C. This can be an acceptable price to pay for being sure you can keep your valuable fuel cell in a pristine condition.

Designers working with these membranes would like to keep the inventory of materials as low as possible, both Pd and Ag are expensive. You can thin the membranes to some extent (and so lessen the cost) by noting that the amount of hydrogen that passes through the membranes depends on the difference in *partial* pressure of hydrogen. You can have 40 Bara of hydrogen on one side and 3 Bara on the other and a certain flow will result. However, your tubes have to be thick enough not to burst under an internal pressure of 37 Bar. What you can do, is to arrange matters so that on the delivery side, there is 3 Bara of hydrogen and 37 Bara of argon. Now you still have the desired hydrogen gradient, but the mechanical forces across the membrane are zero.

*(We deduced this idea during our work on a contract at CDSS Ltd, performed the necessary experiments, submitted a patent application and were then infuriated to find a very similar patent already extent assigned to Engelhardt Industries. Nothing new under the sun, they say.)*

The figure REFORMER 2 shows a layout sketch of a one version of reformer plus membrane device, together with the heat fluxes in and out. This particular cycle was devised at Kettering in 1991 and is called "The Excess Hydrogen Cycle". It does not use a pressure balanced membrane, the quantities are shown for a small test rig. There are doubtless other ways of managing matters

In the arrangement shown in the figure it can be seen that there is a noticeable amount of hydrogen and CO that do not pass through the membrane. This gas is mixed with oxygen and to burned to heat up the reformer and the membrane system. It is quite satisfying to burn the waste hydrogen as part of the process. You certainly don't want to be left with unusable hydrogen that has to be thrown overboard. It would be bad for the efficiency.

This sort of diagram is very typical of the doodlings that chemical engineers use to figure out how to get their plants to work. Once they've got the heat figures they look around to see how they are going to deal with them. Often heat from one plant will be fed to a neighbor, and excess heat might go into a cooling tower or into a water course.

In a submarine, the designer does not have such a wide range of options. He must, more or less, make a plant that is self contained. Some heat can be allowed to go to the sea, but not so much that the submarine might be detected. The designer will note that heat thrown away represents a loss of efficiency and will try to use what high grade heat he has.

While a hydride fuelled fuel cell does not put any waste gases overboard a fuel cell powered by a reformer certainly does; there is a mass of carbon dioxide and probably some CO, O<sub>2</sub> and hydrogen that must leave the boat somehow.

The Canadian navy are at the time of writing developing a reformer to supply hydrogen to a Ballard fuel cell. I think the Canadians, having a world class fuel cell manufacturer in their country in Ballards, are keen to exploit this advantage. The Canadian have recently taken delivery of four Upholder submarines which were built by Vickers for the Royal Navy. Shortly after the submarines went into service the government decided that it couldn't afford them and these nearly new submarines were put up for sale. ( This sudden *volte face* by the British Government is not so silly as it may seem; the change of policy took place around the time of perestroika).

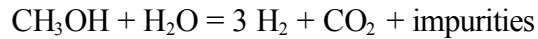
It is assumed that the Canadians will eventually cut one of the Upholders and put a fuel cell plug in it. I believe that there a number of questions still to be resolved about the design of the reformer and the operation of the system as a whole. Original plans to catalytically oxidise away the unwanted carbon monoxide by products have seemingly been shelved and the designers have gone for a palladium membrane system, returning the offgases to the burner. I do not know what plans the Canadians have for disposing of the carbon dioxide.

I still have great reservations about installing a reformer in the body of the submarine. It seems to me that a fractured pipe could flood the compartment with toxic vapours which might then be carried to other parts of the boat. I don't say that it can't be done, but at the moment I am quite

unclear about how the safety audit can be managed. I think it is significant in this regard that the Germans have put their hydrogen and even their oxygen outside the pressure hull.

## APPENDIX - HEATS OF REACTION

The reformer reaction is



We'll ignore these impurities and work out the heat needed to run this reaction. You look up the heats of formation of the reactants in a table and you subtract the RHS figure from the LHS figure. If the answer is negative, heat is being evolved; if positive you need to put heat in

Thus

$$-48.08 \quad -57.08 \quad 0 \quad -94.05$$

$$\text{RHS} - \text{LHS} = -94.05 + 105.12 = + 11.07 \text{ kCal}$$

must be put in to convert one mole of methanol to hydrogen and carbon dioxide.

This is not all, we have to heat up the methanol and water to their boiling point. To do this you look up their specific heats and multiply by the temperature rise. Then you have to add in the latent heat of vaporisation, and finally again the the heat to raise the vapours to 300 °C and the pressure to 20 Bara or whatever. This actually comes out to be quite a large number, some 28.55 kCal/mole of MeOH.

Thus the total energy needed for the reforming operation is 39.76 kC per mole of MeOH reformed.

## APPENDIX – PALLADIUM SILVER MEMBRANES

At the moment, the most common configuration of the membranes is a blind end tube 660 mm long, 1.6 mm outside diameter wall thickness 75 microns; surface area  $3 \times 10^{-3}$  sq m. Mixed gases are applied to the inside of the tube at about 20 Bara.

Under these conditions, with the hydrogen being present at about 70-75 molar percent the tubes pass approximately 0.08 (moles of hydrogen)/second per sq metre at 300 °C.

The cost of a membrane system was something of the order of \$3500/kW in year 2000.

You may think that a blind ended tube is a strange arrangement for a continuously operating process. Originally straight through tubes were used rather like boiler tubes, but they kept failing for no immediately apparent reason. The reason for the failures can be seen by observing the behaviour of a bunch of blind end tubes in actual operation. Astonishingly the tubes move about. This is probably something to do with asymmetric hydrogen concentrations in the walls. In a blind end arrangement the tubes are reasonably free to move as they want to, but in a boiler tube system, there is nowhere for the tubes to go, and the forced strain induces too high stress levels leading to catastrophic fracture.

Having said all this, if I were making a new system I would be thinking of rolling the tubes in to a helix, or making a corrugated plane membrane. Anything to get a counterflow system.

## REFERENCES ON Pd/Ag MEMBRANES

- J B Hunter US Patent 2 773 561 Dec 11 (1956)
- F A Lewis "The Palladium-Hydrogen System" AP (1964)
- J E Philpott Platinum Metals Review Vol 20 No 4 p110 (1976)
- A S Darling Platinum Metals Review Vol 2 p16 (1958) and UK Patent 827681 (1962)
- P M Roberts and D A Stiles Platinum Metals Review Vol 13 No 4 p141 (1969)
- D E Stiles and P E Wells Platinum Metals Review Vol 16 No 4 p124 (1972)
- A G Knapton Platinum Metals Review Vol 21 No 2 p44 (1977)
- K G Musket Journal of the Less Common Metals Vol 45 No 2 p173 (1976)
- DT Hughes, J Levans and I R Harris *ibid* Vol 76 p119 (1970)

*Last revision Friday, 11 November 2005*