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# Economic Thermoelectric Recovery of Low Temperature Heat

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## Abstract

The basic principles of thermoelectric generation and the factors, which determine the conversion efficiency of this process, are outlined. Semiconductor materials for use in the fabrication of thermoelectric modules suitable for operating over the temperature range from ambient to 420K are identified and estimates made of the conversion efficiency of thermoelectric devices fabricated from the best available materials. Procedures for optimising the geometry of commercially available modules for efficient thermoelectric generation are outlined.

Sources of waste heat and naturally occurring are listed and the thermoelectric recovery from exhausted North Sea oil wells considered as a case study. Finally the economics of thermoelectric waste heat recovery are discussed. It is concluded that, provided supportive engineering technology is available, electricity can be thermoelectrically generated on site at a price, which is competitative with current conventional generating utilities.

## Introduction

The effect of global warming on the environment and the uncertainty in the availability and reliability of fossil based fuels has resulted in an upsurge in the identification and development of alternative sources of environmentally friendly sources of energy. In the United States more than 30% of the industrial energy inventory is discharged into the environment as waste heat and of this more than 60% is at a temperature of less than 100C.

Two methods are available for converting low temperature heat into electricity- Rankine cycle engines and thermoelectrics. The Rankine cycle engine, although more efficient, has a number of moving components and a diaphragm which can be unreliable. Thermoelectric generators have no moving parts and can be customised to meet any power requirement. In this paper the possibility of thermoelectric recovery of low temperature heat and in particular marine geothermal is discussed and its economic competitiveness assessed.

## Basic principles

A thermoelectric converter is a heat engine and like all heat engines, it obeys the laws of thermodynamics. If we first consider the converter operating as an ideal generator in which there are no heat losses then the efficiency is defined as the ratio of the electrical power delivered to the load to the heat absorbed at the hot junction. Expressions for the important parameters in thermoelectric generation can readily be derived by considering the simplest generator consisting of a single thermocouple with legs or thermo elements fabricated from n- and p-type semiconductors as shown in Figure 1.

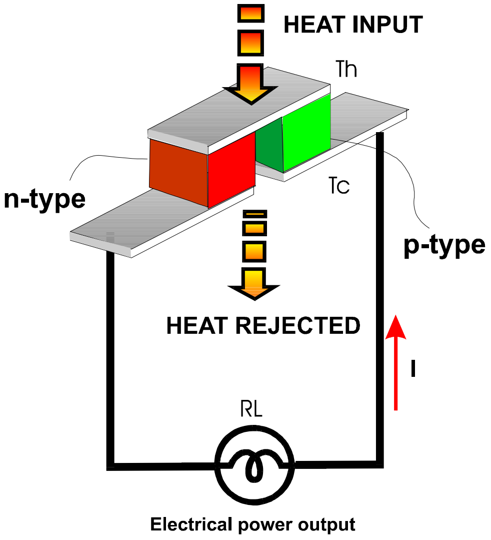


Figure1. Schematic Thermoelectric Unicouple

The efficiency of the generator is given by:

$$\phi = \frac{\text{energy supplied to the load}}{\text{heat energy absorbed at hot junction}}$$

Conveniently the efficiency can be expressed as a function of the temperature over which the device is operated and a so-called 'goodness factor' or thermo-electric figure- of- merit (Z) of the thermocouple materials.

$$Z = \frac{\alpha^2 \sigma}{\lambda}$$

Where $\alpha^2\sigma$ is referred to as the electrical power factor, with $\alpha$, the Seebeck coefficient, $\sigma$ the electrical conductivity and $\lambda$ is the total thermal conductivity. The figure-of-merit is often expressed in its dimensionless form, ZT where T is absolute temperature.

In figure 2 is displayed the efficiency as given by the above expressions as a function of temperature and Z value. Evidently a material with a Z value of 3 when operated with a hot side of 100C would convert heat into electricity with efficiency in excess of 10%.

