

INDUSTRIAL THERMOELECTRIC COOLING AND ELECTRICITY GENERATION

BETWEEN 200 K AND 500 K

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ABSTRACT

A very brief history of thermoelectrics with a description of the phenomena is given. The characteristics of present day materials for the temperature range between 200 and 500 K are presented. The technologies for small and for large systems with their respective particularities and advantages are described. Companies active in thermoelectrics have been contacted, and typical equipments of about ten companies that have product brochures are presented. Thoughts about thermoelectrics, concerning the effect of material and technology improvements on existing and future markets are discussed.

1. HISTORICAL DEVELOPMENT

Thermoelectricity started when Thomas Seebeck (1) discovered in 1822 that an electromotive force is produced by heating a junction between 2 metals. This phenomena is the basis for thermoelectric generators. Jean C.A. Peltier discovered the opposite effect in 1834 (2), that by passing an electrical current through consecutive different conductors a temperature difference was established between consecutive junctions with a transfer of heat from one to the other. The hot junctions give out heat and the cold junctions absorb heat.

The Seebeck effect has been used over the years in thermocouples to measure temperatures. The Seebeck effect for electricity generation and the Peltier effect lay dormant for over a century till improvements in Solid State Physics and work at Leningrad University by Ioffe (3) and his team lead to improved materials that gave a new birth to thermoelectrics.

In the nineteen fifties, based on the work of Ioffe, there was considerable work done on materials in Europe (4) (5) and in North America.

Around 1960 there were over one hundred companies active in thermoelectrics, because in 1959 Dr. Zener predicted thermoelectric materials (6) that would produce cooling with performances equal to those of Compression Cycle Machines using Freon and electricity generators that could compete with steam turbines and alternators, these predictions have not materialized.

In the sixties it was realized that it would not come true before at least several decades. Today it is not even expected, nevertheless there are today applications

where thermoelectrics has its place in the arenas of cooling processes and of electricity generation.

We are concerned with cooling around ambient temperature and electricity generation between ambient and 200° C. The most performing materials are alloys of bismuth telluride (5).

2. FUNDAMENTALS OF THERMOELECTRICS

First the equations that govern thermoelectrics for heat pumps, then for electricity generation and also the material properties are presented.

2.1. Equations for thermoelectric heat pumps

When an electrical current goes through a material which presents thermoelectric properties, heat is transferred across it and a temperature difference is created. Reduced to a "black box" the thermoelectric material becomes a static heat pump.

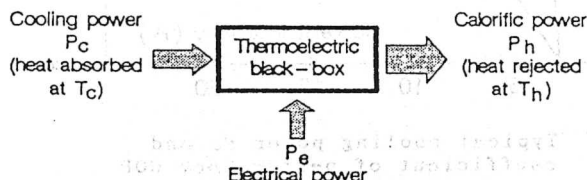


Fig. 1 Thermoelectric "black box"

The above black box is ruled by the following equations :

$$P_c + P_e = P_h \text{ equation of energy conservation}$$

where P stands for power (W) and the indices c for cooling, h for heating, e for electrical

$$P_c = s \cdot I \cdot T_c - \frac{1}{2} R \cdot I^2 / 2 - C \cdot (T_h - T_c)$$

$$P_h = s \cdot I \cdot T_h + \frac{1}{2} R \cdot I^2 / 2 - C \cdot (T_h - T_c)$$

$$P_e = s \cdot I \cdot (T_h - T_c) + R \cdot I^2$$

The piece of thermoelectric material is characterized by :

- s = Seebeck coefficient (V/K)
- R = electrical resistance (ohms)
- C = thermal conductance (W/K)
- T<sub>c</sub> = absolute temperature of cold side in K
- T<sub>h</sub> = absolute temperature of hot side in K
- I = electrical current in amperes

The cooling power  $P_c$ , which we are most interested in, contains 3 terms.

The first one :  $s \cdot I \cdot T_c$  is the total power pumped by the Peltier effect, which is proportional to the Seebeck coefficient, to the current intensity and to the absolute temperature of the thermoelectric material cold side.

The following two terms unfortunately must be subtracted from the first and they reduce it.

The second one  $R \cdot I^2 / 2$  represents the unavoidable Joule effect.

The last one  $C \cdot (T_h - T_c)$  is the result of the thermal conductivity of the thermoelectric conductor due to the temperature difference  $(T_h - T_c)$ . This effect reduces the cooling and heating power, because it transfers heat from the hot side to the cold side.

The curves in Fig. 2 show how the cooling power of a system varies with electrical current.

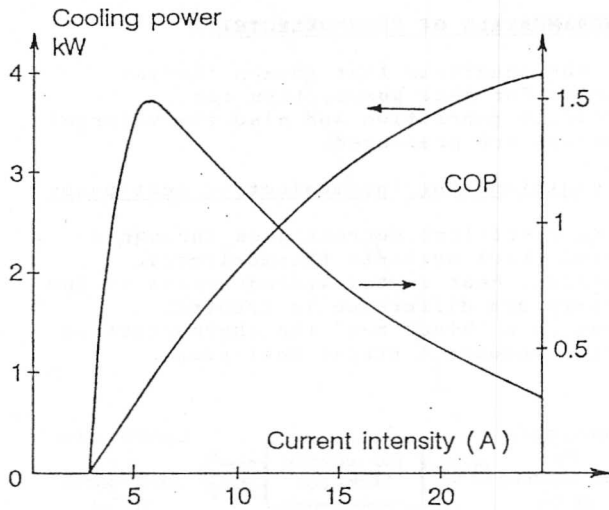


Fig. 2 Typical cooling power  $P_c$  and coefficient of performance COP versus electrical current.

