

MODERN THERMOELECTRIC COOLING TECHNOLOGY

JOHN G. STOCKHOLM
11 rue du Bellay, 78540 Vernouillet, France.

ABSTRACT

The technology of thermoelectric systems with cooling powers of 1 kW or more has evolved considerably over the past 30 years. A review based on patents and some published documents is given for the period 1960-1985 and present day technologies are described. The fundamentals and the technologies for subunits and systems are given. Areas for potential improvement are examined.

1. ONE THERMOELECTRIC MODULE TECHNOLOGY

The greatest number of thermoelectric cooling applications use one single module. The module is single or multiple stage. The technology is simple, the hot side can be soldered, epoxied or compressed with a thermal grease onto the heated sink. The cold side carries the object to be cooled, a structure sometimes compresses the module.

2. LARGE POWERS-GENERAL RULES

2.1 Orders of magnitude.

The thermoelectric material used since the late 1950's is bismuth telluride, the thermoelectric properties have slowly improved but the orders of magnitude are unchanged. Below are some basic facts concerning the three main aspects: thermal, mechanical and chemical:

2.2 Thermal

- cooling power: 2 to 3W per cm² of thermoelectric material
- current density through the thermoelectric material: 1 A per mm²
- typical temperature difference across thermoelectric material: 30°C.
- typical temperature drop between air (2.5m/s) and the cooled side of the thermoelectric material: 4°C; 8°C on the heated side.
- typical temperature drop between water and the cooled surface of the thermoelectric material 2°C; 4°C on the heated side.

2.3 Mechanical

Thermoelectric material has mechanical properties like those of concrete, it has a very low resistance to traction, shear and bending, but it holds up very well to compression. To hold up to shear and bending it must be under compression.

2.4 Chemical

Thermoelectric material is easily poisoned, by elements such as copper and silver. It deteriorates in the presence of water or water vapor, this means that the interfaces of the thermoelectric material must have diffusion barriers to protect them. The volume that contains the thermoelectric material must have a vapor barrier to stop water and water-vapor from reaching the thermoelectric material and its interfaces, copper oxides can build up around a diffusion barrier and deteriorate the thermoelectric material.

3. LARGE POWERS- REVIEW 1960-1985

The technological contributions of the pioneers originate in ideas that are transmitted by patents in papers that are published and in equipments that are built and operated.

Many companies were involved in thermoelectrics in the early sixties an excellent review covers this period. Lynch, 1972 .

There were many inventors with many very interesting ideas, as always many inventors were unable to make even a small unit using their idea because some detail is flawed in that some technological requirement could not be met. These flaws were only known sometimes only many years later. Some of the ideas are reviewed further on.

3.1 Technology from patents

The following short list of inventors, has to leave out many important ones. When dealing with thermoelectric ceramic modules the technology innovations are few, because the electrical circuitry is independent of the heat exchangers. For large systems the use of the heat exchangers to conduct the electrical current leads to many technological ideas.

The most prolific of inventors in thermoelectrics was Elfving who filed over 15 different patents. There are many people who just filed a few, but of importance because they influenced the trend of integrating the thermoelectric material to the heat exchangers. They are Lindenblad of RCA; A.B. Newton of Borg Warner Corp.; C. J. Mole of Westinghouse Corp.

To present some of the ideas it is convenient to classify them by fluids categories: gas-gas, then when there is a liquid there are two basic types, so we present two other categories: those that use a discontinuous tube and those that use a continuous tube . Patent drawings are oriented towards shapes and assembly so the mechanical aspects are predominant. thes are outlined above in 2.3

Gas-gas:

Newton: Assembly of alternating hot and cold heat exchangers that form a cubic type structure as opposed to a planar type structure.

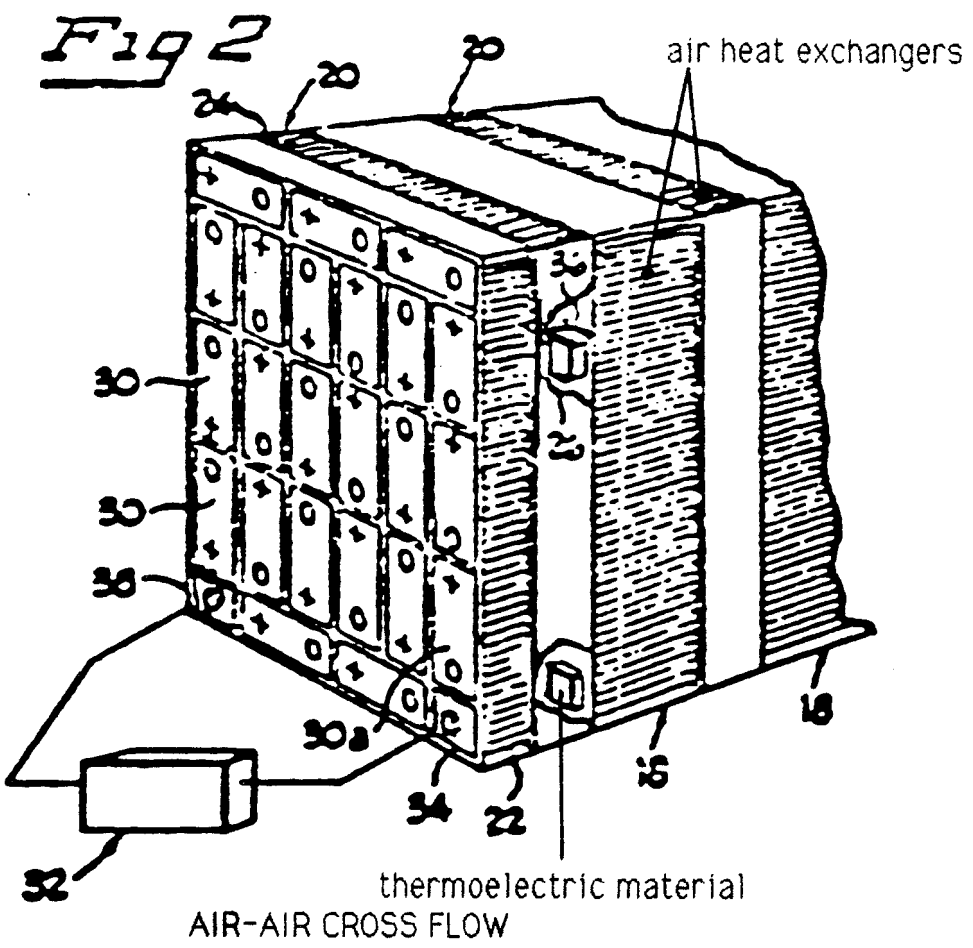


Fig.1 Newton (York Div. of Borg Warner) patent DE 1,801,768 (1967)

Cohé (Westinghouse) : patent US 3,626,704 is on an assembly of alternating hot and cold heat exchangers that are compressed together by wires to form a cubic type structure, no drawing is necessary.

