Thermo-Electric Generators

AZURE ENERGY

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14-7-08 | Azure Energy Ltd

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INTRODUCTION

Thermo-electric generators convert heat directly into electricity, using the voltage generated at the junction of two different metals. The history begins in 1821 when Thomas Johann Seebeck found that an electrical current would flow in a circuit made from two dissimilar metals, with the junctions at different temperatures. This is called the Seebeck effect. Apart from power generation, it is the basis for the thermocouple, a widely used method of temperature measurement.

The voltage produced is proportional to the temperature difference between the two junctions. The proportionality constant a is called the Seebeck coefficient.

A series-connected array of thermocouples was known as a "thermopile", by analogy with the Voltaic pile, a chemical battery with the elements stacked on top of each other. The thermopile was developed by Leopoldo Nobili (1784-1835) and Macedonio Melloni (1798-1854). It was initially used for measurements of temperature and infra-red radiation, but was also rapidly put to use as a stable supply of electricity for other physics experimentation.

George Simon Ohm was probably the most famous user. In 1825 he was working on the relationship between current and voltage by connecting wires of differing resistance across a voltaic pile- pretty near short-circuiting it. After an initial surge of current rapid polarization of the pile caused the voltage to decrease steadily, complicating the measurements. Ohm took a colleague's advice and replaced the voltaic pile with a thermopile, and life became simpler. Note that this is only four years after the discovery of the Seebeck effect.

In 2005 (184years after Seebeck effect was discovered) Jason A. Hopkins (1971-) figured out that the efficiency of the thermopile can be near perfect. These devices can be made with excellent efficiency using a temperature difference as low as 30oC and with a practical mass of material. Nickel alloys and pure metals that where available since the 1860's, and maybe earlier, were used in his thermocouples. The improvement came from thermal resistance management strategies not employed by 19th and 20th Century designers. His design is the first to be suitable for low temperature solar energy systems.

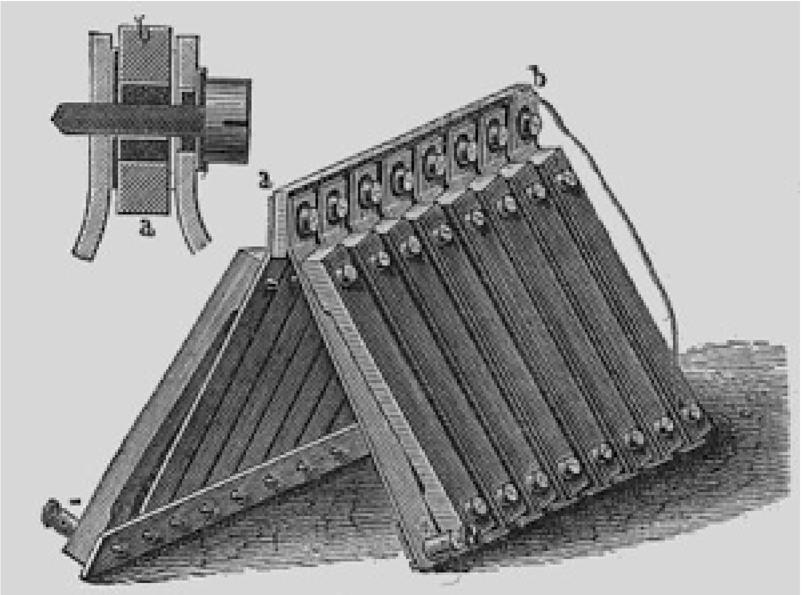
The history shows that all thermoelectric generators developed between 1821 and 2005 operated on radioactive decay or coke or gas combustion as the heat source, hence at 700 to 800oC at the hot ends for the coke and gas. In these applications the efficiency of the conversion of heat to electricity must not have been important. It appears the technology strategy in the past was to increase the voltage of a single thermocouple by using new materials, like semiconductors.

19TH CENTURY THERMOELECTRIC GENERATORS

Here are displayed some early thermo-electric generators or "thermopiles".

The maximum power is obtained from a thermopile when its load resistance is equal to its internal resistance, as with all electrical sources. Since the internal resistance of a chain of thermocouples is very low, this means that it can supply large currents but only low voltages, unless a large number are wired in series.