### 2.2. Equations for electricity generation

The equations are the same, but it is necessary to explicit the load resistance  $R_L$  ( $\Omega$ ). The electrical current  $I$  (A) is :

$$I = s \cdot (T_h - T_c) / (R + R_L)$$

### 2.3. Material properties

An overall parameter, the coefficient of merit  $Z$  is the best practical way to characterize thermoelectric material, it has the dimensions of  $1/K$  :

$$Z = s^2 / (\rho \cdot k)$$

where  $\rho$  : electrical resistivity  $\Omega \cdot m$   
 $k$  : thermal conductivity  $W/(m \cdot K)$

Materials from most manufacturers were characterized by the authors (7).

Typical values are  $s = 200 \mu V/K$   
 $\rho = 10 \mu \Omega \cdot m$   
 $k = 1.6 W/(m \cdot K)$

Most materials that are used today have a  $Z$  at room temperature between  $2.5 \cdot 10^{-3} K^{-1}$  and  $2.8 \cdot 10^{-3} K^{-1}$ .

There are 2 manufacturing processes, one that makes a polycrystalline material by a crystal growing technique such as Bridgman or Zone refining, the other is a sintering process that produces a sintered material.

### 2.4. Mechanical properties

Thermoelectric material with its soldered interfaces is relatively fragile, its properties resemble that of concrete, in that it is extremely robust when prestressed. It can withstand enormous pressure up to 100 MPa, but it has a very weak shear-stress which is for polycrystalline material of the order of 7 MPa, a sintered material is sturdier.

Thermoelectric modules hold up to high compressions values of 50 MPa, but the slightest bending will destroy them. Leong (10) modelled the mechanical stress on a commercial module. Single modules can be mounted to withstand the accelerations and vibrations encountered in rocket propulsion.

### 3. SMALL SYSTEMS TECHNOLOGY

When the cooling requirements are less than 100 Watts, equipment manufacturers, that want to cool an equipment, all use thermoelectric modules.

#### 3.1. Thermoelectric module

A thermoelectric module is a preassembled set of thermoelectric pieces, alternately of type N and type P to form couples (N + P). The couples are placed in series electrically and thermally in parallel between two electrically insulating plates generally of alumina.

A typical module is shown in the photograph Fig. 3.

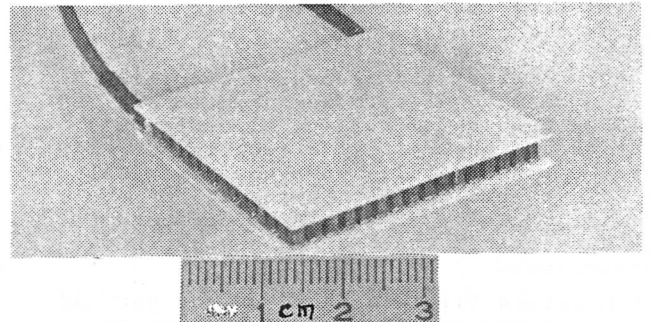


Fig. 3 Thermoelectric module (MELCOR CP 1.4 - 127 - 10L)

Thermoelectric modules in appearance have not changed much over the past 20 years. Progress has essentially been made in the manufacturing techniques and in their performances. These modules are relatively easy to install because the ceramics insulate the electrical circuit from the adjacent heat exchangers. These ceramics give sufficient insulation, on the condition that the equipment need not be tested at more than a few hundred volts.

The maximum temperature difference that a thermoelectric module can produce which corresponds to cooling power = 0 is around  $65^\circ C$ .

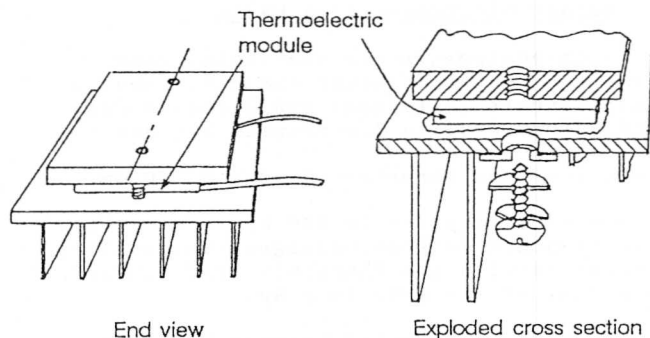
When larger temperature differences are required cascaded modules are used. They consist of several modules put one on top of each other, so that the top surface of the top module for instance can produce a watt of cooling with a large temperature difference.

### 3.2. Assembly procedures

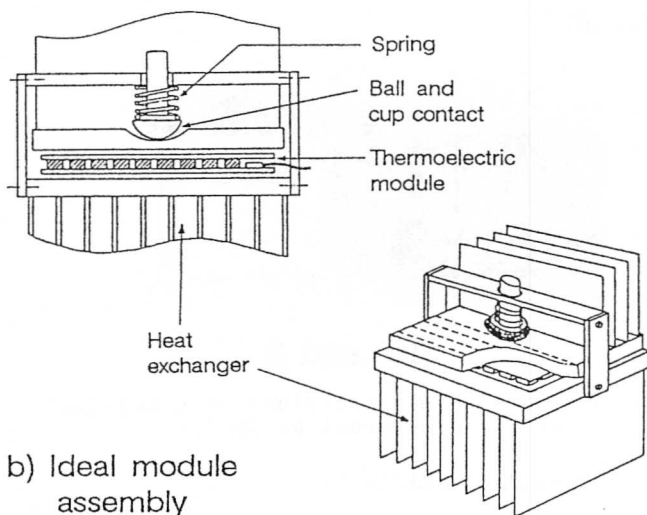
The manufacturers give module assembly procedures. There are some basic rules. The outside surfaces of the ceramics must be sandwiched between two rigid flat plates. A thermal compound is placed at each interface. A common one is Dow Corning G 340 (silicone grease filled with zinc oxide). The tightening procedure requires a certain amount of precaution, because the ceramics of the module are fragile and will crack if pressure is applied unevenly onto them.

