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IMPROVING THE ENERGY EFFICIENCY OF THERMOELECTRIC ENERGY CONVERTERS – REVIEW

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The results of an analytical review of a large number of publications on the problem of improving the efficiency of thermoelectric generators (TEG) over the past decade are presented. An analysis of historical data on the thermodynamic justification of the efficiency of thermoelectric generators is presented. The following areas are analyzed: the problem of increasing the figure of merit Z through the creation of new material science technologies and new materials, the creation of multi-segment thermoelectric elements for a wide temperature range (300 ÷ 1200 K), the efficiency of heat supply to the TEG and cooling. The methods for calculating the thermodynamic efficiency of TEG are presented. It is shown that the efficiency of TEG is limited to $\frac{1}{2}$ of the Carnot value for ZT values of 1-3. Modern materials allow the production of TEG with ZT values less than 1. However, the application of TEG has promising prospects with the increase in the intensity of heat supply and cooling processes. The main directions and trends (physical, chemical, technological) in the creation and improvement of TEG are identified. Some practical solutions presented in the literature, as well as the authors' solution for improving the thermodynamic efficiency of boiler units using TEG, are shown.

Keywords: thermoelectric converters, coolers, generators, energy efficiency, energy and exergy analysis, practical applications.

Introduction

Thermoelectric technologies are the product of modern material science, underpinned by the quantum theory. The development of solar energy is aimed at increasing the technical and economic indicators and efficiency of solar energy converters. The working out of PV technologies consists of the 1st generation (silicone, mono-crystalline, poly-crystalline), 2nd generation (thin films-amorphous, Cd-Te, GIGS), 3d generation (multi-junction-organic, inorganic, pevroskite, dye-sensitized, quantum dot). The first photovoltaic solar cells (PSCs) were crystalline silicon (c-Si) based cells. The PSC coefficient is about 20 %. The PSC disadvantages are the following: high cost and toxicity of their production. The thin-film PSCs are second-generation elements and are made from amorphous (a-Si), microcrystalline (c-Si) or polycrystalline (multi-Si) silicon of multicomponent semiconductor groups A3B5 (GaP, TuP, GaAs) and A2B6 (CdTe), multicomponent semiconductors of CiS, CiGS, CZTS type are materials widely researched for applications in thin-film solar cells and other optoelectronic devices. Second-generation PSCs are more economical to produce and are manufactured in the form of flexible thin films. However, quite low efficiency (about 15 %), toxicity of production, and instability of characteristics hinder their production. Third-generation PSCs are organic elements based on conducting polymers, pigments and organic dyes, organic and inorganic semiconductors, quantum dots on hot electrons and with the division of the solar spectrum. PSCs with solar spectrum division or multijunction ones have the efficiency of 45-46 %, but

they are characterized by high cost. PSCs with parallel division of the solar spectrum have the efficiency of 41-43 % and they are also characterized by high cost. The development of third generation PSCs continues. According to the method of converting solar energy into electrical one, FSEs are divided into diode, photovoltaic and chemical, excitonic and thermophotovoltaic ones. Diode-type PSCs based on bulk crystalline substrates and thin films have been the most widely studied. The main parameters that characterize the efficiency of the PSC are the following: open-circuit voltage V_{oc} , short-circuit current I_{sc} , fill factor FF and efficiency. To determine the characteristics of the PSC, it is also necessary to define the spectral characteristics estimating the quantum yield of the incoming structures (quantum efficiency). Thermoelectric generators have not yet found wide practical application. The industry is mastering the production of thermoelectric coolers. At the same time, the thermodynamic efficiency of thermoelectric converters remains insufficiently high.

Materials and Methods

Thermodynamic justification of the efficiency of thermoelectric generators (historical data)

Thermoelectric and photovoltaic energy conversions are based on the Seebeck, Peltier and Thomson effects (Clausius, 1867, 1879; Thomson, 1856, 1857).

