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# THERMOELECTRIC GENERATORS FROM NEW MATERIALS: POSSIBILITIES FOR THE OIL AND GAS INDUSTRY OF UZBEKISTAN

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## ABSTRACT:

**The possibilities of using thermoelectric generators (TEG) made of new materials for generating electricity from associated petroleum gas flares and their impact on the environment are considered. Thermoelectric materials created in recent years (a solid solution of silicon and germanium doped with phosphorus and iron, a Heusler compound $Fe_2V_{0.8}W_{0.2}Al$, doped silicates) can provide an efficiency of at least 20%, which suggests the prospect of widespread use of TEG in various industries. Important advantage of TEG is the possibility of cascading, which makes it possible to increase the efficiency up to 40% when using new materials. At the same time, at least 2.4 billion kWh of electricity in the amount of 1.1 trillion Uzbek sums can be annually obtained in Uzbekistan from 1.5 billion $m^3$ of associated gas.**

**Keywords: oil and gas industry, energy saving, environmental pollution, thermoelectric generator, thermoelectric material, thermoelectric efficiency, specific (unit) price, cascading possibility of TEG**

## INTRODUCTION:

In recent decades, much attention has been paid all over the world to the creation of methods and devices that make it possible to increase the efficiency of the use of energy resources. The reason for this is the limited reserves of fossil fuels (coal, oil, natural gas), and the harmful effects of traditional methods of producing and using energy on the environment. Approximately 70% of all energy produced in the world is emitted into the environment as waste heat (secondary energy resources). In addition, by-products are formed during the extraction and processing of fossil fuels (for example, associated petroleum gas - APG, flare gases - FG), processing of which into useful species is difficult and not always economically justified. Therefore, this waste is often simply incinerated (Fig. 1). It is also important to use waste heat from compressor stations of main gas pipelines (Fig. 2).

Fig. 1. Oilfield torch

In these issues, Uzbekistan is no exception, where, according to rough estimates, at least 200 billion kWh of waste heat is generated annually, including 1.5 billion m$^3$ of APG, most of the last is burned without any benefit.

It is also necessary to bear in mind the harmful effect of APG and FG on the environment [1]: the gaseous substances that make up their composition are recorded not only at the source of pollution, but also at a considerable distance from it. The maximum dispersion halo (up to 15 km) is typical for hydrocarbons, ammonia and carbon oxides; hydrogen sulfide migrates at a distance of 5-10 km, while nitrogen oxides and sulfur dioxide are noted within 1-3 km from the source of pollution.

In addition to chemical effects, when gas is burned, thermal pollution of the atmosphere also occurs. At a distance of up to 4 km from the torch, signs of oppression of vegetation are observed, and within a radius of 50-100 m - disturbance of the background vegetation cover.

The laws "On the rational use of energy", "On the use of renewable energy sources" apply in Uzbekistan, "Concept of providing the Republic of Uzbekistan with electric energy for 2020-2030" as well as a number of decrees and resolutions of the President and Cabinet of Ministers were adopted to improve energy efficiency of branches of economy. Also characteristic is the order of Cabinet of Ministers 606-F of 07/19/2019, which approved measures to study the potential and feasibility of using waste heat, associated and flare gases in the Republic of Uzbekistan, including gas-pumping units of main gas pipelines.

The most popular and versatile is electrical energy. Therefore, the development of modern methods and devices for generating electrical energy from alternative sources and waste heat using APG and FG is one of the priority areas of the State Scientific and Technical Program, and we will further consider these methods in relation to APG and FG.

Fig. 2. Compressor station on a gas pipeline

Estimates show that only from APG in Uzbekistan, at least 2.4 billion kWh of electricity can be obtained at a cost of 1.1 trillion. Uzbek sums (based on the achieved efficiency value of 20% of the ORC and TEG installations - see below).

At present, mainly gas piston and gas turbine power plants, as well as organic Rankine cycle (ORC) installations [2] are used to generate electricity from waste heat, APG and FG.

Gas piston and gas turbine power plants require complex purification of APG and FG (sulfur impurities should be less than 0.1%). In addition, gas must be supplied to gas turbine plants at high pressure (25-28 MPa), for which a compressor is installed. Therefore, the use of such installations is also limited.