Markus Thermocouple

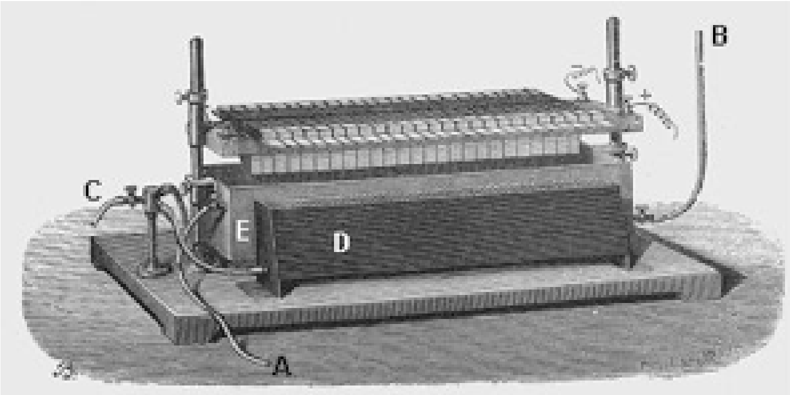


Above: Markus's thermopile: 1864.

The EMF of a single couple was quoted as "One-twentieth of a Daniel cell" which makes it about 55 milliVolts. The negative metal was a 10:6:6 alloy of copper, zinc and nickel, similar to German silver, and the positive metal was a 12:5:1 alloy of antimony, zinc and bismuth. The iron bar a-b was heated and the lower ends cooled by immersion in water. A defect of this design was a rapid increase in internal resistance as the two alloys oxidised at their point of contact.

Markus' thermopile won a prize in 1864/5 from the Vienna Society for the Promotion of Science. [1]

Becquerel's Thermopile



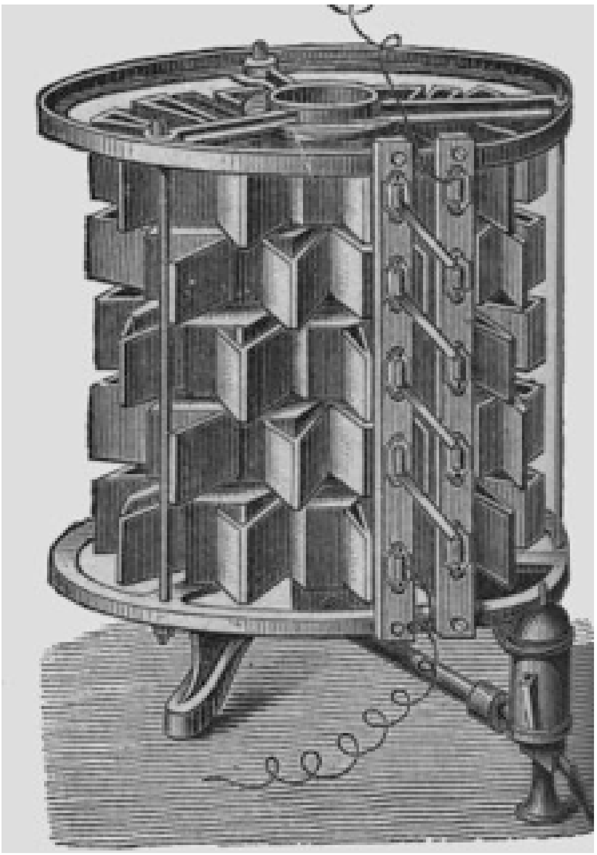
Above: Becquerel's thermopile

This was invented by M. Edmond Becquerel (1820-1891), at a date unknown. The junctions were composed of copper sulphide for one metal, and German silver for the other. It appears that D is a trough of cooling water for the cold junctions, supplied at B and exiting at C. There appears to be another trough on the other side of the central burner E. Gas for the burner is supplied via pipe A.

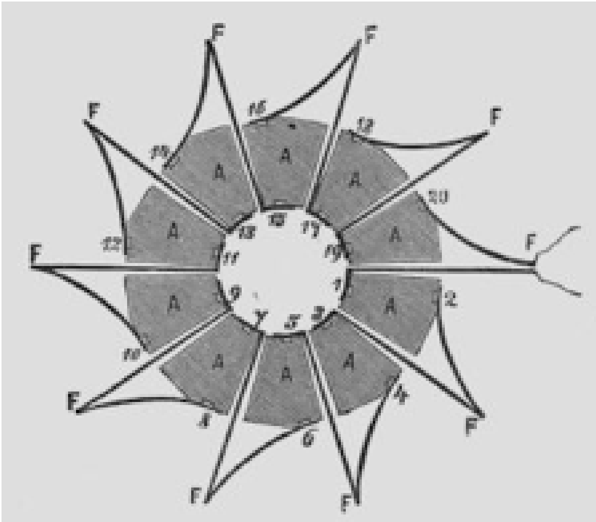
Edmond Becquerel was the father of physicist Henri Becquerel, who discovered radioactivity. [2]

Clamond Thermopile

This pile, developed in association with Mure, used a zinc-antimony alloy for one metal and iron as the other. It was gas-fired, and could liberate 0.7 oz of copper per hour by electrolysis while consuming 6 cubic feet of gas in the same period. The output current was quoted in this outlandish fashion because electroplating was the main application of these devices; possibly practical ammeters did not yet exist. The diagonal connections that join each ring of couples in series can be seen between the two vertical strips. The gas pipe can be seen coming in from bottom right. The little coffee-pot thing in the line is actually a gas pressure regulator. [3]



Right: The Clamond Thermopile



Right: The Clamond Thermopile: plan view.