In 1824 Seebeck T. demonstrated that a temperature gradient causes simultaneously a heat flux and electrical current. In certain materials, mainly metals and semiconductors, the charge carriers (electrons and holes) may move freely within the lattice, carrying thermal energy (heat) as well. In the presence of a thermal gradient, energy is carried from the high-energy (hot) side towards the low-energy (cold) side. As a result, the charge-carrier-based heat transfer generates also a charge gradient (electrostatic potential). Two phenomena are directly proportional, connected by the Seebeck coefficient, α [V/K], or thermopower. The Seebeck effect consists in the fact that if in an open circuit consisting of several dissimilar conductors, a high temperature T_1 is maintained at one of the contacts and a low temperature T_2 at the other one, then a thermoelectromotive force E appears at the ends of the circuit. When the contacts are closed, an electric current appears in the circuit.

A decade later, in 1834, Jean Charles Peltier associates his name with the reverse phenomenon, i.e. a voltage (potential) gradient generates an electrical current and a heat flux, the proportionality constant being the Peltier coefficient, Π [V].

The Peltier effect is that when direct current is passed through a thermoelement consisting of two semiconductors (conductors), heat is released (absorbed) at the point of contact. When electrons move from a p-type material to an n-type one through an electrical contact, they have to overcome an energy barrier and absorb energy from the crystal lattice (cold junction).

Later, in 1854, Thomson W. connected the two coefficients by:

$$\Pi_{a,s} = \alpha T. \quad (1)$$

The Thomson effect is that when the electric current flows through a conductor or semiconductor in which a temperature gradient is created, heat is released (absorbed) in addition to Joule heat.

The effect is explained by the fact that the energy of free electrons depends on temperature. Then the electrons at the hot junction acquire higher energy than at the cold one. The density of free electrons increases with increasing temperature and, as a result, there is a flow of electrons from the hot end to the cold one.

A positive charge accumulates at the hot end, and a negative charge accumulates at the cold end. Processes occur similarly in substances with hole conductivity.

Thus a TEG is defined like this:

Seebeck effect:

$$\alpha = - \frac{\Delta E}{\Delta T}. \quad (2)$$

$$E_1 - E_2 = \alpha(T_1 - T_2). \quad (3)$$

Peltier effect: amount of heat per unit time:

$$q_{\Pi\alpha/\delta} = \Pi_{\alpha/\delta} j. \quad (4)$$

Thompson effect: amount of heat per unit time per unit volume:

$$q_t = \tau(j\nabla T). \quad (5)$$

$$\tau = \frac{q_t}{j\nabla T}. \quad (6)$$

In 1854, Thompson developed the thermodynamic theory of thermoelectric phenomena (Xue and Guo, 2023). Using the theory of reversible cycles (Fig.1), the following relations were obtained:

First thermoelectric relation:

$$\tau = \frac{\Pi}{dT} = \alpha. \quad (7)$$

Second thermoelectric relation:

$$\Pi = \alpha T. \quad (8)$$

or:

$$\tau = T \frac{\alpha}{dT}. \quad (9)$$

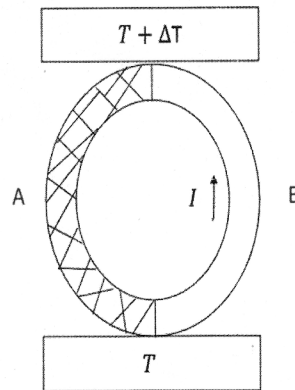


Fig.1. Thermodynamic cycle of a thermoelectric element

In 1956 Ioffe was the first to refer to the ZT -coefficient as figure of merit:

$$ZT = \frac{\alpha_{pn}^2 T}{KR}, \quad (10)$$

where $\alpha_{pn} = \alpha_p - \alpha_n$ are the thermopower of the thermocouple, α_p and α_n being the Seebeck coefficient of the p and n-type thermoelements forming the thermocouple; R is electrical resistance of the thermoelements; K is thermal parallel conductance; T is average absolute temperature at which thermoelectric device is operating.

Ioffe identified that when maximized ZT value resulted in the maximization of the conversion efficiency of generators and coolers.

There is no doubt that ZT is the «true» figure of merit from the thermodynamic point of view. In 1957 Ioffe (Ioffe, 1957) considered that there were mainly two possibilities averaging TE material

properties in devices: firstly, the average over space and secondly, the average over the temperature scale which is denoted here with an overbar.

Kelvin pointed out that the algebraic sum of all forms of energy circulating in the circuit per unit time should be equal to zero:

$$I\alpha\Delta T + I\Pi(T) - I\Pi(T + \Delta T) - I \int_T^{T+\Delta T} (\tau_B - \tau_A) dT = 0, \quad (11)$$

where α is the Seebeck coefficient; Π is the Peltier coefficient; τ is the Thomson coefficient.