The fundamental rule is for the module to be permanently under compression. Lateral components of the compression force  $F$  can be avoided by applying it at the center with a ball and cup contact.

A typical assembly is shown in Fig. 4a and an ideal assembly example is shown in Fig. 4b below :



a) Standard assembly (courtesy of Melcor)



b) Ideal module assembly

Fig. 4 Assembly of a thermoelectric module

## 4. COMMERCIAL EQUIPMENTS WITH SMALL POWERS

There are many scientific equipments that incorporate one or more thermoelectric modules for spot cooling ; The powers involved are often less than a watt.

In the range up to 50 W there are many applications of electronic cooling, dew point meters, blood analysers, photomultipliers, temperature control systems (e.g chemical dopants for semiconductor industry - 5 to + 45° C), optical radiation measurement equipments, photoconductor laser equipments and there are many more.

Equipments that are designed and commercialized to cool specific products or equipments are presented to show the areas already covered by thermoelectrics today.

### 4.1. Picnic coolers

These coolers operate off a 12 V car battery and generate with one thermoelectric module about 20 W of cooling. They can produce ice if it is not too hot outside.

The estimated world production for 1987 is of around 250000 units.

The main North American manufacturer is Koolatron (Brantford, Ontario, Canada), in Europe Electrolux (Luxembourg) and Supercool (Göteborg, Sweden) are the main producers. There are manufacturers in the Far East YAM'S (Hong-Kong) and Commander Highclass Electrical Corporation (Taichung-Hsien, Taiwan). A photograph is shown below of a typical one.



Fig. 5 Picnic Cooler Koolatron model Caddy II

The capacity is of 34 litres, the weight is of 7.7 kg. The temperature inside the cooler can be 26° C below ambient. The maximum electrical power is of 48 W during cool down then it is of 30 W.

### 4.2. Refrigerator/cooler

American and Canadian locomotives are generally equipped with refrigerator/coolers so that the crew can have cold drinking water available. There are several models with shapes that are adapted to available space. Next page is a photograph of such a unit, from Hilan (Kalamazoo, Michigan, USA).



**HYLAN<sup>®</sup>**

**RR-50 FRONTIER**



Fig. 6 Railway refrigerator/cooler  
Hylan RR 50

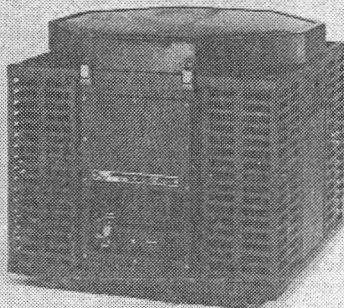
This unit has a useful volume of 46 l. It operates at 74 VDC which is a standard locomotive voltage, it can cool to 30° C below the ambient temperature.

#### 4.3. Military transportation refrigerator

Military thermoelectric equipments for transporting blood, vaccine and drugs are commercialized. Thermopol (Chicago, USA) builds a unit M-50B. It has no moving parts the inside temperature is regulated at 4° C ± 1° C with outside temperatures not exceeding 49° C. The inside volume is of 57 litres and it weighs 35 kg ; A photograph of the unit is shown below with the cover down.

The outside dimensions are :  
64 x 55,5 x 58 cm high

**THERMOPOL<sup>®</sup>**



M-50B STORAGE AND TRANSPORTATION UNIT

Fig. 7 Transportation Refrigerator Thermopol  
model M-50B

#### 4.4. Gas analyzer dehumidifier

One of the constant problems of analyzing gases is the elimination of their water vapor. An equipment is manufactured and

commercialized by Komatsu Electronics Inc. (Minato-ku, Tokyo, Japan). The gas flow rate is of 60 l/s, the dewpoint can be reduced to 1° C with a maximum outside air temperature of 40° C. The cooling is obtained with a module containing 24 couples. The overall weight is 8 kg. It operates off standard network voltages, the maximum power drain is of 140 W.

**Komatsu<sup>®</sup>**

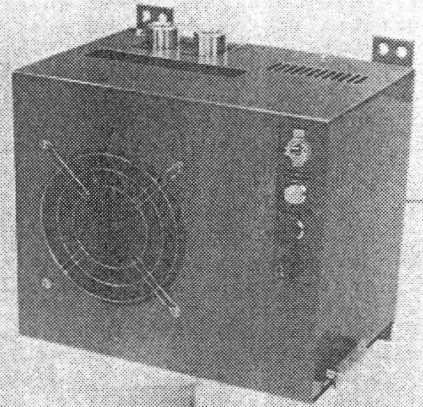


Fig. 8 Gas dehumidifier Komatsu Electronics  
model DH 105

#### 4.5. Adjustable temperature baths

Many such equipments are available, some reject the heat to a water circuit, some to an air circuit. A typical small one, model DA600 B from Komatsu Electronics Inc has :

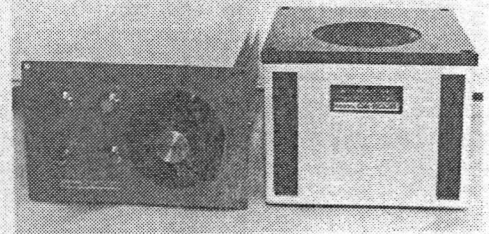
bath dimensions diameter 80, depth 100 mm.