ORC units are designed mainly to operate from waste heat when the temperature of the heat carrying agent is relatively low (no higher than 400°C). These units are, in fact, a conventional thermal power plant (steam boiler - steam turbine - electric generator, Fig. 3), where the working medium - water – is replaced by a low-boiling organic liquid (freons, ammonia), and therefore the entire installation must be hermetical [2]. The use of an organic liquid allows at low temperatures to provide a high vapor pressure required for efficient operation of the turbine. The efficiency of ORC units reaches 20%. However, such installations are complex in design and operation, expensive due to strict requirements for the tightness of the entire installation, the unit capacity is limited (currently up to 15 MW).

Based on the listed disadvantages of devices used at present, it is believed all over the world that direct conversion methods (thermoelectric generators - TEG [3], as well as less studied from the energy point of view methods based on such phenomena as phase transitions ferromagnet-paramagnet, ferroelectric-paraelectric, piezo- and pyroelectricity) are most suitable to convert secondary energy resurses, APG and FG into electricity. The main advantage of these methods are the absence of moving parts, which almost excludes maintenance and repair (not counting the periodic cleaning of heat exchange surfaces from various contaminants), long service life (up to 25-30 years), noiselessness, no harmful emissions, the ability to work from any heat sources. At the same time, the requirements for the quality of heat are minimal - the operating temperature on the hot side must be ensured only.

Fig. 3. External view of the ORC unit [2]

The most studied principle of operation, design and manufacturing technology of TEG. The main indicator of the efficiency of TEG application is the dimensionless thermoelectric figure of merit $ZT = S^2\sigma T / \kappa$, which determines the efficiency of the TEG:

$$\eta_{\text{el}} = \frac{T_{\text{H}} - T_{\text{C}}}{T_{\text{H}}} \frac{\sqrt{ZT+1}-1}{\sqrt{ZT+1}+T_{\text{C}}/T_{\text{H}}}. \quad (1)$$

Here the first factor is the Carnot formula for an ideal heat engine, and the second factor is typical for TEG. $S$, $\sigma$ and $\kappa$ are the Seebeck coefficient, electrical conductivity and thermal conductivity of a thermoelectric material (TEM) respectively, $T = (T_{\text{H}} + T_{\text{C}}) / 2$ is the average operating temperature of TEG, $T_{\text{H}}$ and $T_{\text{C}}$, respectively, are the temperature of the hot and cold sides of the TEG (in K). $S = \Delta U / \Delta T$, $\Delta U$ is the potential difference (thermoelectric power) arising from the temperature difference $\Delta T = T_{\text{H}} - T_{\text{C}}$.

The reliability of TEGs is confirmed by the fact that they have been used in spacecraft for various purposes since 1962, in particular, they are the only sources of power supply for equipment for studying distant planets of the solar system (beyond Mars), when the flight lasts several years and solar radiation is not enough for the operation of photovoltaic generators [4]. TEGs are also used in autonomous power supplies for protection, automation, control and signaling systems of main gas pipelines [5], remote and hard-to-reach facilities [6]. Currently, TEGs are also produced for the utilization of heat from exhaust gases of internal combustion engines, for example, by Alphabet Energy Inc. (California, USA) [7]. One of the interesting options for using TEG in power plants is the Elena thermoelectric nuclear power plant (Kurchatov Institute, Russia) with an electric power of 100 kW and a thermal power of 3 MW (Fig. 4). The developers guarantee its operation for 25 years without any maintenance [8].

It is also important that TEG, unlike other devices, can be easily connected in cascades, in series with respect to the heat flux, which makes it possible to significantly increase the overall electrical efficiency (Fig. 5).

What prevents the use of TEG? Despite the listed advantages, TEGs are currently not widely used due to their high price (more than $ 9000 / kW) with insufficient efficiency of single-stage TEGs (less than 6%) based on common TEM ($Bi_2Te_3$, PbTe, Si-Ge). Multistage TEGs are technologically complex, and the presence of sharp boundaries between the layers, washed out due to thermal diffusion, reduces the service life, especially in the case of superlattices and other nanostructures showing a high dimensionless thermoelectric figure of merit *ZT* > 3 (see below). An efficiency of about 13.5% was achieved in multistage TEG [9] as early as the 60s of the last century, and in 1999 it was about 20% [10] (Fig. 6).

In 2019, it was reported [11], [12] that *ZT* reached 3.6 in the nanostructured Si-Ge solid solution doped with P and Fe, and 5-6 in the $Fe_2V_{0.8}W_{0.2}Al$ alloy. The corresponding efficiency of TEG exceeds 25%. The lower limit of the efficiency of TEG for commercial use is 20% ($ZT \geq 2$) [3], and the above values of *ZT* open up broad prospects for the use of TEG in various fields - in energy, industry, household devices.