The Newton and Cohé patents constitute the base of air-air subunits for large systems where large pieces of thermoelectric material are used and the electrical current goes through the air heat exchangers.

Gaudel: Cubic type structure with compressed thermoelectric material

Fig.1.

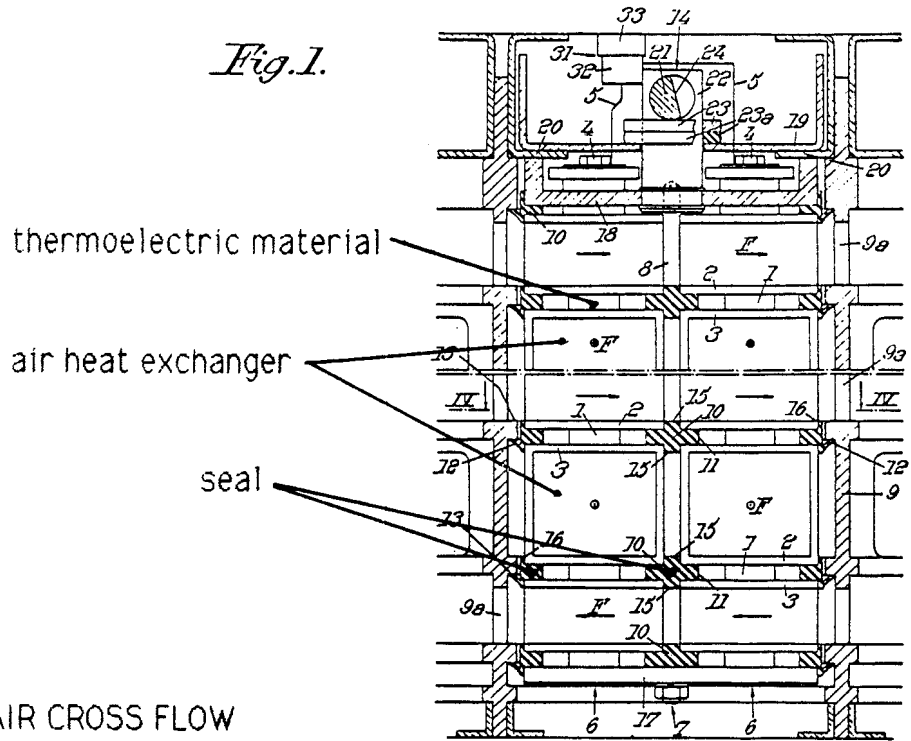


Fig 2. Gaudel (Air Industrie): patent US 4038831 (1977)

Mole: Planar structure.

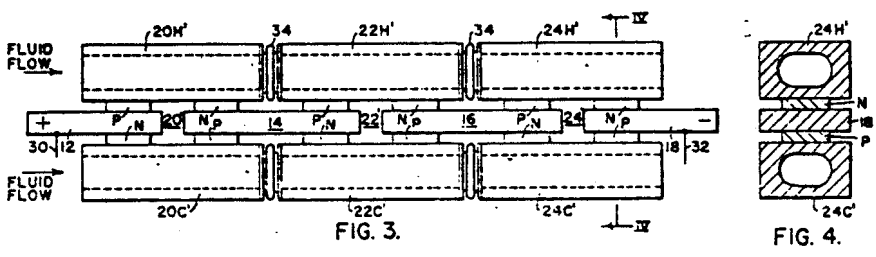
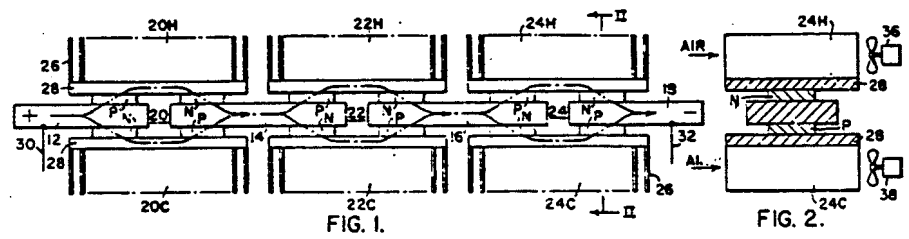
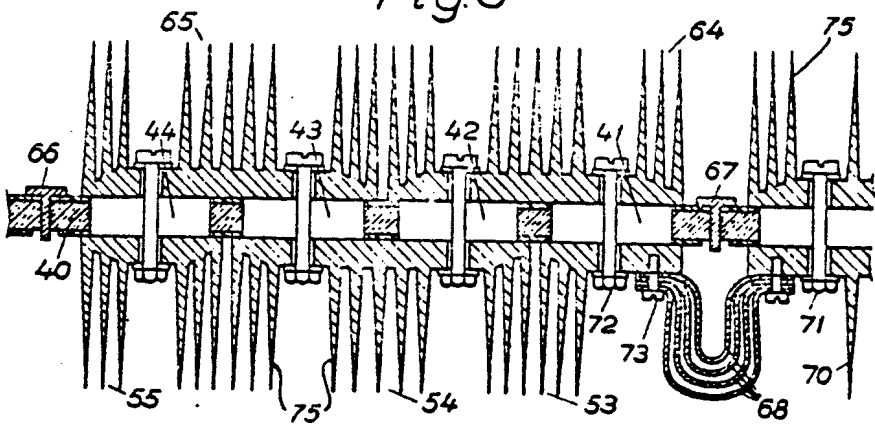


Fig.3 Mole (Westinghouse): Patent US 3,500,650. (1970)

Two pieces of thermoelectric material are in parallel on the electrical circuit, an original design of a 2 stage thermoelectric cooler.

Widakowich : planar structure that uses thermoelectric material that is capped with little pieces of copper.