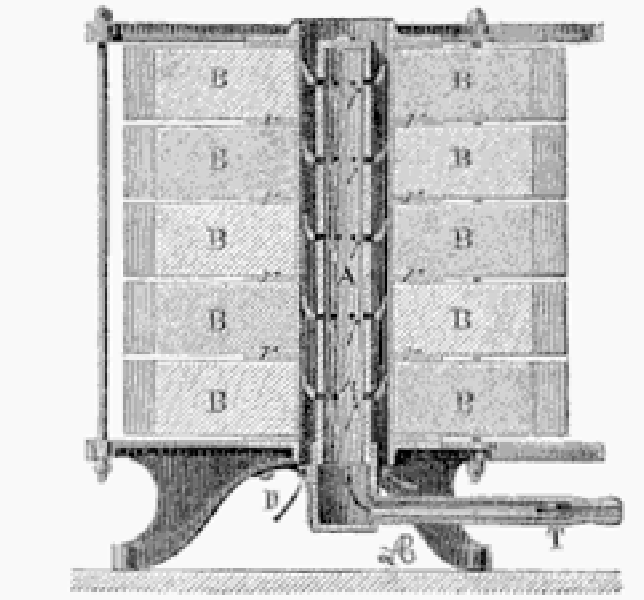
The solid sectors A were made of the alloy, while the cooling fins F were made of sheet iron to act as cooling fins for the cold junctions.

Right: The Clamond Thermopile: reality.

This example is in the History Museum of the University of Pavia in Lombardy, Italy.
Note gas feed with tap running into the centre of the pile.

Right: The Clamond Thermopile: section. Showing the multiple annular burners in the centre of the pile. Gas enters through tube T. [4]

According to the French journal La Nature for 1874, one of these piles was in use at the printing works of the Banque de France, presumably for electroplating.

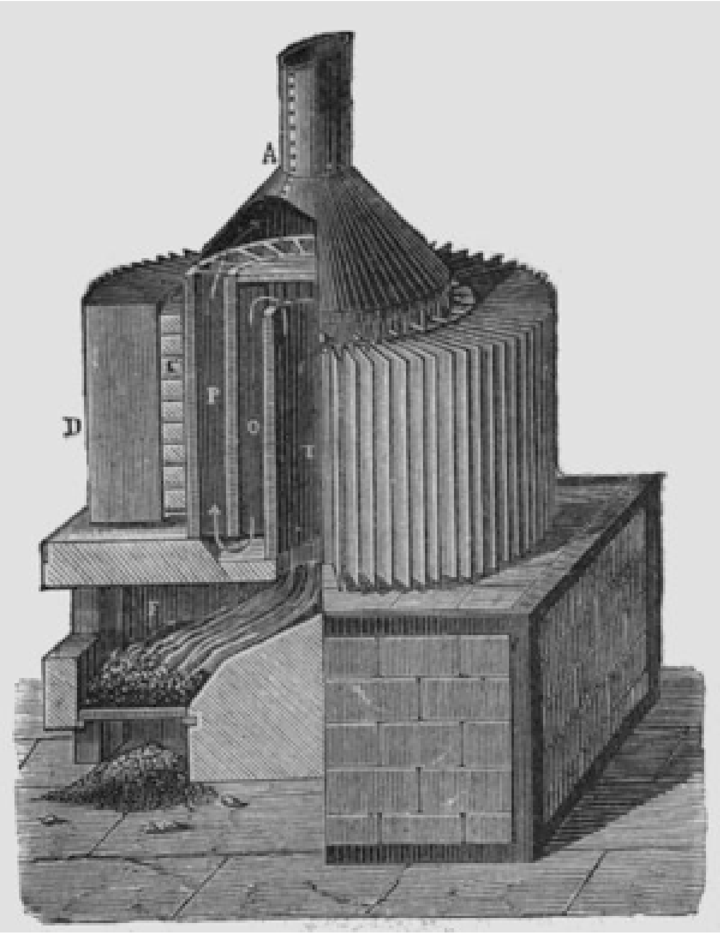


2. — Pile thermo-électrique Clamond. — Coupe suivant l'axe vertical.

