SOLID OXIDE FUEL CELLS FOR MARINE APPLICATIONS

BY

V. W. ADAMS, BA, MPHIL, CPHYS, MINSTP
(Sea Systems Controllerate, Bath)

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ABSTRACT

This article considers the problems of replacing marine diesel-electric generators with solid oxide fuel cell systems. Advantages and disadvantages of employing fuel cell systems and the problems of using middle distillate diesel fuel such as Dieso (e.g. tolerance to sulphur, desulphurization and reforming*) are considered. Projected system, volumes, fuel consumption and costs are compared with those for diesel engines.

Introduction

Recently, renewed interest has been shown in the use of fuel cell generators for marine applications[1,2,3,4]. Summaries of these papers have been given in this *Journal*[5]. Experimental work for marine applications has been reported using either solid polymer or molten carbonate electrolyte fuel cells for surface ships[2] and solid polymer for submarines[4]. This article addresses a longer term possibility, i.e. the future use of the solid oxide fuel cell (SOFC) type for marine auxiliary power and low to medium (approximately 1MW to 2MW) power propulsion applications and higher powers using reformed diesel fuel.

Advantages

The main advantages of replacing diesel-electric generators with fuel cell systems for auxiliary power supplies in marine applications are high efficiency resulting in greater endurance, lower noise output, lower running costs, lower maintenance costs, the generation of d.c. supply for low to medium speed electric propulsion motors, and reduced harmful emissions from the exhaust. Advantages of using SOFCs compared with other fuel cell types are the possibility of direct reforming* of diesel fuel and the elimination of noble metal catalysts.

Disadvantages

The main disadvantages are the very high operating temperature (900–1000°C), the need for d.c. to a.c. conversion for auxiliaries, the need to operate on middle distillate diesel fuel (i.e. gas oil) with currently accepted levels of sulphur, new development costs, and that the development of SOFCs is less advanced than other types of fuel cell.

Fuel

It would be very advantageous if marine fuel cells could operate on reformed diesel fuel since it is likely that, in the foreseeable future, ships will continue to use this fuel for main propulsion. Integrated or 'internal' reforming of diesel fuel is a possibility using SOFCs, and their tolerance to the sulphur content in fuels is an important factor. The presence of sulphur is equally critical for steam reforming catalysts.

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*Reforming is a process that produces a hydrogen-rich gas from hydrocarbon fuels.

TABLE I—*Characteristics and approximate chemical composition of diesel fuels (from Pedley*[6]*)*

1: Straight run distillate (Middle East)
2: Straight run distillate (North Sea)
3: 10% Cat.-cracked stock, 90% North Sea straight run distillate
4: 10% Cat.-cracked stock, 90% North Sea straight run distillate

	1	*2*	*3*	*4*
Density at 15°C	0.84		0.86	0.86
Sulphur* % mass	1.07	0.33	0.16	0.28
Hydrogen content & weight	13.3	13.03	12.96	12.76
Aromatics* content % weight	33†	30.75	31.3	34.6
Aliphatics* content % weight	67	69.25	68.7	65.4

* Compounds which could be used for a theoretical representation of the main chemical classes present in diesel fuel are:

Aliphatics:	Hexadecane $C_{16}H_{34}$
Monocyclic aromatics:	Xylene C_8H_{10}
Bicyclic aromatics:	Napthalene $C_{10}H_8$
Sulphur compounds:	Dibenzothiophene $C_{12}H_8S$

†33% = 18% single ring aromatic:
6% napthalene plus benzothiophene
2.5% dibenzothiophene
6% higher aromatics

Present military specifications for liquid hydrocarbon fuels allow sulphur impurity levels which would cause poisoning of catalysts in fuel cells. The Defence Standard for NATO F-76 fuel (Dieso F-76)[7] gives an upper limit of 1% by mass for sulphur. However, the RN accepts an upper limit of 1.5% by mass for commercial marine gas oil when Dieso is not available, although the specification offered by the suppliers often says nothing about the sulphur content.

For environmental reasons there is an urgent need for legislation on the sulphur content in commercial fuel and diesel exhaust emissions. Typically, about 50% of the particulate exhaust from diesel engines consists of soot and about 25% consists of sulphur compounds and water. The remainder are unburnt fuel, lubricating oil and nitric oxides. The sulphur content and approximate chemical composition of four different fuels are given in TABLE I. European legislation for land gas oil will probably reduce sulphur content to 0.2% by mass in 1993 and similar legislation for marine fuels may follow.