Fig.3



AIR-AIR PARALLEL FLOW

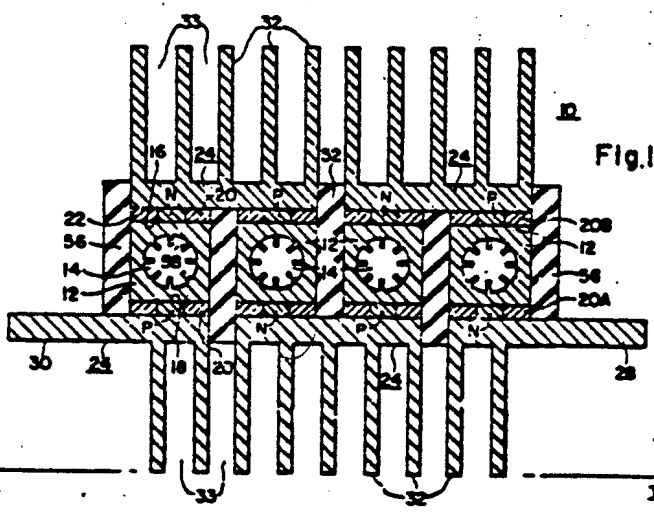
Fig 4. Widakowich (A.S.E.A.): Patent US 3,726,100. (1973)

This patent is interesting because a prototype unit was built on this design by ASEA for the air conditioning of a railway coach of the Swedish railways. The unit was in operation for several years around 1970.

DISCONTINUOUS TUBE TECHNOLOGY:

When the electrical circuit is in direct contact with the water, the majority of the patents are Westinghouse.

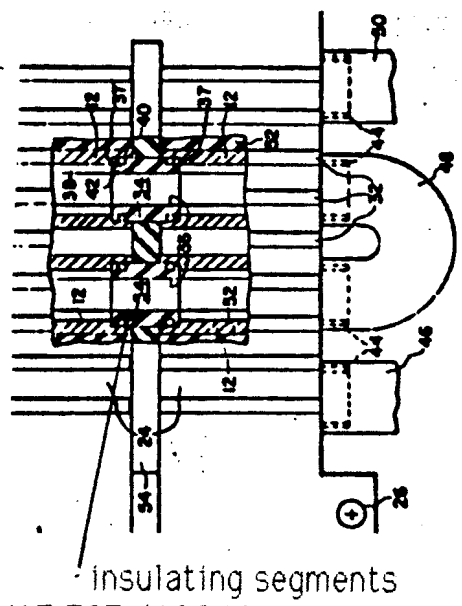
Wepfer: Segments of tube joined by an electrically insulating material.



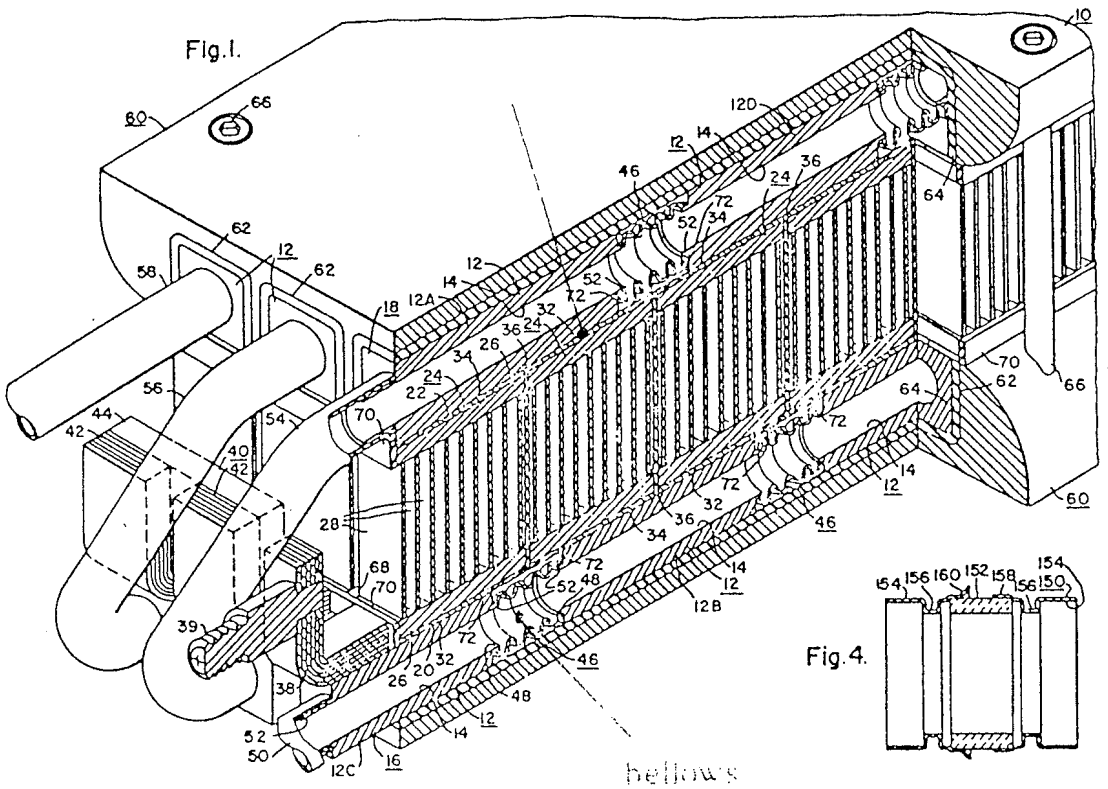
AIR-WATER PARALLEL FLOW

Fig. 5 Wepfer (Westinghouse) : Patent Fr 1,417,727. (1964)

The segmented water tubes are square on the outside for ease of interfacing with the thermoelectric material.



insulating segments



AIR-WATER CROSS FLOW

Fig. 6 Mole (Westinghouse): Patent US 3,178,895. (1965)

This drawing shows the basic concept of the discontinuous tube technology with bellows.