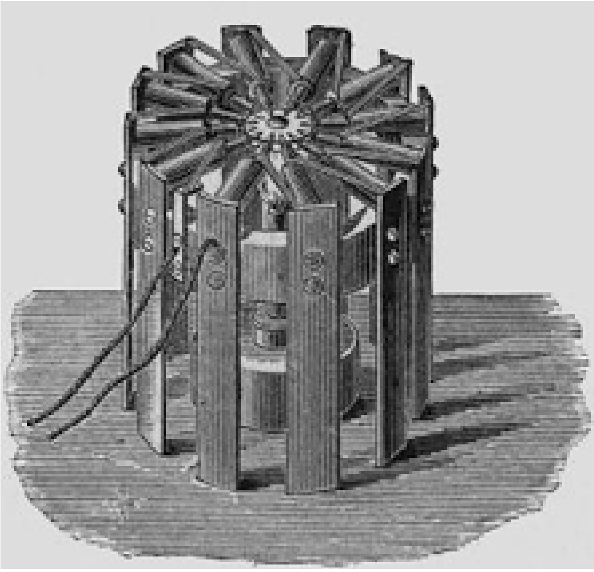
Right: The Improved Clamond Thermopile: 1879.

The EMF of this pile was no less than 109 Volts, with an internal resistance of 15.5 Ohms. The maximum power output was therefore 192 Watts, at 54 Volts and 3.5 Amps.

This pile was fired by coke. The hot junctions were at C, while the cold junctions D were cooled by sheet iron as in the original design above. What purpose was served by the tortuous path T-O-P taken by the hot gases is unclear, because there seem to have been no hot junctions in the inner sections. This beast was 98 inches high and 39 inches in diameter. [5]

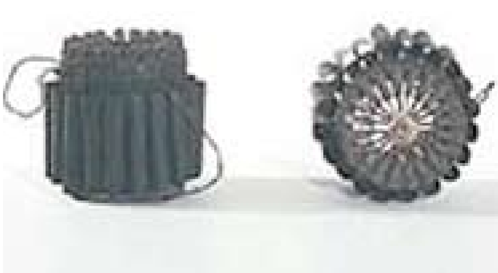


Noe Thermopile



Left: The Noe Thermopile

The hot junctions are the pointed things directed inwards to the central burner. The cold junctions are cooled by radiation and convection from the vertical strips on the outside. The inventor, Fr. Noe, came from Vienna. The output EMF of this pile was about 2 Volts, with an internal resistance of 0.2 Ohm. This was for a pile with 128 couples. [3]

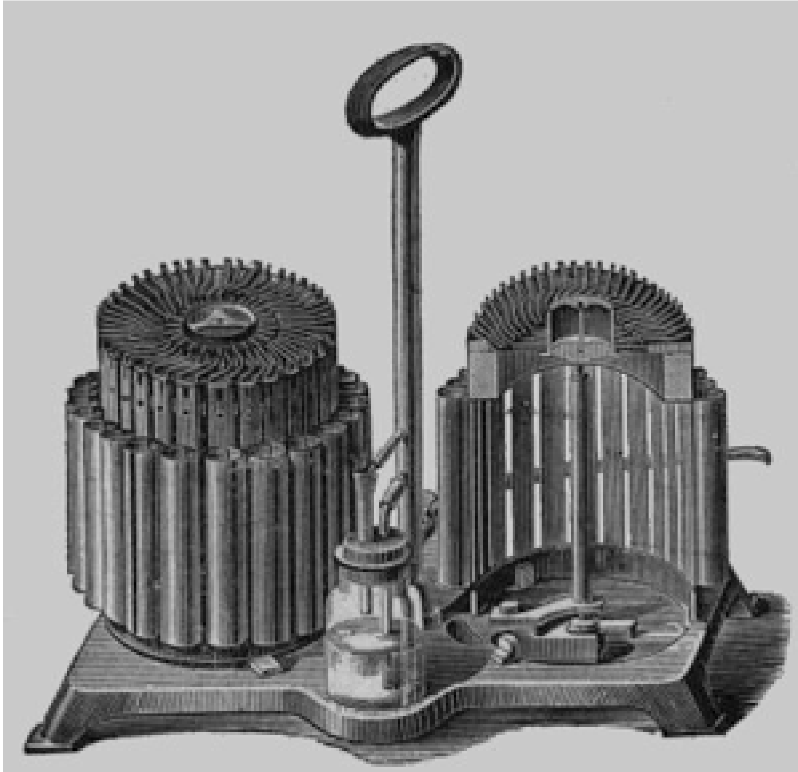


Left: One thermocouple from the Noe Thermopile.
Right: The Noe Thermopile in reality. This example is in the History Museum of the University of Pavia in Lombardy, Italy.

The hot junction is a copper pin in a brass case, surrounded by "an alloy" which is presumably the other half of the junction. The connecting wires visible here on each side were of "German silver". German silver (better known nowadays as nickel silver) is the generic name for a range of bright silver-grey metal alloys, composed of copper, nickel and zinc; it contains no real silver.