Tolerance to Sulphur

It is claimed by Westinghouse[8,p. 584] that the SOFC anode (fuel electrode) can be made with a high tolerance to sulphur; the presence of 50 ppm by volume of hydrogen sulphide in the fuel lowers the operating voltage by only about 5%, causing no damage to the cell. At 1000°C, nickel or cobalt cermet anodes have been assigned[9] sulphur tolerances of 90 and 200 ppm by volume or about 0.021% and 0.047% by mass, respectively. These tolerances are between one and two orders of magnitude lower than the worst accepted sulphur levels in marine fuels. They are, however, one or two orders of magnitude higher than sulphur tolerances for other types of fuel cell, and permit the use of high-temperature methods of sulphur removal, which are more efficient than, for example, the low-temperature methods required by molten carbonate fuel cells to lower the sulphur content in this case to less than 1 ppm by volume[8,p. 585].

Unless legislation causes a change to use low levels of sulphur in fuel, the above tolerances require a sulphur removal system to be integrated with the fuel reformer. Based on a fuel cell sulphur tolerance of 0.047% by mass, a sulphur content in fuel of 1.0% to 1.5% by mass and a diesel fuel consumption of 0.16 kg/kWh (see later), this would mean the removal of between 1.0 and 1.7 tonnes of sulphur per MW of power generated during a typical ship mission of thirty days. This could be reduced to less than 200 kg for fuel with a sulphur content of 0.2% by mass.

Desulphurization

Almost all sulphur in liquid hydrocarbon fuels is present in the form of thiols (based on C_4H_8S), sulphides and disulphides, and thiophenes (based on C_4H_4S). Thiols and disulphides are generally less stable and easier to remove, and hence the effectiveness of a desulpherization catalyst is usually judged by its ability to remove the organic sulphides and thiophenes. The catalytic decomposition of organic sulphur compounds results in the formation of hydrogen sulphide and unsaturated hydrocarbons. However, the thermodynamic equilibrium is usually unfavourable for such reactions below 400°C and higher temperatures can be detrimental to catalyst life.

In practice, hydrodesulphurization is usually preferred where catalytic decomposition occurs in the presence of hydrogen at temperatures between 300°C and 400°C, resulting in the formation of hydrogen sulphide and saturated hydrocarbons with more favourable thermodynamic equilibrium. Often the presence of steam is required to suppress carbon formation and fouling of the catalyst bed. Typical hydrodesulphurization catalysts are a sulphided form of zinc, iron, cobalt, nickel, chromium, molybdenum or tungsten. Retention of the hydrogen sulphide is needed and can be achieved by:

(*a*) a two-step process in which a catalyst is either mixed with an absorbing material or followed by a separate absorption step (zinc oxide or ion oxide is usually the absorbing material in both cases);

(*b*) a one-step process using a material (e.g. nickel) absorbing the hydrogen sulphide (this usually requires the presence of water and is only suitable for steam reforming processes).

Sulphur removal at high temperature is preferable[8, p. 461] because of thermodynamic efficiency and ease of integration into a high temperature fuel cell system. Iron oxide-silica absorbents at about 650°C have been used to remove sulphur levels from about 6000 ppm by volume to about 200 ppm in coal synthesis gas[10].

Fuel Cells and Fuel Consumption

The possibility of internal reforming of fuels with high temperature SOFCs and their moderate tolerance to sulphur make them a more attractive option than other types of fuel cell, which require external or integrated reformers and are intolerant to sulphur. Information on laboratory SOFCs[1,2,11] indicates that, at lower powers, there would be no increase in system weight and size when compared with diesel-electric generators[12] (FIGS. 1 and 2). Approximate