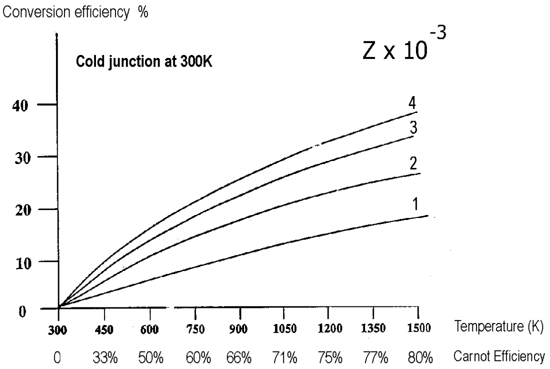


Figure 2. Maximum conversion efficiency as a function of temperature and figure-of-merit (cold junction at 300K)

**Low Temperature Thermoelectric Materials and Performance**

In figure 3 is displayed. the figure-of-merit of a number of established thermoelectric semiconductors identified as suitable for use over the temperature range from room temperature to about 150C (1). Alloys compounds based on the bismuth tellurides exhibit the highest figure-of-merit with $Bi_{2-x}Sb_xTe_3$ the best p-type material and $Bi_2Te_{x-y}\ Se_y$,the best n-type with the average figure-of-merit of the two materials, when formed into a thermocouple, approaching $2.5x10^{-3}K^{-1}$. Alloys/ compounds based on lead telluride possess figures-of-merit around $2.5x10^{-3}$ $K^{-1}$. These are identified by designations such as TEGS-2N this is n-type and indicates a specific semiconductor composed essentially of a compound of lead and tellurium with small additions of electrically active $PbI_2$, while –3P signifies a lead – tin telluride combination doped with sodium and manganese.

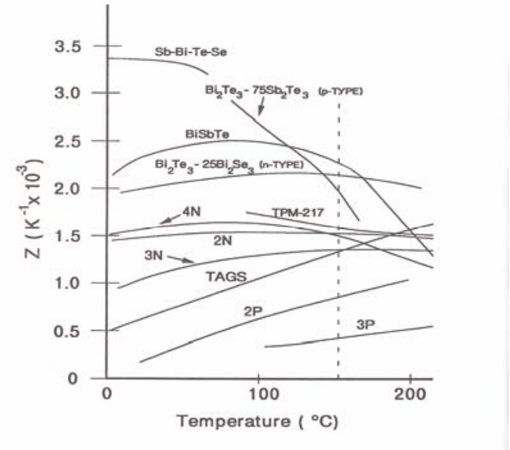


Figure 3. Figure-of-merit as a function of temperature

Materials based on bismuth telluride have a proven track record in device application and are the best "low temperature" thermoelectric materials, capable of converting about 20% of available heat energy, (Carnot fraction) into electricity. A thermocouple fabricated from the best of these materials when the hot and cold junctions are 100C and ambient respectively operates with a conversion efficiency of about 5%. However, substantial improvements can be achieved through the use of functionally graded material or segmentation (2).

**Thermoelectric module and generator**

In a practical generator a large number of thermocouples are connected electrically in series and thermally in parallel to form a module as shown schematically in figure

4 and sandwiched between two electrically insulting but thermally conducting ceramic plates to maintain the device's integrity. Electricity is generated when heat from warm water flowing over the hot side passes through the module and is ejected into cold water flowing over the cold side.