These wires were essential to join the thermocouples together, but reduced its efficiency as they conducted heat away from the hot junctions to the cold ones. The problem is elegantly solved in modern semiconductor versions by using alternate P and N type materials that do not require these connections. [3]

Hauck's Thermopile



Left: Hauck's thermopile.

The EMF of a single couple was quoted as "0.1 of a Daniel cell" which makes it about 110 milliVolts. The current capacity using 30 couples was "capable of making a platinum wire 1.2 inches long red-hot" which is not a very useful sort of spec, since we have no idea how thick the wire was.

The Hauck pile was fired by gas, using something looking very much like a Bunsen burner. The cold junctions were water-cooled by a series of little cylindrical tanks, and there was an obscure little glass device in the middle; possibly to show the rate of gas flow?

These devices appear to have been produced commercially in different sizes, with two or three placed on a common frame. They were used for science education and electroplating. To put a time marker on this, it was 1843 when Moses Poole took out a patent for the use of thermoelectricity instead of batteries for electro-deposition purposes. This was long before practical dynamos and alternators.

In the days when chemical cells needed a lot of attention, something that provided power at the strike of a match must have had its attractions. [4]

Gülcher's thermopile

Left: Gülcher's thermopile: c 1898. This example is in the History Museum of the University of Pavia in Lombardy, Italy.

It looks as if it was gas-fired, with the gas going in through the spigot on the right.

Article from 1875

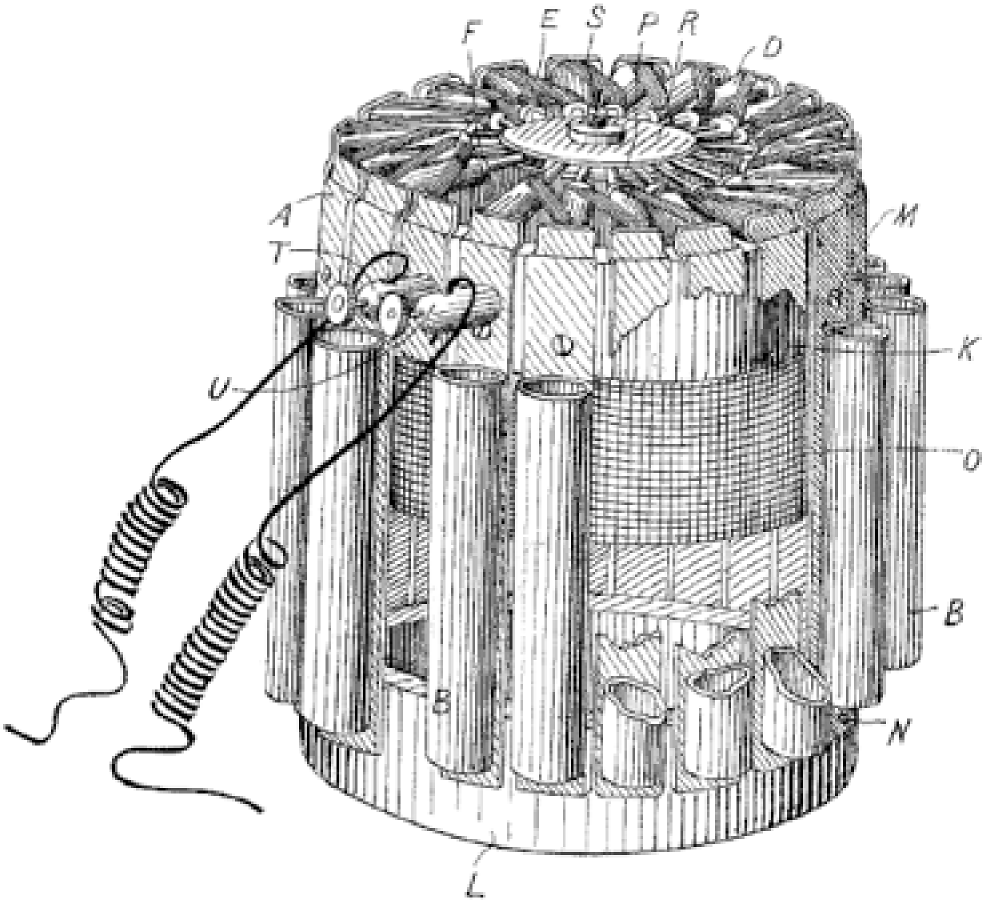
This gives some interesting practical details on the problems of brittle thermocouple materials and the difficulty of avoiding oxidation when iron was used as one half of the couple, as it was in the Clamond pile. There is also the interesting suggestion that petroleum should be vaporised at the cool junctions, reducing their temperature, and the resulting vapour burnt at the hot junctions. [5]

Left: Article in Nature: Nov 18,1875. Doctor Stone reads an article on thermopiles.