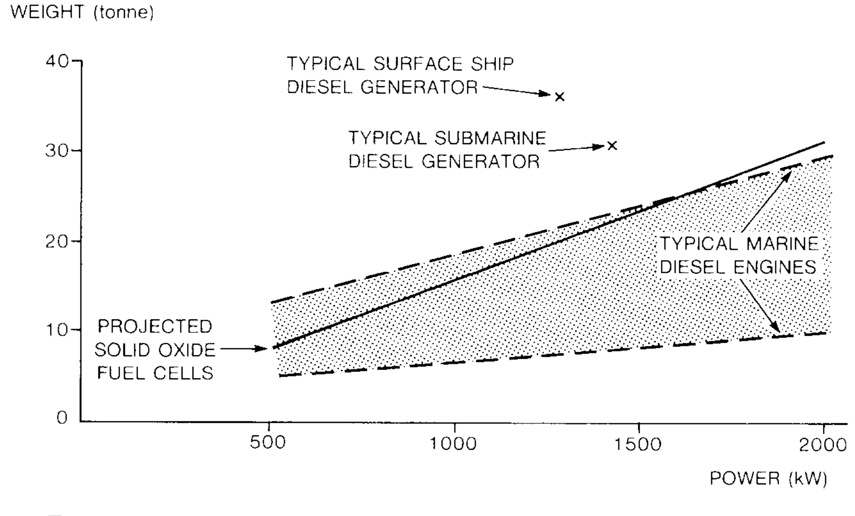

FIG. 1—ESTIMATED WEIGHT AGAINST POWER (LOW POWER UNITS)

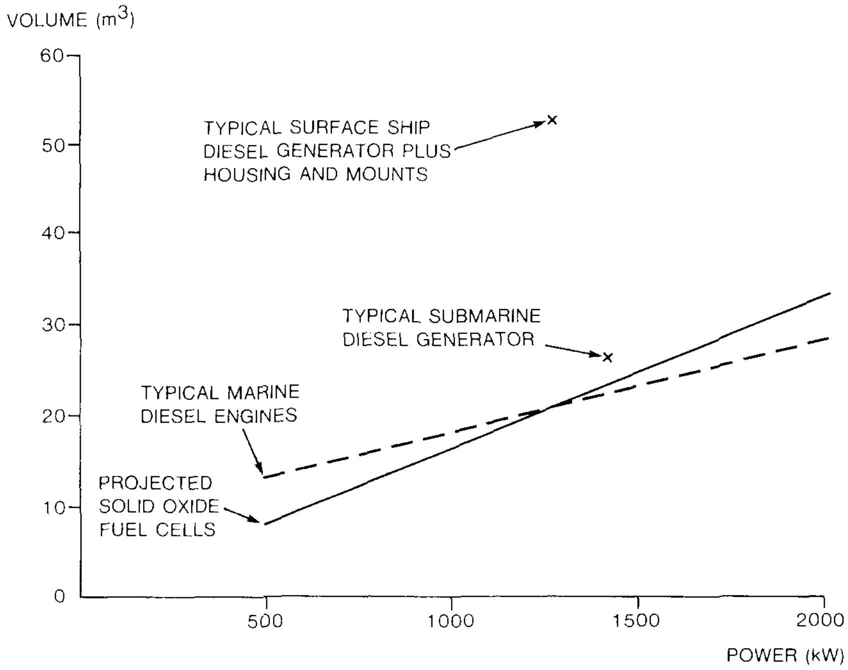

FIG. 2—ESTIMATED VOLUME AGAINST POWER (LOW POWER UNITS)

weights and volumes for higher powered diesel engines, gas turbines[12] and SOFCs are shown in FIGS. 3 and 4, but those for diesel engines and gas turbines do not include the substantial weights and volumes required for the electrical generating components or gas turbine air intake and exhaust ducting. Values for typical surface ship and submarine diesel-electric generators are however, given for comparison.

One design of cell (monolithic [8,p. 607]) has the potential for much greater power densities and lower weights (320 kW/m.^{3} and 1 kW/kg) than those indicated in FIGS. 1 to 4.

SOFCs can utilize the oxygen from an air supply and the hydrogen and carbon monoxide from a reformed fuel, with steam as a by-product. Oxygen ions formed at the cathode,

$$O_2 + 4e^- \rightarrow 2O^{2-},$$

migrate to the anode through the electrolyte where they react with the hydrogen fuel to form water vapour and free electrons to the external circuit,

$$2H_2 + 2O^{2-} \rightarrow 2H_2O + 4e^-.$$

The carbon monoxide is also used as a fuel since, whilst there is some tendency for a shift reaction in the presence of water vapour to convert carbon monoxide to carbon dioxide and hydrogen,

$$CO + H_2O \rightarrow CO_2 + H_2,$$

it can also be used in a direct anode reaction to produce carbon dioxide and free electrons,

$$CO + O^{2-} \rightarrow CO_2 + 2e^-.$$

Catalytic effects are less important at the high operating temperatures of SOFCs and, in principle, fuels can be oxidized but there will be a tendency for them to crack, producing carbon and hydrogen,

$$C_nH_{2n+2} \rightarrow nC + (n+1)H_2.$$

In SOFCs, cracking can be prevented by steam injection and the net result is essentially internal reforming[8,p. 583]:

$$C_nH_{2n+2} + nH_2O \rightarrow (2n+1)H_2 + nCO,$$

followed by rapid oxidation of the hydrogen and carbon monoxide.