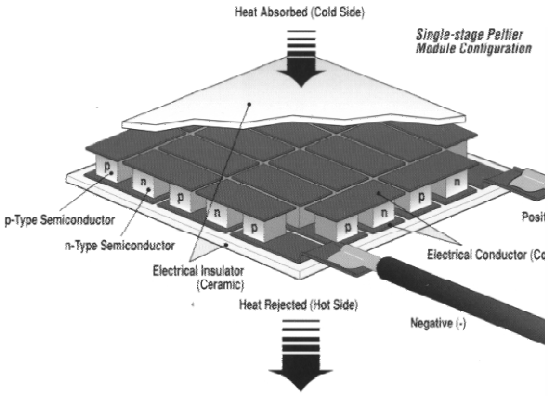


Figure 4. Schematic of a thermoelectric module

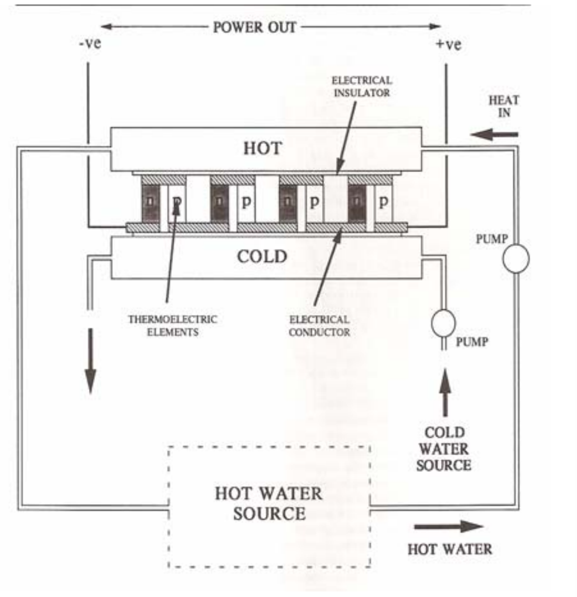


Figure 5. Schematic of a low temperature thermoelectric generating system

A schematic of a low temperature thermoelectric generating system is shown in figure 5. Basically it consists of a parallel plate heat exchanger with the thermoelectric generator modules sandwiched between the hot and cold water flow channels.

**Optimisation of module thermoelements**

For low temperature waste heat to electrical power conversion the thermoelement length should be optimised for maximum power. Usually the required length is shorter than that in the case of refrigeration, where the coefficient of performance is an overriding consideration.

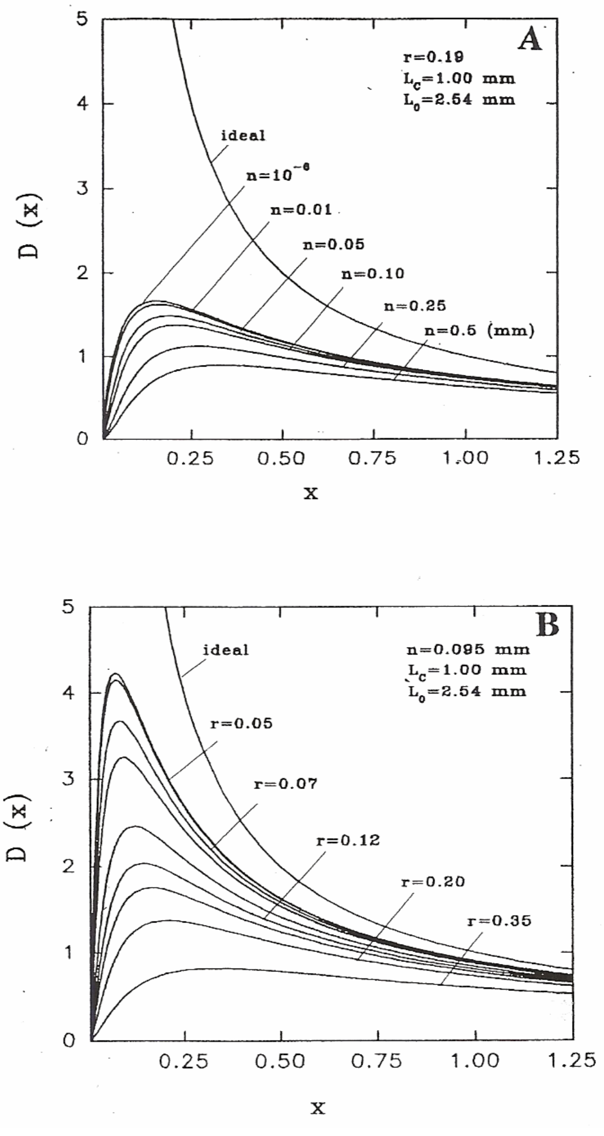


Figure 6. Power output of thermoelectric modules as a function of thermoelement length

(A) Effect of electrical contacting resistance
(B) Effect of thermal contact resistance.

In an ideal model the power output approaches infinity as the length of the thermoelement goes to zero. In practice, as the aspect ratio is decreased the contact resistance effects become more significant and cannot be neglected. In figure 6 is displayed the change in power output of a realist modelled module as a function of thermoelement length (A) Electrical contact resistance and (B) Thermal contact resistance (3).

Conversion efficiency also depends on the thermoelement length. In figure 7 is displayed the change in efficiency with thermoelement length and contact properties. The conversion efficiency of an actual device will decrease with a reduction in length and the effect becomes much more significant when the thermoelement is very short. Consequently the appropriate length is a trade off between the maximum power output and conversion efficiency.
Fortunately in applications such as electrical power generation, employing low temperature and essentially free heat, the conversion efficiency is not an overriding requirement.

Moreover, the decrease in conversion efficiency is not very significant at the thermoelement length that corresponds to maximum power output.