Elfving: Segmented planar water-air structure

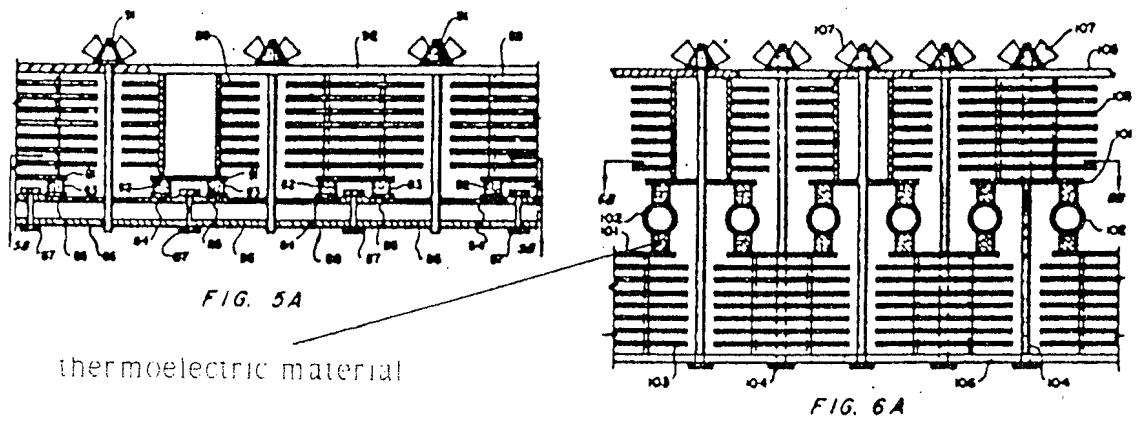


Fig. 7 Elfving Fr 1 541 999 (1967)

The drawing shows the principle of the tightening mechanism. The tubes are segmented.

Elfving: Water-air structure with segmented water tubes and finned tubes for the air heat exchangers.

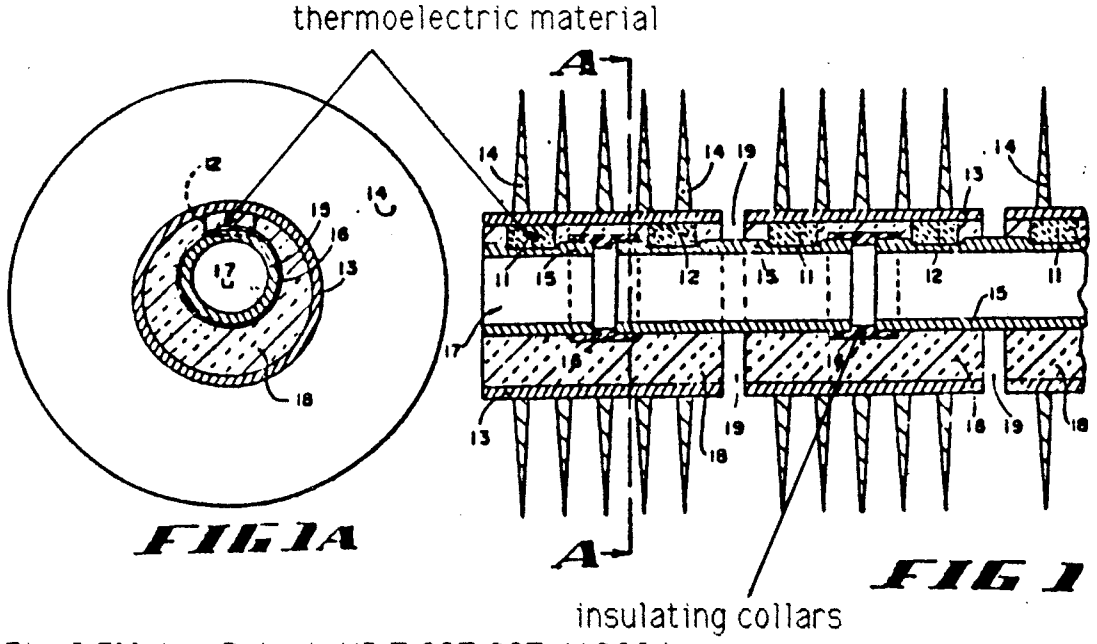


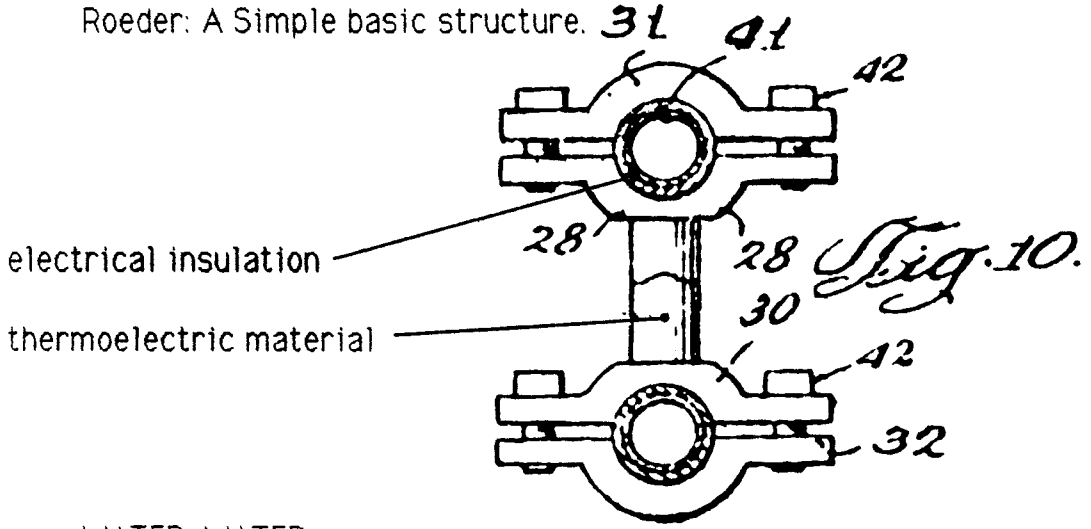
Fig. 8 Elfving: Patent US 3,287,923. (1966)

This concept can be the basis for some new ideas because finned tube air heat exchangers are easy to seal.

CONTINUOUS TUBE TECHNOLOGY

This concept requires that the water tube be electrically insulated from the electrical circuit.

Roeder: A Simple basic structure.



WATER-WATER

Fig 9. Roeder (Whirlpool): Patent US 2,947,150. (1960)

This drawing shows the electrical insulation on the tube and the simple means for tightening the heat conducting collar.

Rich: Planar structure.