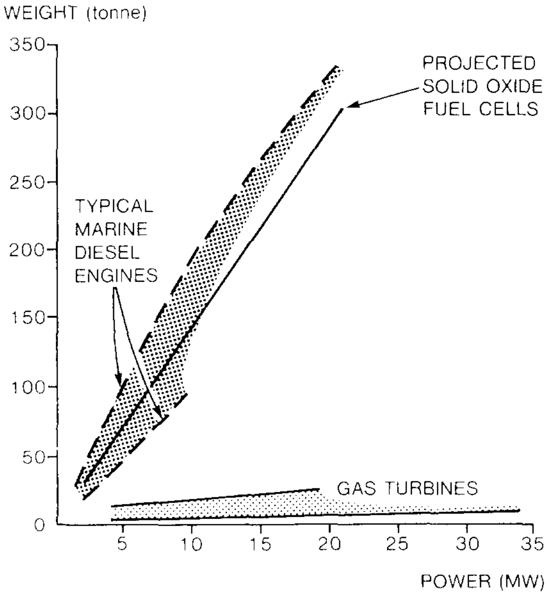

FIG. 3—ESTIMATED WEIGHT AGAINST POWER (HIGH POWER UNITS). WEIGHTS FOR ENGINES AND GAS TURBINES EXCLUDE ELECTRICAL GENERATORS AND DOWNTAKES/UPTAKES

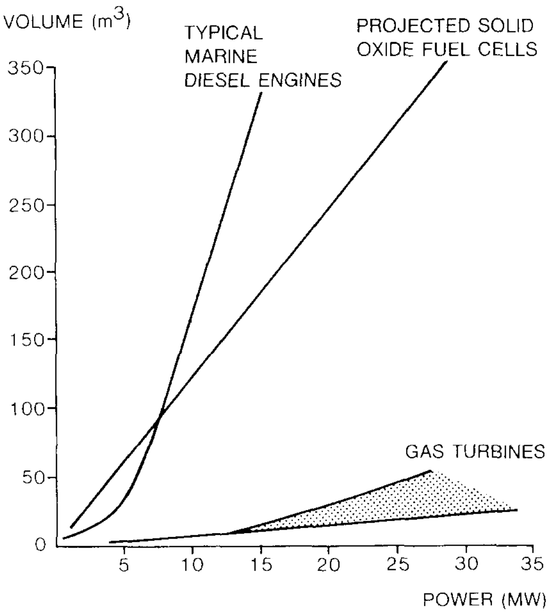

FIG. 4—ESTIMATED VOLUME AGAINST POWER (HIGH POWER UNITS). VOLUMES FOR ENGINES AND GAS TURBINES EXCLUDE ELECTRICAL GENERATORS AND DOWNTAKES/UPTAKES

If it is assumed that reformation of the model compositions given in TABLE I takes place with an efficiency of 90%, this gives approximately 0.26 kg of hydrogen and 2 kg of carbon monoxide per kg of diesel fuel used. Assuming a fuel cell efficiency of 50% and a heating value for diesel fuel of 45.1 MJ/kg the specific diesel fuel consumption may be calculated as 0.16 kg/kWh. The corresponding waste carbon dioxide from the fuel is 2.8 kg/kWh and the oxygen requirement is 0.34 kg/kWh. The overall system could be made more efficient by utilizing the waste heat from the fuel cell system.

FIG. 5 compares fuel consumption for typical marine diesel engines, gas turbines[12] and SOFCs. FIG. 6 compares operational endurances based on 370 tonnes of available fuel, but does not necessarily represent the way in which the Royal Navy operates engines or turbines; nevertheless it suggests considerably improved endurance.