The power consumption is 130 W, it operates under standard network voltages. The cooling is obtained with two thermoelectric modules, the weight of the bath is 6 kg.

The bath can be adjusted between - 8° C to + 70° C within 0.15° C.

Below is a photograph of a unit.

**Komatsu<sup>®</sup>**



**DA 600 B**

Fig. 9 Adjustable temperature bath Komatsu  
Electronics model DA 600 B

#### 4.6. Small air coolers

Air coolers are generally used for cooling electronic devices, the heat is generally rejected to the outside air but can be also rejected to a water circuit.



## 5. LARGE SYSTEMS TECHNOLOGY

### 5.1. Brief history

At the onset of large systems in the nineteen sixties, the first concept was to use the module technology. Large thermoelectric modules were made using large pieces of material with a cross section greater than  $1 \text{ cm}^2$ .

Three companies did development based on this concept :

- RADIO CORPORATION OF AMERICA (10)
- CARRIER CORPORATION (11)
- AMERICAN AIR FILTER (12)

They abandoned thermoelectrics, early on, for many reasons. Since, 4 companies have developed the concept of associating to small individual heat exchangers pieces of thermoelectric material with cross sections in excess of  $1 \text{ cm}^2$ .

- BORG WARNER CORPORATION (13) stopped in the late sixties
- WESTINGHOUSE (14) (15) (16) stopped in the seventies
- ASEA (17) started in the seventies and going strong in the eighties.

A close look at the technological problems related to the particular mechanical properties of thermoelectric material reveals that the concept of macro-modules is not viable.

The concept of associating big pieces of thermoelectric material to a large number of small heat exchangers has considerably evolved technology wise. Westinghouse was the first to demonstrate the reliability of its water and air technologies in military applications.

Asea equipped a passenger railway coach of the Swedish Railways with thermoelectric (air-air) air conditioning (17) in the roof, unfortunately after several years the equipment was taken out and no further development was done.

Air Industrie equipped a passenger railway coach of the French Railways (SNCF) with a centralized thermoelectric (air - air) air conditioning unit below the coach floor (9). The first unit was installed in 1978, it was replaced by a more powerful unit in 1981 and it has been in daily operation since.

So today Air Industrie which has become TNEE Air Industrie Thermoelectrics is the only manufacturer of large thermoelectric systems.

### 5.2. General technology

Medium (kilowatt range) and large (tens of kilowatts range) systems consist of an assembly of subunits.

The following description corresponds to ideas that have been around since the nineteen sixties. Each company has had to study how to make the concept of using the heat exchangers as electrical conductors work and to develop a valid subunit technology.

#### 5.2.1. Description of subunit electric circuit

The air heat exchangers are used as electrical conductors and the heat conducting collars which are electrically insulated from the water tubes also conduct electricity from a N type piece of thermoelectric material to a P type piece.

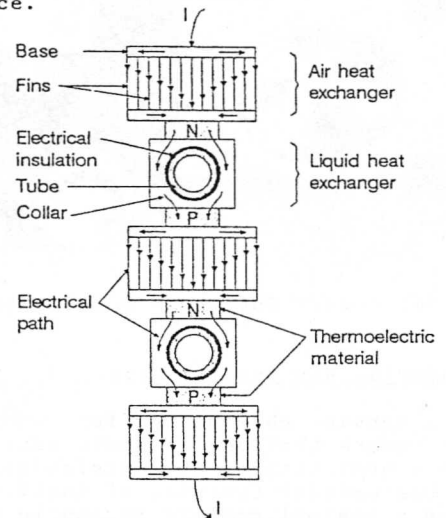


Fig. 14 Schematic of electrical path through heat exchangers for large systems

The electrical current exits from N type material on the cold side and it enters the P type material also on the cold side. This is why along the electrical path, there is alternately N and P type material.

The cooling power from a piece of thermoelectric material (thermoelement) is proportional to its cross section and to the current density, typical values are :

- . cross section :  $150 \text{ mm}^2$
- . current density :  $1 \text{ A/mm}^2$

#### 5.2.2. Thermoelectric material configuration

For large systems in excess of 10 kW one uses thermoelements (each piece is of  $150 \text{ mm}^2$ ). For smaller systems in the kilowatt range one uses polarized modules instead of thermoelements.

A polarized module is an array of n couples (N + P) with an extra piece (N or P) that determines the polarity of the module. The photograph below shows these 2 configurations besides a traditional thermoelectric module that has 2 ceramic plates on the lower and upper surfaces.

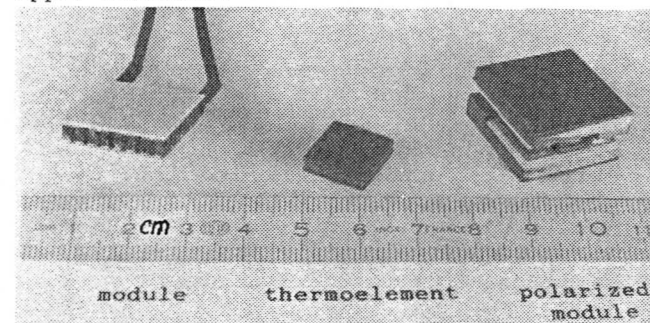


Fig. 15 Photograph of one piece of thermoelectric material (thermoelement) between a thermoelectric module and a polarized module.