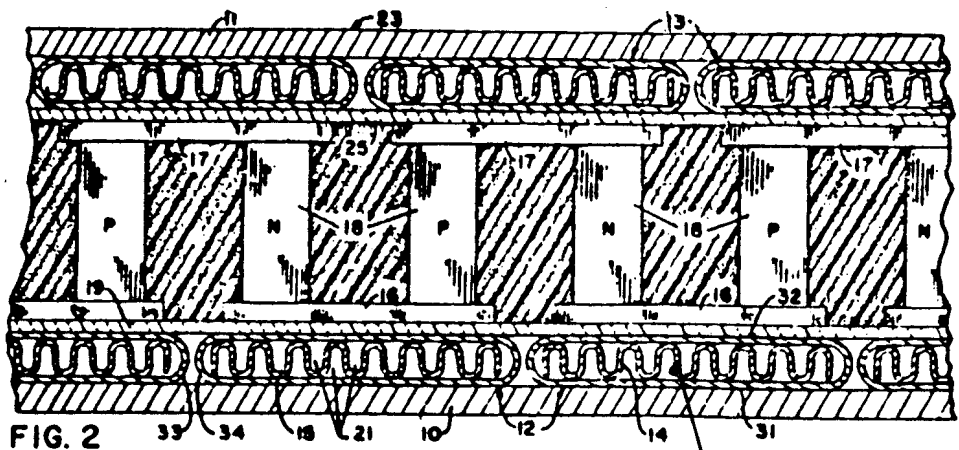


FIG. 2

WATER-WATER

flat water tubes

Fig 10 Rich (Carrier Corp.) Patent US 3,006,979 (1961).

Flat tubes are used with interior reinforcement so as to hold up well to compression. The water tubes are insulated from the electrical circuit.

Benicourt: Multilayer structure.

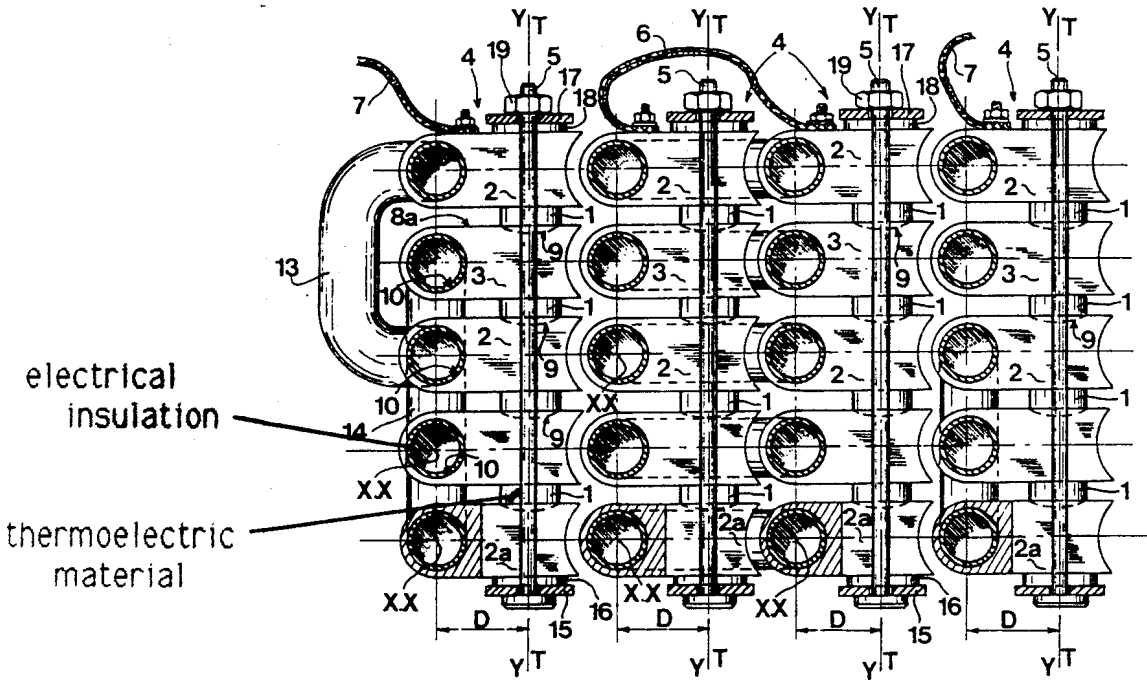


Fig. 2

Fig 11. Benicourt (French Navy) : Patent US 4 499 329 (1985)

The collars are electrically insulated from the continuous tubes and the thermoelectric material is under compression.

The main companies involved in large systems who have contributed to the development of thermoelectric technology are RCA, Whirlpool (Sickert, 1960), Carrier, Borg Warner, Westinghouse and Air Industrie.

3.2 Technology from published documents

Radio Corporation of America (RCA):

This company was the pioneer, but they realized early on, that the expectations concerning thermoelectric material properties, that would lead to systems with performances that would be, on par, with compression cycle systems, eg Freon systems would not materialize in a foreseeable future.

Carrier Corporation:

This company worked on naval applications. Hudelson, 1960. They built in the mid 1960's a thermoelectric air conditioning system for the headquarters of Johnson S C in Racine Wisconsin. The system consisted of about 30 decentralized air conditioning units with heat rejection to a water circuit. I visited the installation in 1973, the system was operating, the problem was the non availability of spares, especially concerning the power supply and controls, so several of the units were not in operation.

Unfortunately Carrier Corporation were unwilling to talk about the system because after completion of the system, they had decided to stop this activity.

Borg-Warner Corporation:

This company was very active, but published practically nothing, so it is very hard to know all that they did. Newton, 1965. Their main activity was in small compact systems that used ceramic thermoelectric modules. The York Division with A. B. Newton was very active in the R and D field for large systems using large thermoelectric pieces between electrically conducting air heat exchangers.

Westinghouse Corporation:

This company has been the most active over the longest period of time. They pioneered the large systems with large thermoelectric pieces integrated to the heat exchangers. The air-air structures with a wire to compress the thermoelectric material remains the best concept. They developed systems where the water circuit consists of electrically and thermally conducting blocks that transfer the heat efficiently to the water but have the drawback of putting the water in contact with the electrical circuit. Mole, 1968; Mole, 1972.

Air Industrie:

This company was a late comer to thermoelectrics having only started in this area in 1973. The company started by developing and building an air conditioning system for a passenger railway coach that is in daily operation today after over 10 years of operation without a single thermoelectric failure. Stockholm, 1982. In 1985 they brought out a large scale water-water system for naval applications. Stockholm, 1988.

3.3 Contributions from the 1960-1985 period

The most important contribution is of no doubt the performance stability of bismuth telluride for periods well in excess of 10 years. This statement must include that this is on the condition that the thermoelectric material is properly interfaced with adequate diffusion barriers and that the mechanical stresses on it from the system, are compatible with the thermoelectric material and its interfaces.

The ceramic thermoelectric module technology that was developed in the 1960's, when installed correctly, is now a proven reliable product. It saves the user from having to be concerned about the direct interfacing of the thermoelectric material, the user must follow the thermal and mechanical supplier's instructions on the installation of the module.