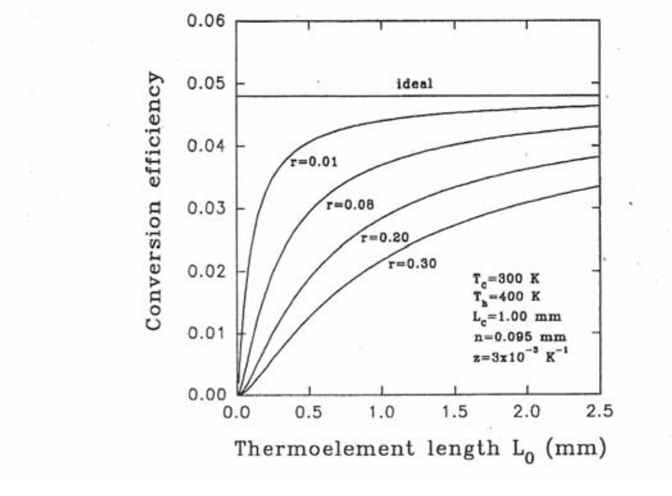


Figure 7. Conversion dependence on thermoelement length

**Sources of Low Temperature Heat**
Vast quantities of low temperature heat (ie below 150C) are available on earth from a variety of sources and can be conveniently divided into naturally occurring and waste heat.

***Waste Heat***
All utilities / industries use some form of energy. This is supplied at a high temperature and subsequently rejected at a lower temperature into the environment. The most convenient form energy is utilised is as electricity, when only about 35% of the energy provided is converted into electricity. The remainder appears mainly in the cooling water . Generally the cooling water is raised from 10C to around 25C and in a 2000MW power station more than 4000MW is ejected as waste heat. Consideration of the global energy inventory is outside the scope of this paper.

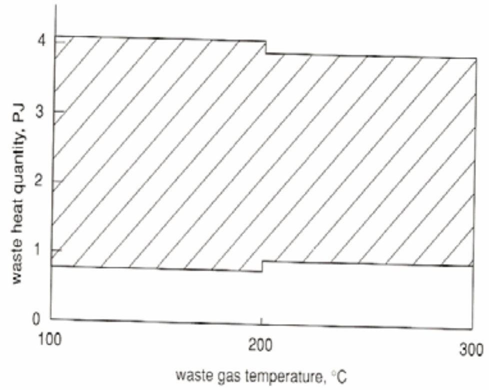


Figure 8A. Temperature distribution of heat in the potteries, brick building and bulk refractories industries

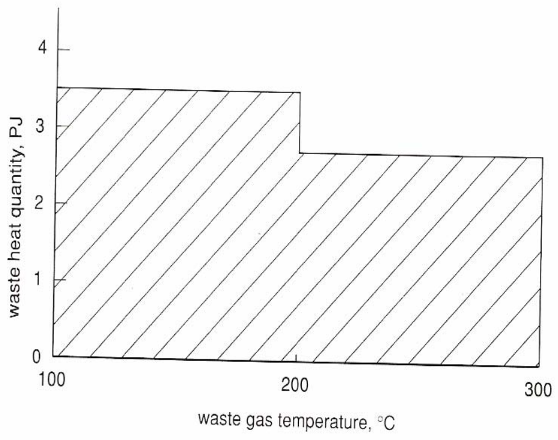


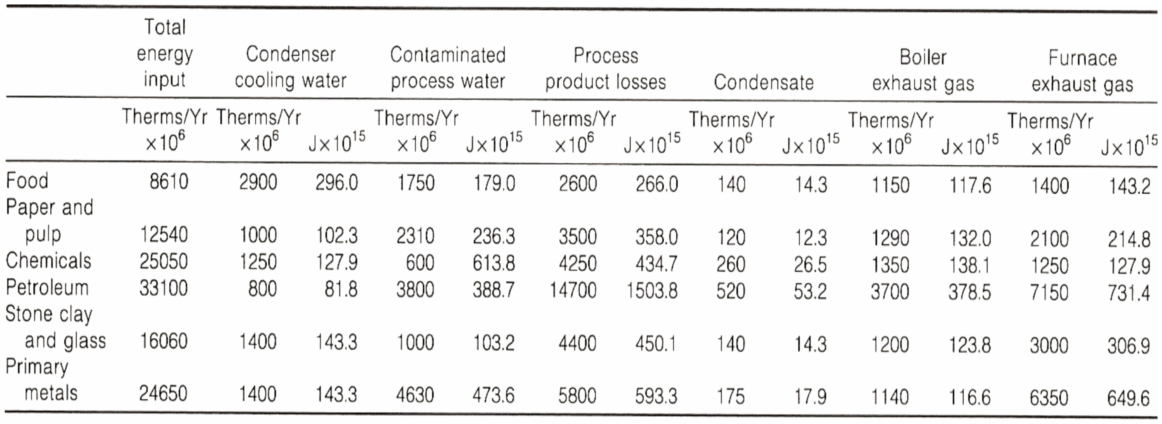
Figure 8B. Temperature distribution of heat in the aluminium industry