The technology depends on the type of fluid (gas or liquid) of the heated side and of the cooled side, so a description is given for the 3 combinations of gas and liquid.

### 5.3. Building block concept

The three configurations all use the building block concept, an example is shown below in Fig. 16 where a water-air block shows one with a liquid and with a gas. The air-air and water-water building blocks use the same concept except that the heat exchangers on the 2 sides of the thermoelectric material are similar.

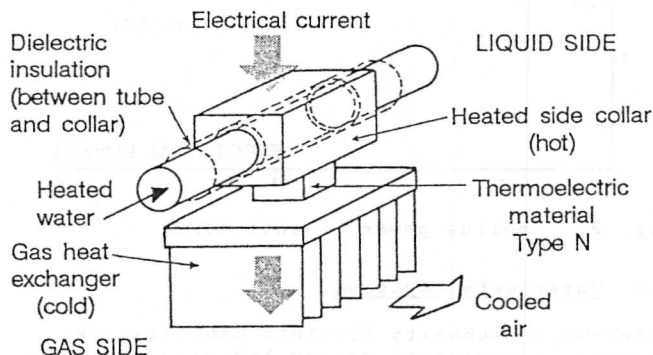


Fig. 16 Building block

Each liquid building block "uses" a small length of the tube upon which a thermally and electrically conducting collar is tightly fixed, in fact the blocks are assembled onto Continuous Insulated Pipes (CIP) which support the other components. This technology for a liquid circuit is extremely robust and reliable.

Adjacent air heat exchangers are positioned by a seal, as shown in the photograph below for air-air subunits.

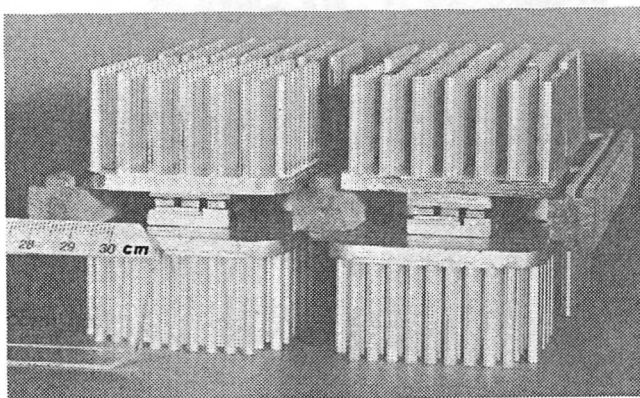


Fig. 17 Photograph of buildings blocks with pin type air heat exchangers

## 6. SUBUNIT DESIGN

Subunits can be tailored to specific applications by using standard components. in certain cases where the constraints are very specific it can be necessary, to obtain a maximum optimization, to design special heat exchangers.

### 6.1. Air-air subunits

Several types of air heat exchangers are standard. A typical subunit is PR2 which is shown below in Fig. 18

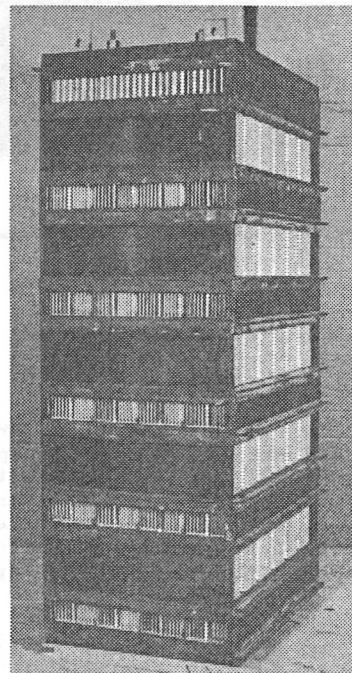


Fig. 18 Air-air PR2 subunit

This subunit is for a system using cross flow, this is generally found preferable to counter flow, because the air ducting is simpler.

### 6.2. Water-water subunits

The standard subunit PE925 has a tubing with a inner diameter of 17 mm ; Its dimensions are 850 x 250 x 310 mm and it weighs 52 kg ; A photograph is shown below.

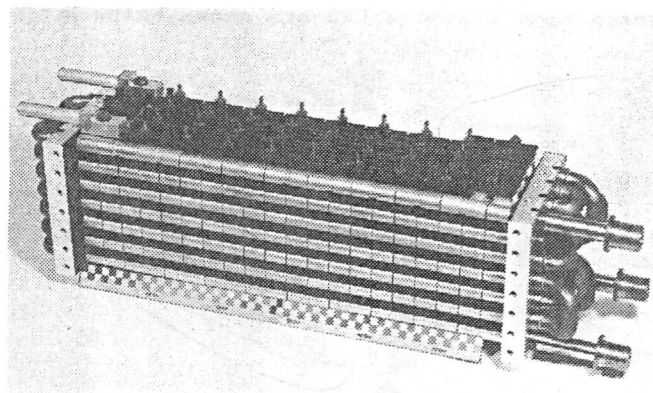


Fig. 19 Subunit PE925

6.3. Water-air subunit

The subunit EA504 uses standard components of the previously described subunits, the dimensions are 480 x 510 x 170 mm and it weighs 34 kg ; A photograph is given below.