Physical Society, Nov. 13.—Prof. Gladstone, F.R.S., president, in the chair.—The President stated that since the last meeting of the Society, Prof. Everett's important work on the Centimetre-Gramme-Second System of Units had been published by the Society. The book is based on the recommendations of a committee of the British Association, and consists of a collection of physical data concisely presented on the above system, a complete account being added of the theory of units.—Dr. Stone then read a paper on Thermopiles. He has recently been engaged in some experiments with a view to ascertain the best alloy for use in thermopiles. The thermo-electric power of a metal or alloy appears to be quite unconnected with its power for conducting heat or electricity, or with its voltaic relation to other metals, neither does it appear to have any relation to specific gravities or atomic weights. The thermopiles employed were of a form slightly modified from that employed by Pouillet in his demonstration of Ohm's law. Alloys are frequently more powerful than elementary metals, thus: 2 parts antimony and 1 part zinc have a negative power represented by 22·70, while that of antimony is 6·96 or 9·43, and of zinc is 0·2. A strange exception, however, is that of bismuth and tin, for while the power of bismuth is + 35·8, when the two metals are alloyed in the proportion of 12 to 1, the power becomes − 13·67. Dr. Stone first used a couple consisting of iron and rich German silver (that is, rich in nickel). This was characterised by great steadiness, but the electromotive force produced by moderate differences of temperature was not great. He then used Marcus's negative alloy, consisting of 12 parts antimony, 5 of zinc, and 1 of bismuth, but the crystalline nature and consequent brittleness of this mixture were found to be great objections to its practical use. It occurred to Dr. Stone that the addition of arsenic might diminish the brittleness without injuring the thermo-electric power, and on trial it was found that an alloy of zinc, antimony, and arsenic, with a little tin, formed a much less brittle mass than Marcus metal, with quite as great or greater thermo-electric power. A set of twelve couples of this alloy and German silver was exhibited. The electromotive forces of this set and of a similar one of twelve iron and German silver couples were determined by Mr. W. J. Wilson, and found to be, for one alloy and German silver couple with difference of temperature of 80° C., [illegible] of a Daniell's cell. The electromotive force of one couple of the iron and German silver set was [illegible] of a Daniell's cell. The ordinary method of applying heat by a trough of hot water is objectionable, for the water short-circuits some of the current. This is evident from the fact that if oil heated to the same temperature be substituted, a considerably greater deflection is obtained. Another method suggested by the author, which would tend to economy, is to allow petroleum to volatilise in the neighbourhood of one face of the pile, thus chilling it, and to ignite the mixture of air and gas so produced at the other face. Clamond's pile, consisting of iron and an alloy of zinc and antimony, was employed for some time, but although good results were obtained, the iron is liable to rust at the connections.—Dr. Guthrie remarked that in researches of this nature the main object in view was to ascertain what relation, if any, existed between the direction of the current and the amount of heat-flow. He referred to the experiment with a tangle of fine platinum wire, by which it is found that if either end of the wire be heated, a current flows towards the tangle, and this takes place however well the tangle may be annealed. Dr. Guthrie suggested that the great effect which alloying one metal slightly with another has on its position in the thermo-electric series may perhaps be connected with its change in conducting power for heat.—Mr. Walenn referred to experiments which he made some years since on thermopiles when used at high temperatures. The most powerful currents were obtained with a couple in which amalgamated copper was employed, but the power was soon lost in consequence of the volatilisation of the mercury. Subsequently he employed wires of wrought iron and German silver, and although the results were not specially remarkable at moderately high temperatures, the power became great when the connections were raised to a red heat.—Prof. Foster called attention to Matthiessen's table of the electric conductivities of metals and alloys in relation to the use of the latter in thermopiles. The fact shown by Matthiessen that the conductivities of alloys are greatly influenced by changes of temperature, will probably, he considers, be found to have some connection with their thermo-electric action. He also mentioned, as a fact which should be remembered when considering the construction of thermopiles, that the presence of minute traces of impurity completely changes the electric conductivity of a metal.

THERMO ELECTRIC GENERATOR IN THE 20TH CENTURY

Yamamoto



第壹圖

Above: Yamamoto patent: 1905.

This thermopile was patented in Japan in 1905 by one Kinzo Yamamoto. Few other details are known; much information was destroyed in the Tokyo Earthquake of 1923.

The P-type material is made of bismuth, antimony and zinc in the proportions: Bi:Sb:Zn=12.0:48.0:36.8. In the figure, D is a P-type "Bullet" and E is a Nickel electrical connection. (Probably that should be nickel-silver: see above)F is the pin to collect heat flow from the flame. A is an electrical and thermal metal connection. B is a cooling fin

This design has an unmistakable resemblance to the Noe thermopile in fact it appears to be a very faithful copy. It was presumably intended for powering radios.