These relationships have been tested experimentally and are used in practice.

$$I \frac{\Pi(T)}{T} - I \frac{\Pi(T+\Delta T)}{T+\Delta T} - I \int_T^{T+\Delta T} \frac{\tau_B - \tau_A}{T} dT = 0. \quad (12)$$

Taking into account the irreversibility of processes, one can obtain:

$$-\frac{Q_1}{T_1} + \frac{Q_2}{T_2} = \int \lambda \left(\frac{1}{T} \frac{dT}{dl} \right)^2 dl + I^2 \int \frac{\zeta}{T S'} dl, \quad (13)$$

where ζ is the resistivity of the conductor; λ is the specific linear thermal conductivity of the conductor; S' is the cross-sectional value.

$$Q_\lambda = \frac{T_1 T_2}{\Delta T} \left\{ \frac{1}{T_1} \left[\left(\lambda_a \frac{dT}{dl} \right)_a + \left(\lambda_b \frac{dT}{dl} \right)_b \right]_{T=T_1} - \frac{1}{T_2} \left[\left(\lambda_a \frac{dT}{dl} \right)_a + \left(\lambda_b \frac{dT}{dl} \right)_b \right]_{T=T_2} + \frac{I^2 R_\Omega}{T_2} \right\}, \quad (14)$$

where $\Delta T = T_1 - T_2$

By determining the temperature gradient at the ends of the thermoelectrode $\frac{dT}{dl}$, one can obtain equations for the efficiency.

Thermodynamic substantiation of thermoelectric processes was carried out in (Samoylovich et al., 1953).

The efficiency of a thermoelement is defined as the ratio of electrical power to the amount of heat removed from the heater:

$$\eta = \frac{I^2 R_E}{Q_1} = \frac{E^2}{4 R_E Q_1}, \quad (15)$$

where E is thermoelectric power.

The presence of irreversible phenomena of thermal conductivity and electrical conductivity leads to a decrease in efficiency.

According to the said above one can write:

$$\eta = \Delta T \left\{ \frac{[(\lambda_a \zeta_a)^{1/2} + (\lambda_b \zeta_b)^{1/2}]^2}{\bar{E}^2} + \frac{1}{2} (3T_1 + T_2) \right\}^{-1}, \quad (16)$$

where \bar{E} is the average differential thermopower in the temperature range of ΔT .

The second thermoelectric relation is not a consequence of thermodynamics, but it is a ratio of regularities related to the kinetics of thermoelectric phenomena.

For metal alloys, equation (16) can be replaced by:

$$\eta_{met} = \Delta T (20,1T_1 + 21,1T_2)^{-1}. \quad (17)$$

Example: At temperatures $T_2=300\text{K}$ and $T_1=800\text{K}$, the efficiency is 2.2%.

Using semiconductors makes it possible to increase the efficiency of the thermoelement. Thus, an increase in the efficiency of thermoelements can be achieved by using more advanced semiconductor materials.

In 1947 TEG based on PbS and ZnSb was manufactured, showing a conversion efficiency higher than 5% when operation under a temperature difference of 400K (Telkes, 1947).

Results and discussion

Analysis of modern publications and assessment of thermodynamic efficiency of thermoelectric generators

Modern publications provide the following relationships to determine the TEG efficiency.

A thermoelectric generator can convert heat into work in the presence of heat sources with different temperatures (Fig.1).

The hot junction absorbs heat from a source with temperature T_1 :

$$Q_r = \alpha_1 \cdot T_1 \cdot I. \quad (18)$$

And the cold junction releases heat with temperature T_2 :

$$Q_x = \alpha_2 \cdot T_2 \cdot I. \quad (19)$$

If there is a potential difference and an electric current circulates in the circuit, then the work done by the electric current is equal to the product of the current strength and the potential difference.