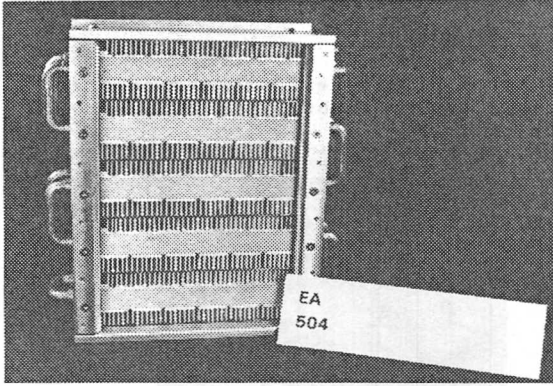


Fig. 20 Subunit EA504

7. MEDIUM AND LARGE SYSTEMS

The medium systems are from 1 to 10 kW and the large systems from around 10 kW upwards. In practice, the authors distinguish the borderline by the thermoelectric material. When polarized modules are used we are in the medium range and when thermoelements of 1.5 cm<sup>2</sup> are used one is the large range.

A medium system will have just a few subunits, while a large system generally consists of many subunits that are grouped into units or cabinets.

Cabinets are connected with their fluid circuits in parallel. Their electrical circuits are preferably in parallel but often they are grouped together in sets of 2, 3 or 4 in series electrically so that the operating voltage can be of several hundred volts.

Some typical examples are given below.

7.1. Air-air system

A group of 4 subunits PR2 are shown below.

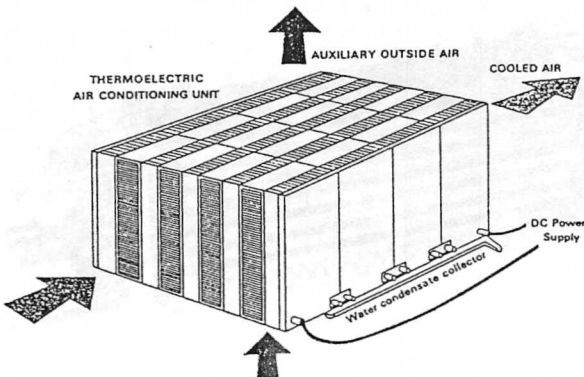


Fig. 21 Air-air unit 4TPR2

The air to be cooled (or heated) goes from left to right and the air from the auxiliary heat sink goes from bottom to top.

The cooling power is given below as a function of the electrical input power.

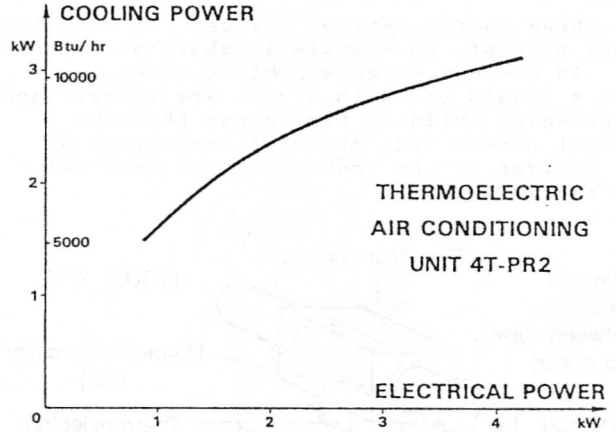


Fig. 22 Cooling power of unit 4TPR2

7.2. Water-water systems

Water-water subunits fit into cabinets like drawers. A practical design has plug in electrical connections at the back, with the water connections in the front. A photograph of a prototype cooling cabinet with 10 subunits is given below.

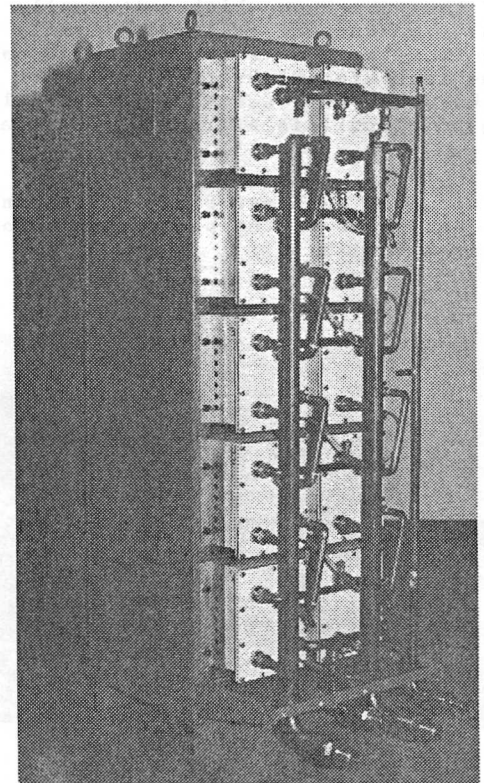


Fig. 23 Photograph of thermoelectric water-water cabinet 10T925

This cabinet is 600 mm wide, 870 mm deep and 1800 mm high.



The fluid circuitry between subunits depends on the water flow rates and the required temperature differences between inlet and outlet of each circuit. A typical configuration, is the one shown in photograph Fig. 23 where the cold water circuit consists of 2 circuits in parallel each one having 5 subunits in series. The auxiliary circuit (heated circuit) consists of 5 circuits in parallel with on each circuit 2 subunits in series.

Cabinets can be tailored to a wide variety of dimensions.

The cooling performances for producing chilled water at 20° C and 30° C for cooling electronics as a function of the heat rejection loop's inlet temperature are given below fig. 24.