Thermattaix

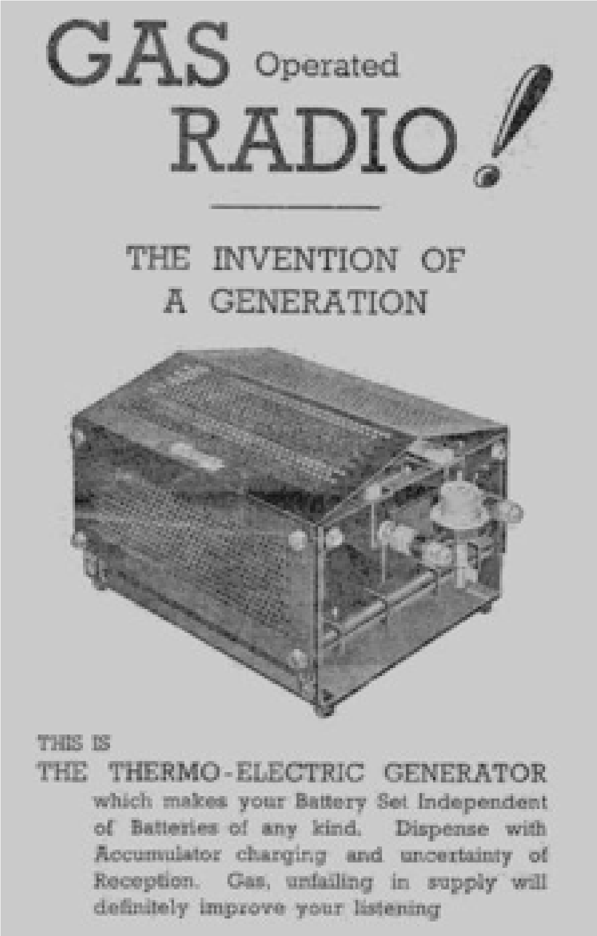
It appears that Great Britain was rather slow in electrification compared with other European countries. Light could be provided by gas, and heating by coal, but electricity was needed to run radios and a gas-fired thermopile was one way to get it. Alternatively, you took your lead-acid filament accumulator into town to get it charged for you, which was somewhat less than convenient.

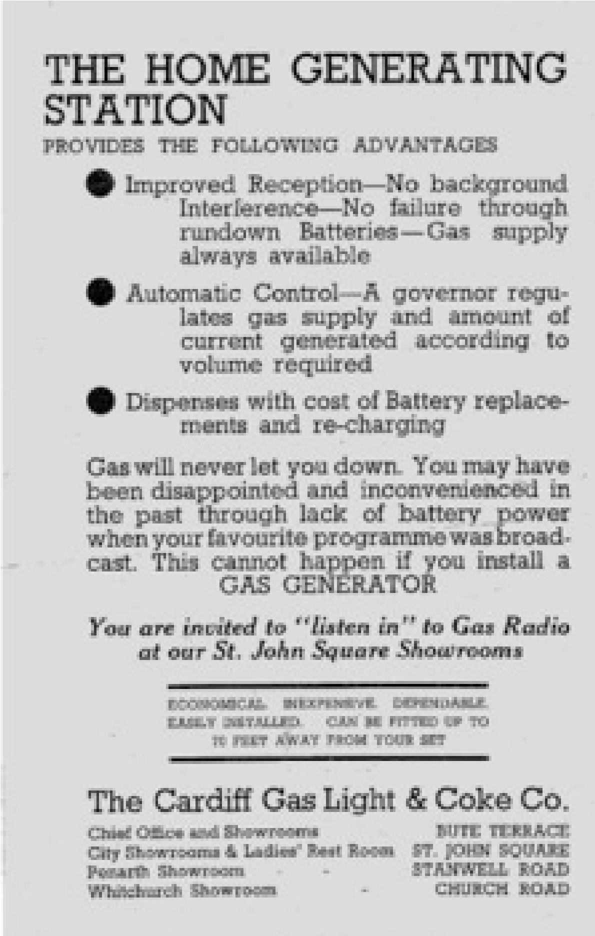
Above: The Thermattaix: circa 1925. This example is in the Science Museum in London.

The voltmeter on the front registers from 0 to 10 Volts a suitable voltage range for charging accumulators running 6.3 Volt valve heaters. The black knob below the meter obviously controlled something- presumably the gas supply. It appears this device was designed to charge lead-acid accumulators rather than power the radio directly. This may have been because output voltage fluctuations would have had little effect on accumulators, but would have been very bad for the filaments of valve heaters.