$$W = I \Delta E = \alpha(T_1 - T_2). \quad (20)$$

Thermoelectrodes have their own electrical resistance and when current passes, Joule heat is released, which reduces useful work:

$$W = \alpha(T_1 - T_2) - Q_J. \quad (21)$$

Thus, in a thermoelectric generator, Peltier heat Q_r and heat removed by thermal conductivity through thermoelectrodes Q_K are taken from the hot source. In this case, Joule heat is released in the thermoelectrodes, which determines heat losses:

$$Q_1 = Q_r + Q_K - \frac{1}{2} Q_J. \quad (22)$$

Peltier heat (Q_x), Q_K heat coming from the hot source by means of thermal conductivity through the thermoelectrodes and Joule losses in the thermoelectrodes are supplied to the cold source:

$$Q_2 = Q_x + Q_K + \frac{1}{2} Q_J. \quad (23)$$

The useful work produced by the installation according to the first law of thermodynamics is equal to:

$$W = Q_1 - Q_2 = \alpha(T_1 - T_2) - Q_J. \quad (24)$$

Let us determine the heat loss due to the thermal conductivity of the electrodes. Provided the electrodes are thermally insulated, heat loss is determined by the formula:

$$Q_K = (l_1 S_1 + l_2 S_2) \frac{T_1 - T_2}{l} Q_J, \quad (25)$$

where λ_1, λ_2 are thermal conductivity coefficients of thermoelectrode materials; S_1, S_2 are cross-sectional area of thermoelectrodes; l is length of thermoelectrodes.

Joule heat loss is determined by:

$$Q_J = I^2 r = I^2 \left(\frac{l_1}{\zeta_1 S_1} + \frac{l_2}{\zeta_2 S_2} \right), \quad (26)$$

where ζ_1, ζ_2 are electrical conductivity resistivity of materials.

The generated electrical power is equal to:

$$P = I^2 R, \quad (27)$$

where I is the current strength; R is external load resistance.

The current strength is defined as:

$$I = \frac{\alpha(T_1 - T_2)}{R + r}, \quad (28)$$

where: r is the internal resistance; $\alpha = \frac{1}{2}(\alpha_1 + \alpha_2)$ is the average value of the Seebeck coefficient.

The efficiency of a thermoelectric generator is:

$$\eta = \frac{D}{Q_Y} = \frac{\alpha^2 (T_1 - T_2) R}{(R + r)^2} \times \frac{1}{\frac{\alpha^2 T (T_1 - T_2)}{R + r} + K(T_1 - T_2) - \frac{\alpha^2 (T_1 - T_2)^2 r}{2(R + r)^2}}, \quad (29)$$

where $T = (T_1 + T_2)/2$.

After transformations we get:

$$\eta = \frac{T_1 - T_2}{T_1} \times \frac{m / (m + 1)}{1 + (m + 1) / ZT - (T_1 - T_2) / ZT_1 (m + 1)}, \quad (30)$$

where $m = r/R$, $\eta_c = (T_1 - T_2)/T_1$.

The maximum power is released under the condition $R=r$, and the efficiency is equal to:

$$\eta = \eta_c \times \frac{1}{2(1 + \frac{2}{ZT})}. \quad (31)$$

The maximum efficiency value is achieved at a value of $M > 1$, $m_{\max} = M = \sqrt{\frac{T_2}{T_1} + ZT/2}$, which

does not correspond to the maximum power. The electrical power of the TEG current source supplied to the external load is maximum at $m = 1$. The external load uses 50% of the total power generated, and 50% is spent on the internal resistance of the source. At $Z > 1$ $m=M > 1$, the efficiency of the thermoelement approaches the efficiency of the Carnot cycle. According to the relation with m_{\max} , the efficiency, corresponding to the maximum power of the thermoelement, reaches the value $\eta = 1/2 \cdot \eta_c$ (half the value for the Carnot cycle). Thus, the efficiency of TEG depends on two factors, namely the temperature difference between hot and cold sources (Carnot cycle efficiency) and the Ioffe coefficient ZT . The dependence of ZT on temperature is shown in Fig. 2.