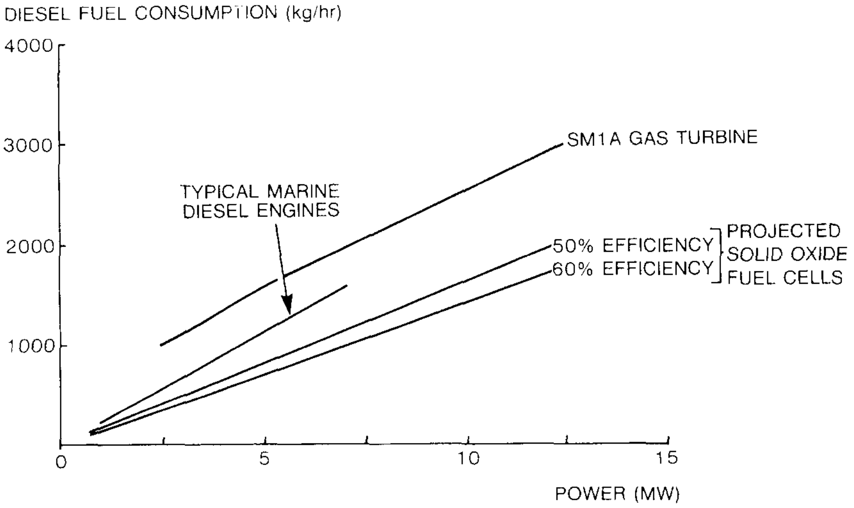

FIG. 5—ESTIMATED FUEL CONSUMPTION AGAINST POWER

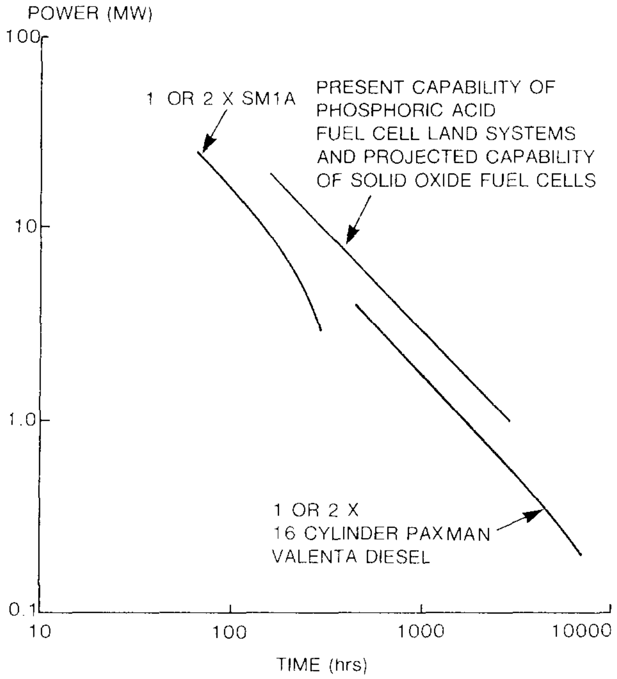

FIG. 6—POWER AGAINST ENDURANCE FOR 370 TONNES OF FUEL

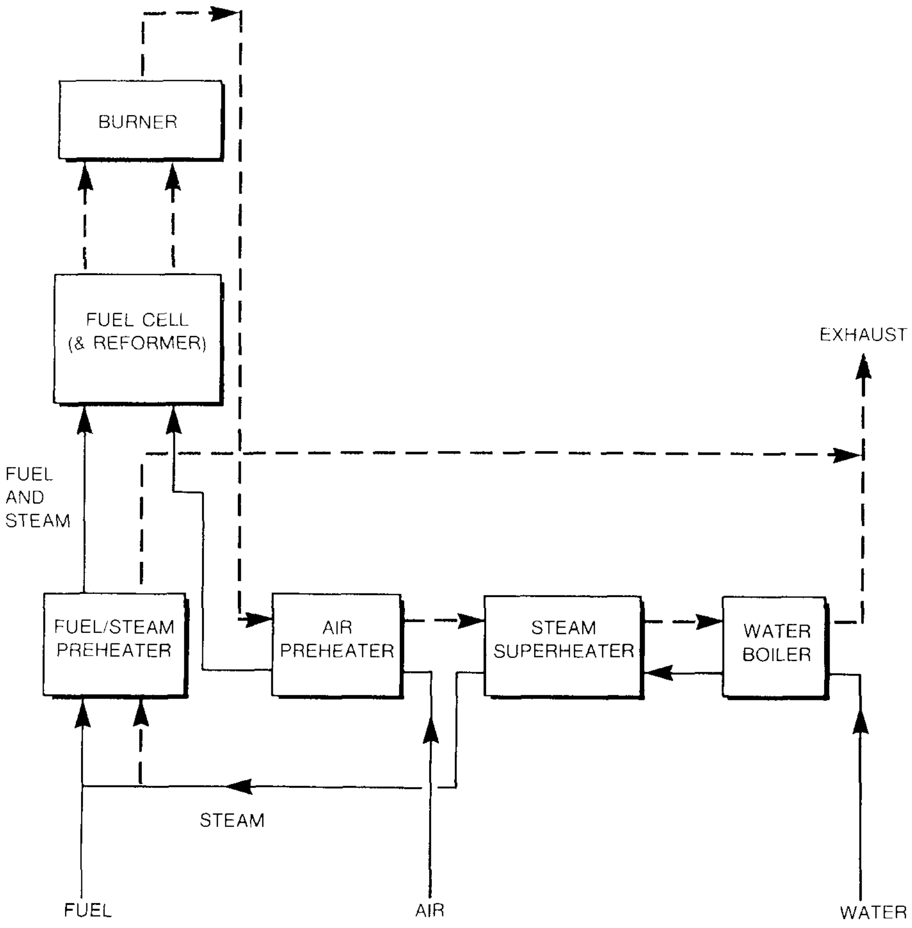

FIG. 7—SOLID OXIDE FUEL CELL SYSTEM FUELLED BY NATURAL GAS
based on Appleby & Foulkes[8]

System

A typical system configuration needs to include preheaters for the fuel and air supplies to the fuel cell stack(s) as well as a desulphurizer.

A natural gas-fuelled system designed by the Argonne National Laboratory[8,p. 585], is shown schematically in Fig. 7, where fuel is mixed with steam to stabilize against carbon formation, and then preheated before entering the fuel cell stack. Residual fuel leaving the fuel cell stack at 1000°C is burned to provide hot gases to preheat the incoming air and to generate steam. Some of the steam is added to the incoming fuel and the remainder used to preheat the fuel. This system would need to incorporate a desulphurizer if the fuel is Dieso or other middle distillate diesel fuel.

Designs for a marine diesel-fuelled system would need to incorporate desulphurization, be compact and consideration given to how much of the waste heat from the fuel cells can be used for preheating, and further utilized in a combined heat and power system. Fig. 8 shows a possible schematic layout which incorporates these features and is based on a solid oxide fuel cell plant proposal for electricity and heat supply to a building[13]. The problems of diesel oil reformers which incorporate desulphurization are being addressed experimentally for surface ship applications using either solid polymer or molten carbonate fuel cells[2].