The magazine Amateur Wireless, in April 1929 carried an advert for the Thermattaix, apparently claiming that it could work your wireless set by gas, petrol, electricity or steam. It goes on to claim that amongst their customers were gas companies, the Italian airforce, architects of note and big game expeditions in Africa and India.

Cardiff Gas Light & Coke





Above: Advertising blurb for the thermo-electric generator. Probably printed on the other side of the page above. These were sold in South Wales during the 1930's. Picture kindly provided by John Howell.

Above: The gas-fired thermo-electric generator: 1930s

Russia post WW2

Below: A Russian thermo-electric generator based on a kerosene lamp.

This was manufactured in the 1950's, once again to power radios. The output voltage(s) are unknown, but since a picture is known to exist of it powering a valve radio, HT must have been generated somehow, possibly by a vibrator power supply. In this context a vibrator is an electromechanical device, similiar to an electric bell, that chops low-voltage DC into crude AC that can be applied to a step-up transformer. They were widely used in car radios before semiconductors arrived.

Remote Areas

These machines are alive and well, being used in remote places where small amounts of electricity are required and the complications of an internal-combustion engine and alternator are not welcome. Modern versions use a thermopile made up of a series array of lead-tin-telluride semiconductor elements, rather than simple thermocouples. These thermojunctions are were considered more efficient than simple thermocouples, and have been available since the mid-1960s. They are commonly used (working in reverse, of course) to cool the little sofa-side beer refrigerators which are now quite common. [7] [8]
Thermoelectric generators can also be heated by radioactive decay, and such devices are used to power interplanetary space probes and the like, where distance from the sun means that solar power is not an option. See: Free Dictionary: RTGs

Boilers

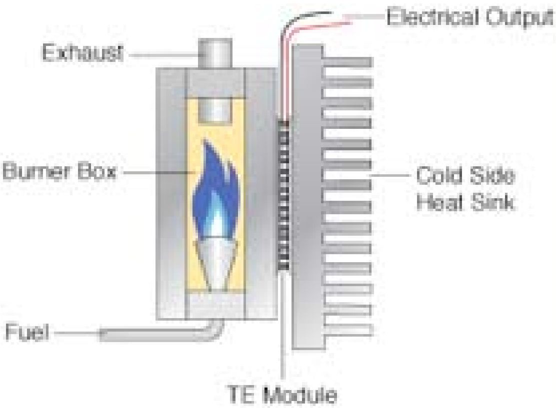
They are used in central heating boilers to control the pilot-light valve. When the pilot is burning, the thermopile generates about 750 mV- enough to actuate a small solenoid that keeps the pilot valve open. This sadly doesn't mean you can run a central-heating system with no electric power, as the main gas valve is operated by mains power switched by the room thermostat; in any case, the pump wouldn't run.

Above: A modern thermo-electric generator or thermopile made by Honeywell for boiler control.

Tellurex

The voltage output is 750 mV with the "Cold" Junction at 416 degC (780 F) and the Hot Junction at 760 degC. (1400 F) I know that 416 degC is not exactly cold, but this thing is mounted inside the boiler combustion chamber. Assuming Ni/NiCr thermocouples are used, we can deduce from this that the device contains about 55 thermocouples in series.

So why is a thermopile used for this job? Presumably because it is very simple and reliable; it is hard to see how a thermopile could fail to the danger state- it can hardly generate electricity when it isn't hot.



Tellurex's current design of gas powered TEG

THERMO-ELECTRIC GENERATORS IN THE 21ST CENTURY

With the awareness of the need for renewable energy researches are now looking the thermoelectric generator to be used with solar energy generated heat. Companies like Azure Energy and researcher Jason Hopkins now have designs suitable for use in low temperature solar energy systems.

Above is part of an 83% efficient thermocouple designed by Jason Hopkins for use in solar energy equipment. Some of his patents are about making thousands of these devices to reach a useful power out.

CONCLUSION

The Electricity source of most of the 19th Century may become the source for the 21st Century as well.

Reference

[1] Electricity in The Service of Man published in its 3rd edition in 1896; the thermopile section appears to have been written much earlier, and certainly before 1888. It was originally published in Germany and was written by Dr A R Von Urbanitsky.

[2] Electricity and Magnetism, 1891.

[3] From Electricity in the Service of Man

[4] Picture from La Nature 1874.

[5] Electricity in the Service of Man

[6] English Nature, not to be confused with the French journal of the same name.

[7] This gives a very good account of semiconductor thermojunctions and how they work: Thermoelectrics by Tellurex (external link)

[8] For one example of modern gas-fired thermoelectric generation, see: Global Thermoelectric. (external link)

Major source http://www.dself.dsl.pipex.com/MUSEUM/POWER/thermoelectric/thermoelectric.htm