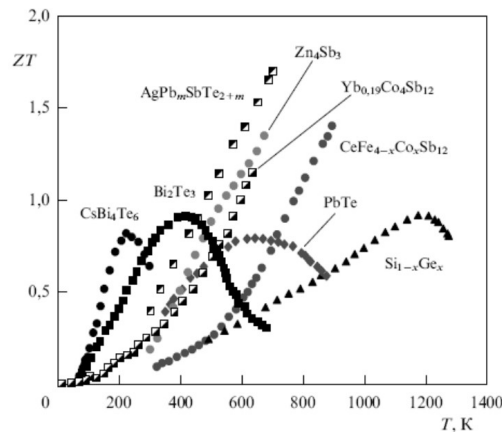


Fig. 2. ZT in the function of temperature (T.M. Tritt et al., 2008)

Taking into account eq.(31) and equation for m_{max} the value of the maximum efficiency can be determined by the formula:

$$\eta_{TEG} = \eta_c \frac{m^* - 1}{m^* + T_1} \quad (32)$$

where $m = r/R$, and $m^* = \sqrt{Z^* \frac{T_1 - T_2}{2} + 1}$.

$$Z^* = \left(\frac{\alpha}{\sqrt{S_1 \lambda_1} + \sqrt{S_2 \lambda_2}} \right)^2$$

The efficiency depends on the electrical and thermal properties of thermoelectrodes and their geometric dimensions. Efficiency also increases in multilayer thermoelements. The diagram of a multilayer thermoelement is shown in Fig. 3.

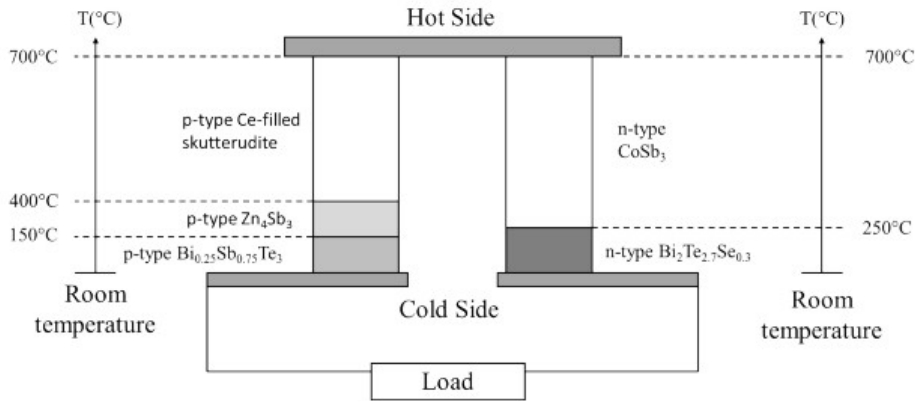


Fig. 3. Multilayer thermoelement diagram

Entropy method

Entropy at the TEG input:

$$\Delta S_{in} = \frac{Q_1}{T_1} \quad (33)$$

Entropy at the output of the TEG:

$$\Delta S_{out} = \frac{Q_2}{T_2} \quad (34)$$

Entropy change in TEG:

$$\Delta S_T = \Delta S_{in} - \Delta S_{out} = \frac{Q_1}{T_1} - \frac{Q_2}{T_2} \quad (35)$$

Entropy change during electricity production:

$$\Delta S_e = I_{sc} V_{oc} - I_{me} V_{me}, \quad (36)$$

where I_{sc} is the short circuit current; V_{oc} is the open circuit voltage; I_{me} V_{me} are the maximum power point.

Entropy efficiency is defined as:

$$\eta_S = \frac{\Delta S_{in} - \Delta S_T - \Delta S_e}{\Delta S_{in}} = 1 - \frac{T_0 \Delta S_{gen}}{\Delta S_{in}} \quad (37)$$

The relation for calculating the energy efficiency of thermoelements is given:

$$\eta_{EX} = \frac{1}{\left(\frac{1+m}{m} + \frac{(1+m)^2}{m} \frac{1}{2T_H} - \frac{\eta_T}{2m}\right)}, \quad (38)$$

where $m = R/r$; Z is a quality factor; $\eta_T = 1 - T_X/T_H$ is a conversion factor.

The maximum value is achieved at optimal load when:

$$m_{OII} = \sqrt{\frac{1+Z(T_H+T_X)}{2}}, \quad (39)$$

this implies:

$$h_{EX}^{\max} = \frac{m_{OII} + 1}{m_{OII} + T_X/T_H}. \quad (40)$$

Practical application of TEG

Numerous publications present the results of the practical application of semiconductor thermoelements (De Vos et al, 1981; Anaticchuk, 1979; Anaticchuk et al., 2013; Nolas et al., 2001; Zebarjadi 2015; Tohidi et al., 2022; Beretta et al., 2019). Thermoelectric coolers are most widely used. The industry has mastered the production of thermoelectric coolers of various cooling capacities and applications (Rawat et al., 2017; Rosa, 2012).