However, some idea of the magnitude of the waste heat associated with major industrial users in the UK is given in figures 8A and 8B (4). The United Kingdom's Energy Technology Support Unit investigated the energy levels and temperatures of waste heat from a number of major industries. The figures show waste heat divided into difference temperature bands enabling the potential heat available within the low temperature range to be ascertained. A distinction is also made between dirty (hatched) and clean categories of heat as at higher temperatures dirty waste heat may well be more destructive and substantially increase recovery costs.

The major heat US users of energy are collected in table1.

### ***Naturally occurring heat***

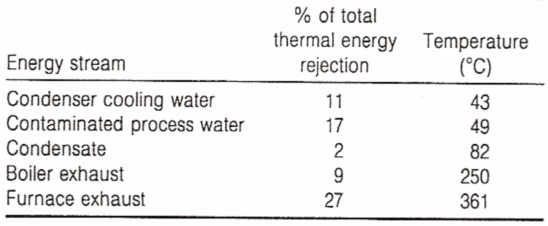
Geothermal heat is the Earth's natural energy which is derived from the radioactive decay of long lived isotopes of uranium, thorium and potassium. Geothermal heat sources vary considerably in quality and accessibility and are generally classified as those with temperature ranging from 50-200C (high enthalpy) and other sources less than 150C (low enthalpy). Techniques have been developed to extract heat from hot dry rock (HDR) systems where there is sufficient natural fluid flow available to transfer the heat to the surface (6). A study has also been undertaken to assess marine based geothermal generation employing thermoelectrics as covered in the case study.



| | Total energy input | Condenser cooling water | | Contaminated process water | | Process product losses | | Condensate | | Boiler exhaust gas | | Furnace exhaust gas | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Therms/Yr $\times 10^6$ | Therms/Yr $\times 10^6$ | $J \times 10^{15}$ | Therms/Yr $\times 10^6$ | $J \times 10^{15}$ | Therms/Yr $\times 10^6$ | $J \times 10^{15}$ | Therms/Yr $\times 10^6$ | $J \times 10^{15}$ | Therms/Yr $\times 10^6$ | $J \times 10^{15}$ | Therms/Yr $\times 10^6$ | $J \times 10^{15}$ |
| Food | 8610 | 2900 | 296.0 | 1750 | 179.0 | 2600 | 266.0 | 140 | 14.3 | 1150 | 117.6 | 1400 | 143.2 |
| Paper and pulp | 12540 | 1000 | 102.3 | 2310 | 236.3 | 3500 | 358.0 | 120 | 12.3 | 1290 | 132.0 | 2100 | 214.8 |
| Chemicals | 25050 | 1250 | 127.9 | 600 | 613.8 | 4250 | 434.7 | 260 | 26.5 | 1350 | 138.1 | 1250 | 127.9 |
| Petroleum | 33100 | 800 | 81.8 | 3800 | 388.7 | 14700 | 1503.8 | 520 | 53.2 | 3700 | 378.5 | 7150 | 731.4 |
| Stone clay and glass | 16060 | 1400 | 143.3 | 1000 | 103.2 | 4400 | 450.1 | 140 | 14.3 | 1200 | 123.8 | 3000 | 306.9 |
| Primary metals | 24650 | 1400 | 143.3 | 4630 | 473.6 | 5800 | 593.3 | 175 | 17.9 | 1140 | 116.6 | 6350 | 649.6 |

Table 1 Major US users of heat energy

Waste heat energy resources from those identified are condenser cooling water, contaminated process water, process product losses, condensate, boiler exhaust gas and furnace exhaust gas. The percentage of energy rejected and average rejection temperature in the various waste streams are given in table 2. (5)



| Energy stream | % of total thermal energy rejection | Temperature (°C) |
|---|---|---|
| Condenser cooling water | 11 | 43 |
| Contaminated process water | 17 | 49 |
| Condensate | 2 | 82 |
| Boiler exhaust | 9 | 250 |
| Furnace exhaust | 27 | 361 |

Table 2 Percentage from waste rejection sources and their temperature

Ocean thermal energy has also attracted serious consideration. There are several areas of oceans, particularly in the tropics where the temperature of the surface water may be 20-25C higher than the water at a depth of 500m and in some regions, for example the Red Sea, similar temperature changes occur over considerably shorter distances ( 7.) During the early 1980's considerable research effort was mounted in Japan (8) and USA (9) to develop ocean thermal energy conversion systems (OTEC).