The integration of large pieces of thermoelectric material directly to the heat exchangers and using these to conduct electricity from one piece to another is now a proven technology.

- For air systems it is very practical.

- For liquid systems there are two different technologies, one is to put the electrical circuit directly in contact with the water, which does create problems and the other is to electrically insulate the electrical circuit from the water tubing so that the tubing can be grounded.

4. FUNDAMENTALS

The design of large systems requires that the fundamental thermal aspects be studied in great detail, so as to obtain good performances; But the following areas, that are so often neglected, must also be carefully studied: thermoelectric material interfacing and shear stress, sealing techniques and liquid circuitry.

4.1 Thermal aspects

This topic is covered in detail in thermoelectric books. Heikes, 1961 and in heat transfer books. The fundamental rule is to reduce all temperature differences between the thermoelectric material and the working fluids. (paragraph 2.2) One must also keep to a minimum parasite heat transfer that goes directly from the cold side fluid to the hot side fluid, bypassing the thermoelectric material, and heat to the outside.

4.2 Structural aspects

The mechanical properties of thermoelectric material require that the structure satisfy two requirements: Allow levels of compression in excess of 5 MPa on the thermoelectric material , while keeping the shear stress on the thermoelectric material to levels well below 5 MPa.

The shear stress comes essentially from the difference in thermal expansion of the hot side and the cold side heat exchangers. The segmentation of the heat exchangers makes it easy to install between the heat exchangers components that will take up the thermal expansion.

- For air heat exchangers an elastic seal is an efficient way of absorbing any thermal expansion parallel to the interface of the thermoelectric material.

-For liquid heat exchangers, there are several techniques: compressible material, bellows and "O" Rings. The drawback of having segmentation on a liquid circuit is the the circuit's water tightness reliability decreases.

The compression on the thermoelectric material ensures that the soldered interfaces between the thermoelectric material and intermediate parts (caps), or directly onto the heat exchangers, do not separate, because separation leads to high electrical resistance and to arcing.

4.3 Thermoelectric material interfacing

There are several alternatives each one with advantages and disadvantages

4.3.1 Direct soldering to the heat exchanger. This gives the lowest thermal and electrical interface resistances, values are in the order of:

- electrical interface resistance = 10^{-11} ohm*m² (0.1 microhm*cm²)
- thermal interface resistance = 10^{-6} K*m²/W (0.01K*cm²/W)

4.3.2 Pressure contact at interface. It is very difficult to get a reliable low resistance interface directly on the surface of the thermoelectric material, a thin foil of indium has been used, but it is an

expensive metal.

An efficient way is to solder onto the thermoelectric material copper or aluminium caps. A diffusion barrier, for example nickel must be in between the thermoelectric material and the caps as copper is a notorious poison for bismuth telluride alloys.

The outer surface of the caps can be flat (plane), a sphere or a cylinder. When the interface must conduct heat and electricity, a silver based silicone grease is used. The interface resistance varies considerably with pressure. When the pressure is below 0.5 MPa then the dispersion of the resistance values can be several fold, so in practice it is necessary to have interface pressures in excess of 1 MPa but the interface resistances are 10 times greater than with a soldered interface;

- electrical interface resistance = 10^{-10} ohm*m (1 microhm*cm²)

- thermal interface resistance = 10^{-5} K*m²/W (0.1 K*cm²/W)

When the interface consists of two coaxial cylinders or two concentric spheres then the above values increase considerably with the difference in radii of the two interfacing parts. There will always be a small difference in radius because of the manufacturing tolerances. The above interface resistances given for planes will increase by 50 to 100 % when the interfaces are cylindrical or spherical and the difference in radii is of the order of a percent.

4.3.3 Choice of interfacing. The choice depends on design compatibility and on quality control.

Design compatibility:

- 1) There must be the physical possibility of soldering in situ the thermoelectric material to one or both heat exchangers.
- 2) The shear stress at the interface must be below 5 MPa

Quality control of the individual pieces of thermoelectric material:

Pieces of thermoelectric material with metallic caps are easy to quality control. Electrical resistance is an important parameter and we have found Stockholm, J. 1985 that on an ingot (polycrystalline material) or batch (sintered material) basis, the Seebeck coefficients and the thermal conductivity can be measured on a sample basis , on the condition that pieces are chosen with electrical resistances at the high end and at the low ends of the resistance range. The correlations are linear in the ranges encountered for one ingot or for one batch.

In many cases it appears that the caps do protect somewhat the thermoelectric material

Direct soldering is more compact, because it avoids intermediate

parts however small, but quality control of the soldering is generally very difficult.

4.4 Air sealing technology

The thermoelectric material must be reliably sealed from the air circuit especially when the cooled air produces condensation, as is the case in air conditioning. there are two types of structures: planar and annular.

4.4.1 Gas-gas. The layered structure makes sealing relatively easy. The best technology for gas-gas systems is the multilayered, cubic type structure.

4.4.2 Gas-liquid. In the case of gas-liquid, there are two types of structure. the sealing is different for each type.

a) Planar design

A planar structure is relatively easy to seal, for compactness a multilayered structure is the best.

b) annular design.

An annular design where the water tube is in the center and an outer cylinder has the fins, is practically impossible to seal if the outer cylinder is in two half cylindrical shells.

When the outer cylinder is a complete cylinder but segmented axially, then the sealing can be done by "O" rings. the difficulty in this case will reside in putting the thermoelectric material into place and in some instances soldering it in situ. This is another area for development

4.5 Liquid circuitry

There are two factors that have an influence on the choice of the liquid circuitry, the first is that liquids and especially water tend to **degas**, which creates air pockets so the number of high spots in a system should be kept to a minimum. The other factor is that the geometry of the air circuit should be such that the condensation can be eliminated by gravity

4.5.1 High spots. When tubes are vertical there is a high spot for each one, this is not acceptable, so tubes must be horizontal. A layer of horizontal tubes may be in a horizontal or in a vertical plane. The configuration with horizontal planes leads to the minimum number of high spots, this layout is chosen for liquid-liquid systems. For gas-liquids systems we will examine two configurations: parallel and cross flow.

4.5.2 Liquid-gas systems. In the case of liquid-gas systems, there are other constraints, the main one being the evacuation of condensate from the cooled air. A horizontal air velocity greater than 2.5 m/s will certainly entrain water droplets, but when the water droplets are created

they must be evacuated immediately, otherwise they can fill up the space between fins and create clogging. There are two configurations that depend on the relative flow of the air and of the water:

a) Parallel flow.