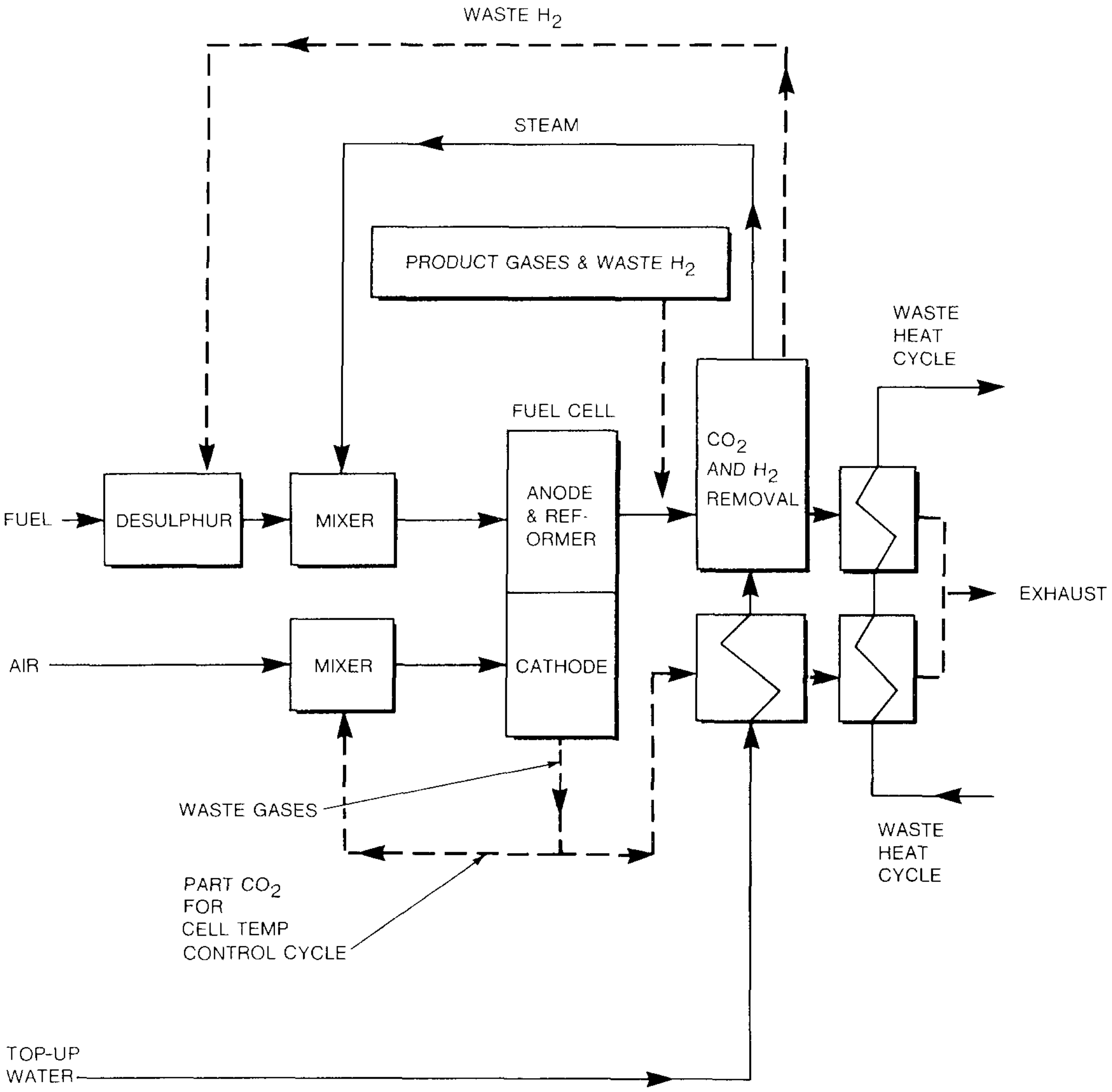

Fig. 8—Solid oxide fuel cell system fuelled by diesel fuel

based on Drenckhahn & Schramm[13]

Costs

The capital cost of a typical 750 kW naval marine diesel-electric generator is about £500k, or £660/kW. The development and capital costs for marine SOFCs are unknown, and the estimated installed capital costs for other types of large (MWs) commercial fuel cell generating plants vary from about £350/kW to £650/kW[8]. Also, fewer replacement modules throughout the life of a ship may be expected.

Overall through-life running costs for typical naval marine diesel engines comprise support and fuel costs. Assuming a 25 year lifetime for a surface ship with 30% usage the overall support costs are about £1.8M and the fuel costs about £2.8M/MW of installed power. The support costs for a fuel cell system are unknown but maintenance costs and mean time between module replacement will probably be less than that for diesel engines. Based on the fuel consumptions in FIG. 5 and the same lifetime and usage assumed above for diesel engines, the projected fuel costs for SOFCs are about £1.8M to £2.1M/MW. Fuel costs could be reduced further by utilizing the waste heat from the fuel cell system and improvements in cell performance.

Conclusions

The potential advantages of fuel cell systems to replace diesel-electric generators on ships outweigh the disadvantages, with the exception of tolerance to sulphur contamination. Savings in overall through-life costs are to be expected by changing from diesel-electric generators to fuel cell systems.

The tolerance of solid oxide fuel cells to sulphur content in the fuel is one and two orders of magnitude lower than currently accepted levels in middle distillate diesel fuel, but one or two orders of magnitude higher than other types of fuel cell. Unless the sulphur tolerance of cells can be improved, or legislation causes a change to use very low levels (less than 0.05% by mass) of sulphur in fuel, this is a limitation, and sulphur removal will need to be integrated with the fuel cell plant.

The acceptance of fuel cell systems for marine applications depends on the ability to use the fuel, already carried in ships to supply main propulsion systems. Experimental work directed at the use of reformed fuel for either solid polymer or molten carbonate fuel cells in ship applications has started[2]. The status of solid oxide cells is less advanced and only laboratory units have been demonstrated but development programmes for larger power levels are underway[11], and diesel fuel based systems are being studied[14].

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