Solar ponds have been employed in many parts of the world as an energy storage device. A modification of the solar pond is the so called salt gradient stabilised solar pond. A salt density gradient is established with increase in depth. Solar energy is collected with an efficiency of up to30% and heats up the pond to temperatures of up to 90C in locations where the average insulation is 200W/m2. About 50W/m2 can be extracted form the pond. The maximum Carnot efficiency is about 18%.

## Marine geothermal thermoelectric generation (MGTG)

Renewable energy sources such as wind, wave tidal power etc are all to some extent variable and unpredictable from the point of power generation. Consequently they are not really satisfactory in meeting the requirement of a steady load.

Redundant oil wells have a big advantage in that an accessible route to the reservoir of heat has already been established. At the sea surface the temperature varies around 10C and in the strata beneath the sea exceeds 100C. The rock temperature beneath the North Sea increases at around 25-35C with each kilometre of depth. Although in some regions the gradients can be a high as 47C per kilometre. At a typical well depth of 5km the temperature is around 120-170C. The temperature range of potential redundant wells can be grouped into three temperature ranges 20-80C, 80-110C and 110-190C.

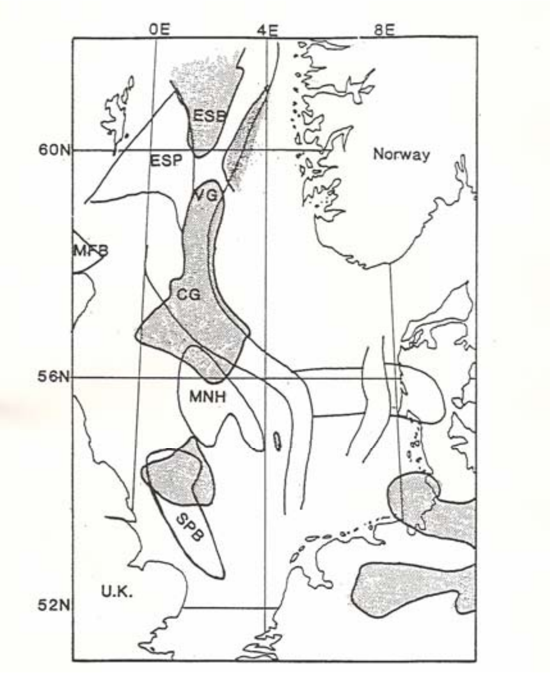


Figure 9. Areas of the North Sea with Rock Temperatures of 200C at Depth Less than 6 km ( dark areas)

In figure 9 North Sea areas with sub-sea rock temperatures at 200C at depth of less than 6km are shown shaded.

## The generating system

The first use of low temperature waste heat recovery using thermoelectrics was considered by Matsuura and Rowe (10). In 1992 the United Kingdom's government decided to commence decommissioning of off-shore oil platforms. Hydrocarbons which have collected beneath the North Sea are normally extracted by pumping sea water from the surface into the subterranean reservoir via an injection pipe and forcing the hydrocarbons to the surface platform through an extractor pipe. The two pipes are called a doublet (figure 10). Oil reserves are located typically at depths of around 3 km and the oil temperature at this working depth is around 100 K. Generating electricity from this low temperature heat source using conventional methods is not possible and the possibility of employing thermo-electrics has been considered as a possible alternative (11). The use of Peltier devices in the Seebeck mode for electrical power generation employing low temperature waste heat is well established (12).

Information relating to actual platform performance and operation is commercial property. A realistic doublet flow rate based on available information on reservoirs and platforms is around 4000litres a minute. Operating at an input temperature of 90C and sea temperature of 10C gives a Carnot efficiency of 22 percent and a maximum operating efficiency of around 4.5%. Each extractor thus has a potential to produce a maximum of 1MW(e) continuous. Assuming that ten pairs of doublets can be accommodated on a single platform, each platform could produce around 10MW(e).