Gas-liquid systems where the two fluid flows are parallel, and the layer of tubes is vertical, then the U bends are at the inlet and the exit of the air flow. A planar structure requires that the fins be either of the pin type or perforated so that the condensate is evacuated by gravity. An annular structure is difficult because the fins that are normally radial, will be at all different angles with respect to vertical and some will accumulate water.

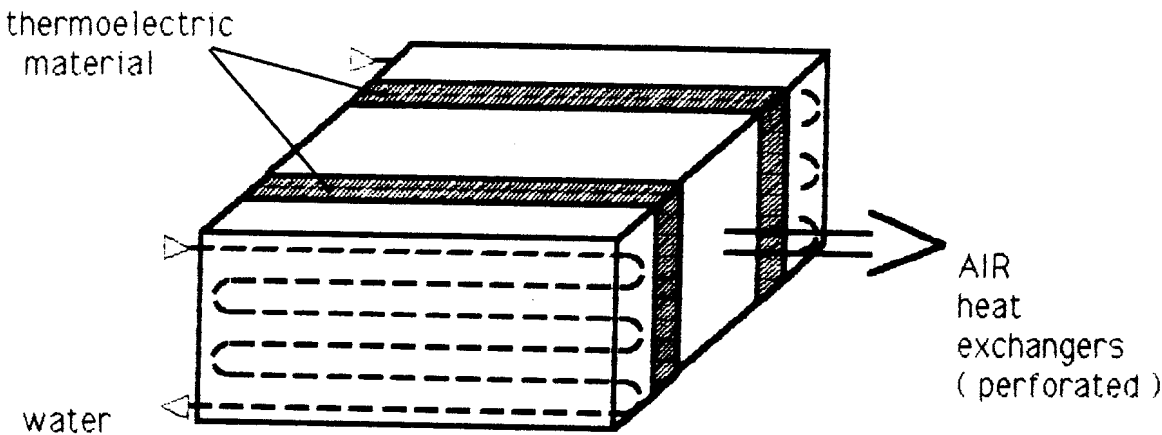


Fig. 12 Schematic of water-air subunit with vertical planes

b) Cross flow

This system with a horizontally layered structure will only allow condensate evacuation at the end of each subunit, unless an annular design is used so that the water droplets can fall between the outer tubes.

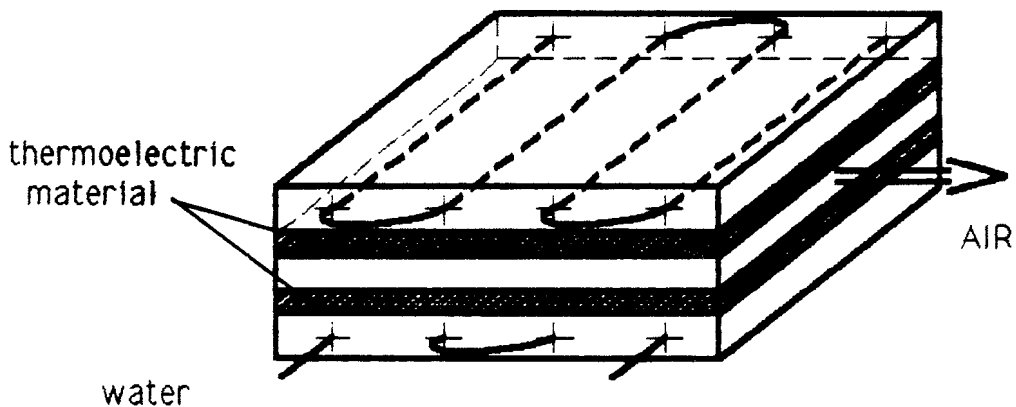


Fig.13. Schematic of water-air subunit with horizontal planes

5. SUBUNIT TECHNOLOGY

The technologies are classified by the combination of fluids.

5.1 Gas-gas.

The most efficient susystem is a cubic structure. Westinghouse manufactured in the 1960's subsystems consisting of columns of 2*2 individual air heat exchangers per layer, tightened by a wire. Air Industrie in the 1970's developed subsystems with layers of 6*4 individual air heat exchangers per layer, with up to 10 layers of thermoelectric material.

There are different ways of interfacing the thermoelectric material as has been shown in paragraph 4.2. The seal can be a prefabricated one that can also participate in the stability of the structure, or added on after the structure is put together, in this cas it does not participate in the structure.

Condensing atmospheres require a design that allows continuous elimination of the condensate, this can be obtained with horizontal air flow and a fin configurationn that does not stop the water drops from falling out by gravity.

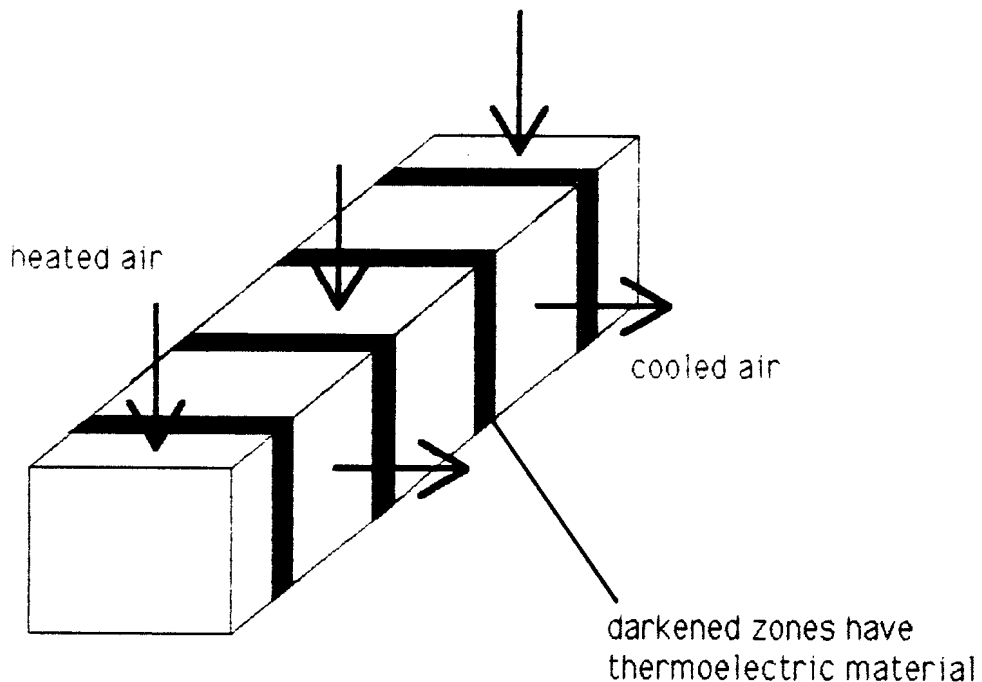


Fig.14. Air-air subunit

5.2 Liquid-liquid

There are several levels of options.