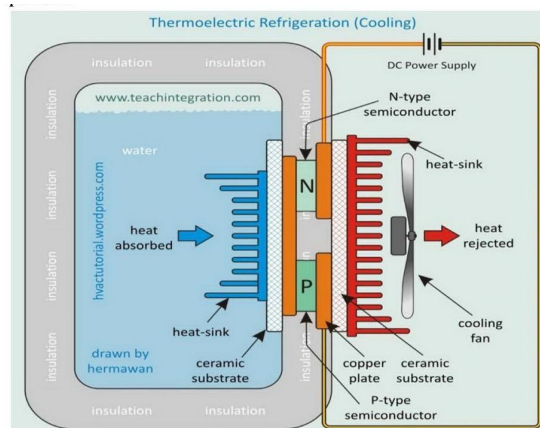


Fig. 4. Thermoelectric cooler circuit

Fig. 4 shows the thermal diagram of a cooler with intensified heat supply and removal.

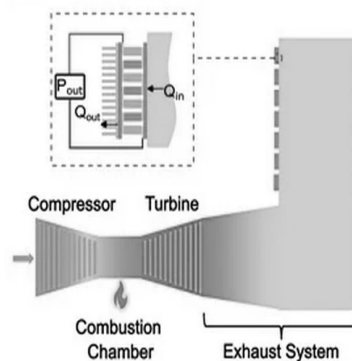


Fig. 5. Diagram of a thermoelectric generator in a gas turbine

Fig. 5 shows the thermal diagram of a TEG for a gas turbine (Alsaghir and Bahk, 2023). The thermoelectric module is installed on a General Electric LM 6000 PC turbine with a capacity of 46 MW. The exhaust gas temperature at the turbine outlet is 500°C, and the mass flow rate is 130 kg/s. The geometric dimensions of the module are 0.5 x 0.5 m², with a length of 2 m. The thermoelements have several segments. The generated power ranges from 9.2 kW to 10.3 kW. The overall efficiency of the TEG is about 8 %.

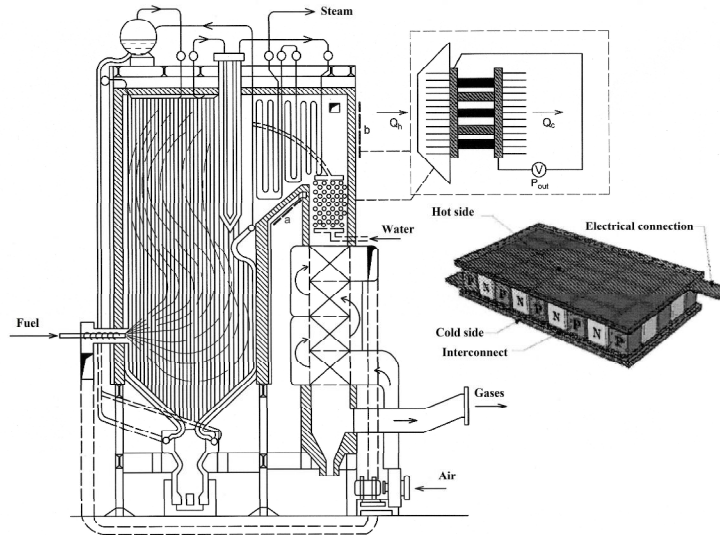


Fig. 6. Scheme of a thermoelectric generator of a steam boiler

The authors propose a thermal diagram of the TEG, shown in Fig. 6, as applied to steam boilers. The TEG is installed in the boiler flue at the outlet of the furnace. The temperature of the flue gases drops to 150-180°C. At the same time, electricity is generated in an amount sufficient for consumption for one’s own needs.