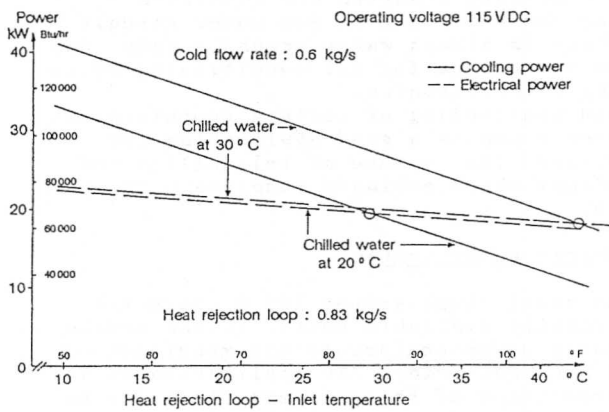


Fig. 24 Thermoelectric water chiller 10T925 performances for electronic cooling.

### 7.3. Water-air system

When the cooling power is in the kilowatt range, a single subunit is installed in a

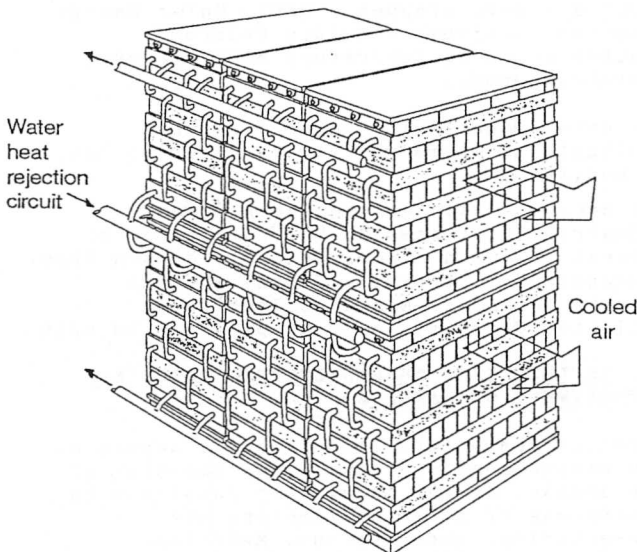


Fig. 25 Air-water unit for air conditioning.

caseing, for large cooling powers subunits can be arranged in parallel and in series. The air cooling system shown in Fig. 25 has 2 circuits in parallel and each circuit has 3 subunits in series. Such a unit has a nominal cooling power of 15 kW.

### 8. WHEN DO THERMOELECTRICS PREVAIL

For very small cooling powers such as those for spot cooling of electronic components, thermoelectrics is the ideal solution. When the cooling powers reach up to 50 W, thermoelectrics is still often the most economical solution.

When the cooling powers are between 50 W and 1 kW, a thermoelectric system is competing generally with compression cycle system using a Freon. In this range, thermoelectric systems are often more costly and are always less efficient (require more electrical power) than compression cycle systems, so thermoelectric system will only be retained if some other characteristic or characteristics prevail.

For large systems, compression cycle systems are always more economical than thermoelectric systems. At the nominal rating thermoelectric systems are less efficient than compression cycle systems. In this range a thermoelectric system is only valid if it presents one or more important advantageous characteristics.

#### SPECIFIC ADVANTAGES OF THERMOELECTRIC SYSTEMS

The following characteristics constitute under certain circumstances a prevailing reason to choose thermoelectrics.

##### - Redundancy and reliability

For high reliability compression cycle systems require a complete back-up unit. A thermoelectric system is consisted of subunits, should one or two fail it can be short circuited with a loss in cooling power that is about half the ratio of short circuited subunits to the total number of subunits.

Thermoelectric systems are basically static so have high MBTF's for example Air Industrie's thermoelectric air conditioning on a passenger railway coach has an MBTF in excess of 500 000 subunit-hours.

##### - Flexibility of operation

A general characteristic of compression cycle system is that the COP decreases as the cooling power is reduced ; On the other hand thermoelectric systems have two very important characteristics :

. when the cooling power is reduced the COP increases. Generally when the cooling power is below 50 % of the nominal thermoelectric systems are more efficient (higher COP) than compression cycle system.

. when the operating voltage is double the nominal voltage, the cooling power can increase by 30 to 50 % . This is a tremendous advantage when extra cooling is required.

## - Transient mode

Thermoelectric systems have little thermal inertia, also as, it has just been indicated, the voltage can be considerably increased : the time to reach steady state operation can be divided by 2 compared to a compression cycle system.

## - Quietness and safety

Thermoelectric systems having no moving parts, except for pumps and fans are by concept very quiet. They contain no thermal compression fluid that can constitute a health hazard.

## 9. DEVELOPMENTS AND PROTOTYPES

First developments which are taking place with thermoelectric materials that are commercially available are presented. then the influence of better thermoelectric materials on the developments of thermoelectric system will be examined.

### 9.1. Small cooling and electricity generating powers

There is a continuous flow of new components or equipments that require cooling. The markets are in many areas.

For medium and large systems it is convenient to classify applications by the fluids (liquid or gas) that are used on the cooled and heated sides.

### 9.2. Air-air systems

In the 500 W range interesting development is being done on the air-conditioning for breathing masks (Midwest Research, Kansas City, Missouri, USA). The main advantages are reliability and flexibility of operation.

Also in this range would be the cooling of mobile carts for transporting food or medications,, etc...

In the 1 kW range cooling, electronic cooling represents an important future market. Equipments are already commercially available but above 1 kW it is all in the prototype stage (TNEE - Air Industrie, Rueil Malmaison, Hauts de Seine, France).

Humidity control for specific environments is an area of development. A typical example is where paper is manipulated because paper is very hygroscopic.