In a thermoelectric marine farm concept a number of platforms are linked together with submarine cable. Estimates of the length of cable can be made based upon each cluster comprised of five platforms separated by about 12km with the distance from the closest platform to the shore about150 km.

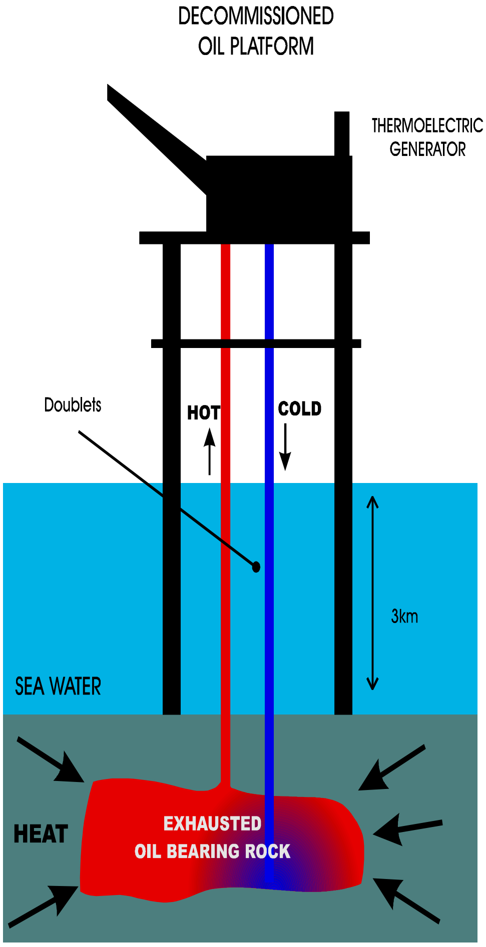


Figure 10. Marine geothermal thermoelectric generation (MGTG)

## Optimisation of module geometry and economics

A starting point when considering the economics of MGTC is the projected life time of the operating system. The usable lifetime of the marine generator depends upon the rate of heat extraction. If the thermal conductivity of the rock is 4Wm-1K-1, the local temperature gradient is 25C/100m and the heat conducting surface replenishment area $10^6$m2 then the rate of replenishment is around 1MW. As the temperature of the extracted water decreases with time an estimate of approximately twenty years can be made of the effective lifetime of the heat reservoir.

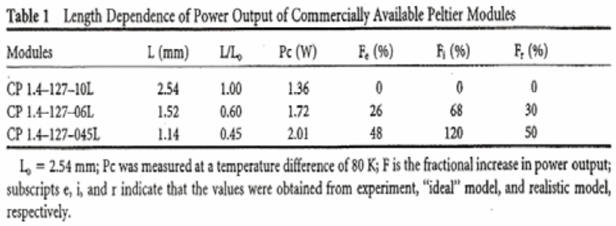


Table 1 Length Dependence of Power Output of Commercially Available Peltier Modules

| Modules | L (mm) | $L/L_0$ | Pc (W) | $F_e$ (%) | $F_i$ (%) | $F_r$ (%) |
|---|---|---|---|---|---|---|
| CP 1.4–127–10L | 2.54 | 1.00 | 1.36 | 0 | 0 | 0 |
| CP 1.4–127–06L | 1.52 | 0.60 | 1.72 | 26 | 68 | 30 |
| CP 1.4–127–045L | 1.14 | 0.45 | 2.01 | 48 | 120 | 50 |

$L_0$ = 2.54 mm; Pc was measured at a temperature difference of 80 K; F is the fractional increase in power output; subscripts e, i, and r indicate that the values were obtained from experiment, "ideal" model, and realistic model, respectively.