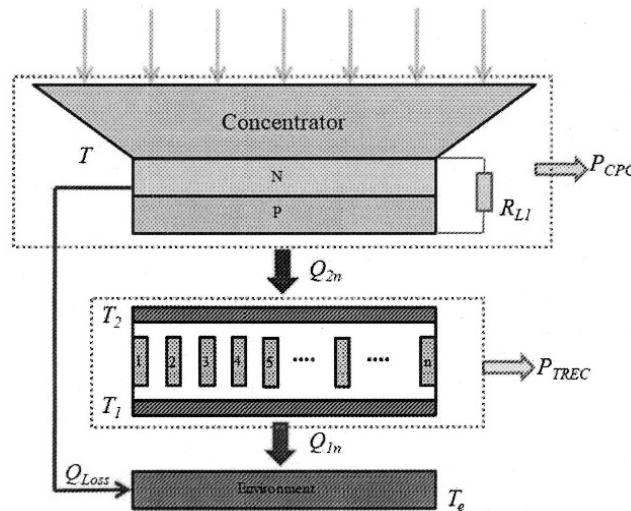


Fig. 7. Scheme of thermoelectric solar energy generator

Fig. 7 shows a diagram of a TEG with a solar concentrator. The concentration of solar energy allows increasing the amount of energy input, but the problem of cooling remains. The efficiency is defined as

$$\eta_{TREC} = \frac{\eta_{PTREC}}{Q_{2n}} = \frac{Q_{2n} - Q_{1n}}{Q_{2n}}, \text{ where } Q_{2n} = Q_{in} - P_{pv} - Q_{loss}.$$

Conclusions

The review results of literature sources indicate a slight increase in the thermodynamic efficiency of thermoelectric generators and coolers through technological improvement of the Ioffe coefficient ZT . Modern technologies provide a ZT value from 1 to 2. Analyzing the functions for the energy efficiency of generators and coolers, one can see that efficiency can be increased by intensifying heat transfer when supplying heat to the generator and, especially, cooling. At low efficiency values (10-15 %), there is a need to remove a significant amount of heat, $Q_2 = (1 - \eta_{TEG})Q_1$. With a small area of thermoelectric batteries, there is also a problem of heat removal. Surface ribbing is used both on the heat supply and heat dissipation sides. At the same time, forced ventilation is installed in the coolers. Analyzing the possible applications of TEGs, their usage in exhaust gas ducts of gas turbine units and internal combustion engines is shown. The authors point out the possibility of using TEGs in thermal circuits of steam boilers to generate electricity for their own needs and autonomous power supply.

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ПІДВИЩЕННЯ ЕНЕРГОЕФЕКТИВНОСТІ ТЕРМОЕЛЕКТРИЧНИХ ПЕРЕТВОРЮВАЧІВ ЕНЕРГІЇ – ОГЛЯД

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Представлено результати аналітичного огляду великої кількості публікацій щодо проблеми підвищення ефективності термоелектричних генераторів (ТЕГ) за останнє десятиліття. Наведено аналіз історичних даних щодо термодинамічного обґрунтування ефективності термоелектричних генераторів. Аналізуються наступні напрямки: проблема підвищення добротності Z шляхом створення нових матеріалознавчих технологій і нових матеріалів, створення багатосегментних термоелектричних елементів для широкого діапазону температур (300 ÷ 1200 К), ефективність теплопостачання ТЕГ і охолодження. Наведено методи розрахунку термодинамічної ефективності ТЕГ. Показано, що ефективність ТЕГ обмежена ½ значення Карно для значень $ZT = 1-3$. Сучасні матеріали дозволяють виготовляти ТЕГ зі значеннями ZT менше 1. Проте застосування ТЕГ має багатообіцяючі перспективи зі збільшенням інтенсивності процесів теплопостачання та охолодження. Визначено основні напрямки та тенденції (фізичні, хімічні, технологічні) створення та вдосконалення ТЕГ. Аналізуються залежності розрахунку ККД термоелектричних генераторів та методи його підвищення. Показано деякі практичні рішення, наведені в літературі, а також авторське рішення щодо підвищення термодинамічної ефективності котлоагрегатів з використанням ТЕГ. Цей аналіз демонструє значний прогрес у розвитку термоелектричних генераторів, проте також підкреслює існуючі обмеження, які потребують подальших досліджень і вдосконалень. Підвищення ефективності матеріалів та оптимізація технологій охолодження і теплопостачання є ключовими факторами, які можуть привести до значного прориву у використанні ТЕГ в різних галузях. Окрім того, інтеграція нових матеріалів та інженерних рішень в реальні промислові процеси, такі як котлоагрегати, має потенціал для значного підвищення загальної енергоефективності.

Ключові слова: термоелектричні перетворювачі, охолоджувачі, генератори, енергоефективність, енергетичний та ексергетичний аналіз, практичне застосування.