Biological environments can be easily controlled by thermoelectric systems. The advantages are reliability and reversibility (heating and cooling).

Electronic shelters that are isolated require highly reliable electricity generation and cooling. Thermoelectric electricity generators have been developed and commercialized for this application. The choice of cooling depends on the availability of electric power.

Military vehicles under certain environments require air conditioning ; Thermoelectrics which is very robust has been examined and continues to be for this application.

Railway locomotives often require air-conditioning. Thermoelectrics in the most robust cooling equipment that can operate with high outside temperatures in excess of 55° C (TNEE Air Industrie).

Earth moving equipment can use the same type of thermoelectric equipment.

A passenger railway coach has been in operation for 10 years with thermoelectric air conditioning (TNEE Air Industrie). This market is being explored and thermoelectrics is interesting in temperate climates, especially as it heats and cools the coach.

### 9.3. Water-air systems

In the small range there are medical applications such as heating and cooling pads (Marlow Industries Inc, Dallas, Texas, USA).

These systems can be used either to cool air or to cool water. Navies are interested because the water can be sea water circuit and there is always water around a ship. The cooled air can be for air conditioning or the cooling of electronics. On land the cooling of certain computers and computer rooms is a good application for thermoelectrics because of reliability and redundancy which avoids a complete back-up system.

### 9.4. Water-water systems

In the small range around 100 W there are commercially available units. In the medium and large power equipments are manufactured (TNEE Air Industrie). The application is for the production of chilled water that can be used for many purposes (electronic cooling, air conditioning).

### 9.5. Large scale electricity generation

Ten years ago many Universities, Research Institutes and Companies were very interested in electric power generation using the thermal gradient in the sea. It is called Ocean Thermal Energy Recovery (OTEC).

Today all have stopped : SERI (Solar Energy Research Institute - Golden Colorado), Electrotechnical Laboratory MITI (Sakura, Ibaraki, Japan).

The developments will serve for other applications where waste warm (liquid) heat is available.

The area of waste gaseous heat from industrial processes is being examined by several research organizations : Nippon Steel (Nakahara-Ku; Kawasaki, Japan) and the Georgia Technical Research Institute, (Atlanta, Georgia) is developing a 5 kW unit.

## 10. INFLUENCE OF THERMOELECTRIC MATERIAL IMPROVEMENT ON MARKETS

Material characterization results depend on the measurement procedures and the size of the sample. In the laboratory samples with dimensions of a few millimeters are characterized under vacuum. Material manufacturers like to characterize assemblies of couples when the element size is of the order of 1 mm. Equipment manufacturers of

large system need to characterize samples of 1.5 cm<sup>2</sup>. These three procedures give different results : the laboratory results on samples of several mm are generally about 10 % higher than those measured in ambient air on samples of 1.5 cm<sup>2</sup>.

Thermoelectric material characteristics of pieces of 1.5 cm<sup>2</sup> vary quite considerably (7). Sintered material can be manufactured with a dispersion of material characteristics of less than  $\pm 5\%$ . Polycrystalline material varies considerably between manufacturers and also between ingots from the same manufacturer. In one ingot the coefficient of merit Z can vary up to  $\pm 10\%$  and between ingots up to  $\pm 20\%$ .

The authors have seen two trends over the past ten years. The first is that the dispersion between production batches is decreasing which leads us to state that quality control has considerably improved over the years.

The second trend is that the average coefficient of merit Z for thousands of pieces of 1.5 cm<sup>2</sup>, has increased regularly over the years to reach  $Z = 2.5 \cdot 10^{-3} \text{ K}^{-1}$

Every few years breakthroughs are announced, sometimes concerning new thermoelectric materials, sometimes concerning bismuth telluride, but so far nothing has materialized.

Basic work is now being done on bismuth telluride, it seems that it is possible to master the final composition for crystalline material and also to control the crystal quality. The authors believe that a 20 % improvement in the Z factor may be obtainable within a year or two. Any further extrapolation is hazardous but it does seem that with a continued effort in the understanding of the undoped, then of the doped material, future improvement up to around  $Z = 3.5 \cdot 10^{-3} \text{ K}^{-1}$  is feasible.

The improvement in Z will open up the markets in two ways :

- first it will increase the market for a given product by making the equipment more performing and more economical

- secondly it will open up new applications because with the prior performances the equipment was not competitive with other processes.

The first step will be accomplished already with materials of  $Z = 3.0 \cdot 10^{-3} \text{ K}^{-1}$ . The second step will start when Z exceeds  $3.2 \cdot 10^{-3} \text{ K}^{-1}$ .

In large systems especially the values of the 3 material parameters  $\rho$ ,  $s$  and  $k$  for a given value of Z are very important and certain values of  $\rho$ ,  $s$  and  $k$  always at the same Z can increase the performances by 10 or 20 %.

## 11. CONCLUSION

Small thermoelectric systems (cooling and electricity generation) are in a regularly expanding market as they are used in more and more areas.

The main advantage is that thermoelectric system are simple and reliable.

Medium size cooling systems of 500 W or more are now commercially available.

Some large systems are going into series production in military areas where one or more of the specific advantages of thermoelectric cooling systems are the prevailing factors in choosing thermoelectric.

The medium range between 1 and 10 kW constituted a gap for lack of viable technology ; The gap can be filled by using a technology developed for large systems with polarized modules because it is a rugged technology with good performances.

More and more medium and large systems will be installed as the specific advantages of thermoelectric systems are recognized. The thermoelectric material improvements that are seen for the next few years will increase existing markets and open up new ones.

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