5.2.1 Segmented tubes. Segmented tubes at the present time have the electrical circuit in contact with the water.

Advantages:

Direct heat transfer from the thermoelectric material to the water, without the thermal barrier of an electrical insulator. The system can incorporate easily a design that reduces the shear stress due to differential thermal expansion on the thermoelectric material.

Disadvantages:

The liquid generally water is in contact with the electrical circuit, so the voltage must be limited to several volts to reduce the safety hazard and electro-corrosion of the parts in contact with the water.

It is conceivable to electrically insulate the inside of the tube, this would enable the water circuit to be grounded and the system to operate at higher voltages. The problem is that it is very difficult to have a reliable insulating coating on the inside of a cylindrical surface and the insulation will reduce the heat transfer.

5.2.2 Continuous tubes. A large system is being built by TNEE for a naval application that has grounded continuous water tubes.

Advantages:

The tubes can be grounded and the electrical circuit can be operated at several hundred volts hence reducing considerably the amperage required for a large power system. Safety is another factor

Disadvantages:

The dielectric insulator between the electrical circuit and the outside of the **grounded water tubes** does constitute a thermal barrier. It is much **easier to insulate well** between two metallic surfaces than between a **metal and water**. Over the past few years this thermal resistance between **two metal surfaces** has been reduced to acceptable levels, following intensive R and D.

5.3 Liquid-gas

This is the biggest area for development. the first option is whether the subassembly is with a segmented or a continuous water tube.

A system is being built at the present time by Westinghouse Corporation for a naval application that has segmented tubes and two layers of thermoelectric material. The segments along the water circuit are sealed by "O" rings which also have the function of reducing shear stress on the thermoelectric material.

For large systems the future appears to lie in a continuous grounded tube technology, to enable operation at several hundred volts.

Air conditioning applications require the evacuation of condensate, there are several available designs. The most promising design for the future appears at the present time to be an annular design with a continuous grounded tube and for the air heat exchangers consisting of completely cylindrical shells with transverse fins. The problem is that at the present time no-one has come up with valid technologies for the interfacing of the thermoelectric material and to keep it under compression.

6. SYSTEM TECHNOLOGY

A system consists of a cabinet containing subunits, a power supply and controls.

The size of a subunit is generally limited by its weight, so that it can be put into place by one or two people without mechanical lifting devices, this means a mass of around 50 kg.

6.1 Built-in redundancy.

A cabinet will contain for example 8 or 10 subunits electrically in series, should one fail electrically then it can be easily electrically bypassed, while leaving the fluids going through it. Obviously if the failure is a water leak, the leak must be repaired. When a subunit is taken out of the electrical circuit and if the overall voltage on the cabinet is maintained then the remaining subunits individually see a higher voltage, so the electrical current and the electrical power increase, but the cooling power decreases much less than the ratio of 1 subunit to 10 subunits. In fact on a water-water system undergoing testing, the cooling power drops only by 3%. If the system is adequately dimensioned and the power supply has available extra voltage then the cooling power can be maintained at the expense of electric power.

6.2 Power supplies.

Thermoelectric systems require direct current, the ripple generates Joule heating so it should be reduced to a level where the effect is negligible. In practice a 5 to 10% ripple is acceptable.

The technology of high amperage (several hundred amperes) power supplies is evolving, the switching is faster, so that transformers and selfs are considerably reduced in size, compared to those operating under 50 or 60 Hz.

6.3 Control systems.

With the advent of the microprocessor, all the controls and safety controls can all be included in a small package. The transducers used to detect the presence of fluid flow should preferably be static. It is advisable to have several redundant safety measurements, for example:

air circuit:

- check on fan amperage
- physical check on air flow with a pressure drop transducer.
- maximum air temperature

water circuit:

- presence of water (by using an electrode)
- presence of water flow (pressure drop transducer, or flow detector based on two close by temperature probes).
- minimum and maximum water temperature.

electrical circuit:

- maximum operating voltage
- maximum and minimum amperage
- for grounded water circuit: periodic check of insulation of

electrical circuit with respect to ground.

7. CONCLUSIONS

In the 1960's people expected thermoelectric cooling systems to have performances equal to those of freon systems, this did not and probably will not materialize.

The reliability of the thermoelectric material and the reliability of well designed large systems has been proven.

The people in 1960 paved the way for today's thermoelectrics, all the basic ideas are now in public domain patents. But to improve performances, to decrease volume, mass and cost, there are still some ingenious technologies to be developed.

Thermoelectric cooling with its performances of today has potential uses in areas where certain advantages prevail such as modularity and reliability and it constitutes no hazard to the environment.

REFERENCES

Hudelson, G. D. 1960. Thermoelectric air conditioning of totally enclosed environments. Electrical Engineering, June 1960. pp. 460-468

- Lynch, C. J. 1972 Thermoelectricity: The breakthrough that never came. Uneven Z (M.I.T. Press), pp. 47-57
- Mole, C. J. Purcupile, J. C. 1968. Recent developments on direct transfer thermoelectric cooling for shipboard use. ASHRAE Annual meeting, Lake Placid N. Y. 1968
- Mole, C. J. Foster, D. V. Ferenchak, R. A. 1972. Thermoelectric cooling technology. IEEE Transactions on industry applications. vol1A-8 No.2, March/April 1972. pp. 108-125.
- Newton, A. B. 1965. Designing thermoelectric air conditioning systems for specific performance. ASHRAE Transactions July 1965, pp.133-147.
- Sickert, R. G. 1960. A thermoelectric refrigerating system for submarines. Electrical Engineering, May 1960, No. 5 vol. 79 pp. 364-371
- Stockholm, J. G. Pujol-soulet, L. Sternat, P. 1982. Prototype thermoelectric air conditioning of a passenger railway coach. 4 th Int. Conference on thermoelectric energy conversion. U. of Texas at Arlington 1982.
- Stockholm, J. G. Schlicklin, P. M. 1988. Thermoelectric cooling for naval applications. 7 th International conference on thermoelectric energy conversion. University of Texas at Arlington 1988.