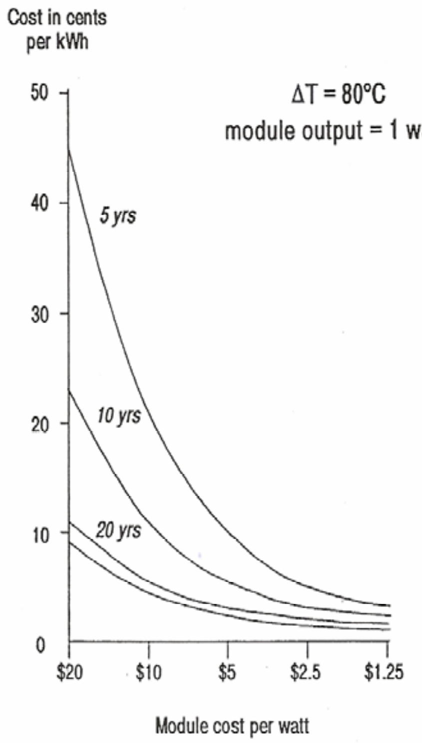


Figure 11. Cost of electricity as a function of module cost and operating time

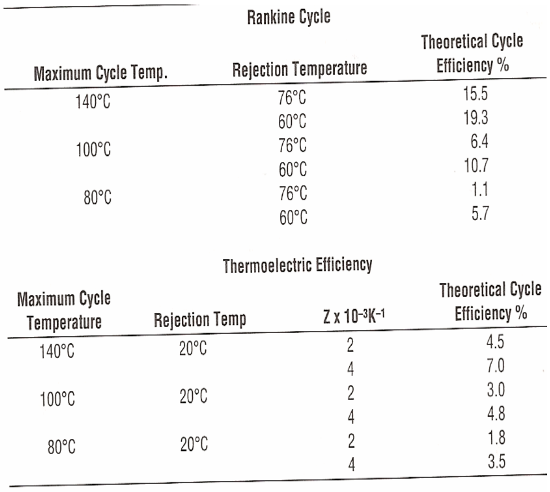
A costing estimate assumes that the pumping gear and inlet and outlet pipe work and appropriate pumping gear is in place. The generating costs depends essentially on that of the thermoelectric converters .with the most expensive items likely to be thermoelectric module. Consequently, their optimisation for economic power generation is considered in some detail.

The beneficial aspects of reducing the thermo element length are evident from table3. Three commercially available modules differing in element length are subjected to a temperature difference of 80C. The calculated cost of generating power using thermoelectrics is displayed in figure 11.

Power generating modules are available in bulk purchase at a cost of around $5. Evidently electricity can be generated on site over a 20 year period at a cost of less than 2 cents per kilowatt hour. The construction/assembling costs are considered to be of similar magnitude as the modules then the systems generating costs will be around 4-5 cents per kilowatt hour. This compares very favourably with the commercially price of between 5 and 7 cents paid for electricity generated by conventional methods.

## Discussion and conclusion

The only alternative technology to thermoelectrics that can be employed in low temperature heat recovery are heat engines employing Rankine cycle. A comparison of the efficiency of both is shown in table 4. Evidently thermoelectric conversion is significantly lower than that of an organic Rankine cycle. Nevertheless thermoelectric generators possess a number of design advantages over Rankine cycles. They have no evaporator, condenser, working fluid, pressure vessel or turbo generator. In addition they are robust and the method of generating electricity is environmentally friendly.



Rankine Cycle

| Maximum Cycle Temp. | Rejection Temperature | Theoretical Cycle Efficiency % |
|---|---|---|
| 140°C | 76°C | 15.5 |
| | 60°C | 19.3 |
| 100°C | 76°C | 6.4 |
| | 60°C | 10.7 |
| 80°C | 76°C | 1.1 |
| | 60°C | 5.7 |

Thermoelectric Efficiency

| Maximum Cycle Temperature | Rejection Temp | Z x $10^{-3}K^{-1}$ | Theoretical Cycle Efficiency % |
|---|---|---|---|
| 140°C | 20°C | 2 | 4.5 |
| | | 4 | 7.0 |
| 100°C | 20°C | 2 | 3.0 |
| | | 4 | 4.8 |
| 80°C | 20°C | 2 | 1.8 |
| | | 4 | 3.5 |

Table 4 Comparison of Rankine cycle and thermoelectric efficiencies.

In situations where the cost of fuel is negligible or very low, the efficiency is not a major consideration, although the systems efficiency will be a factor in determining the final size of the generating system. Capital investment and the lifetime of the conversion system are the dominant factors. Thermoelectric devices are inherently reliable, but are expensive. Consequently a reduction in module cost is a main objective. The availability of low cost Chinese manufactured devices has dramatically improved the economic competitiveness of low temperature heat recovery employing thermoelectrics and provides the capability of generating electricity on site from low temperature heat at a cost which is competitive with conventional utilities.

The locations of majority of North Sea oil are remote from land and local power distribution networks and implementation of the scheme would incur additional cost of several hundred kilometres of transmission cable. More favourable locations near shore would be economically viable.

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