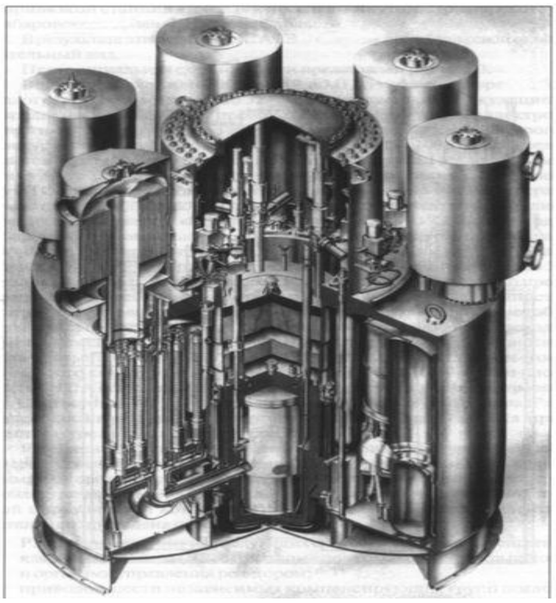
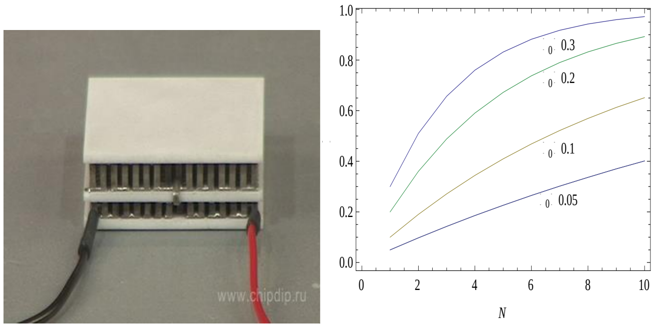


Fig. 4. Thermoelectric nuclear power plant "Elena"




*a* *b*

Fig. 5. Cascade connection of thermoelectric modules (*a*) and dependence of the total electrical efficiency on the number of stages (*b*). The numbers at the curves are the efficiency of one stage

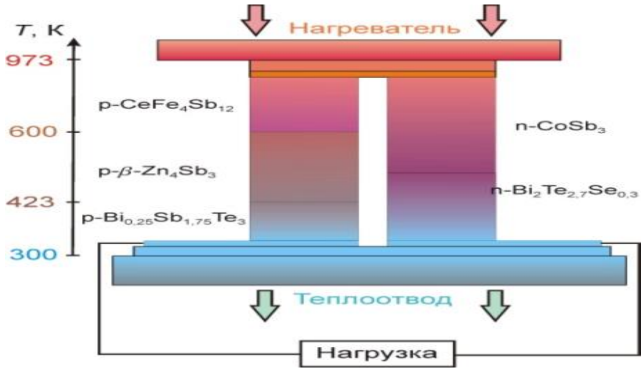



Fig. 6. Multistage structure that ensured record efficiency ηel [3]

It should be noted that the commercial feasibility of using various energy converters is determined by the combination of the power output price (the ratio of price to generated power), electrical efficiency $\eta_{el}$ and operating costs, including the cost of the primary energy carriers used (coal, oil, natural gas). Usually, to compare devices that generate electricity, including those using renewable sources and secondary energy resources, the electric efficiency $\eta_{el}$ is used in combination with a reduced price. This is not entirely correct, although, of course, the latter affects the price - the higher the efficiency $\eta_{el}$, the greater the generated electrical power and the lower the reduced price, all other things being equal. In this regard, secondary energy resources (including APG and FG, as well as partially renewable energy sources) have an important feature - in them, primary energy for conversion is free and even harmful to the environment and, accordingly, to people, and amount of this energy should be reduced as much as possible. Proceeding from this, researchers [13, 14] drew attention to the fact that in relation to renewable energy sources and secondary energy resources, the efficiency criteria of converters should be revised. Namely, in this case, the reduced price and current operating costs of energy converters are decisive, and the efficiency $\eta_{el}$ is a secondary indicator. Here we specially highlight the electrical efficiency $\eta_{el}$, since we only consider the methods of generating electricity. Therefore, and also taking into account the prospects of using TEG for converting the energy of the Sun [15-20], an intensive search for new TEMs is underway all over the world [21-25].

TEM must meet a number of requirements: 1) be produced from available, widespread and cheap raw materials; 2) be harmless to the environment and people in terms of composition and technology; 3) be resistant to oxidation, which simplifies the protection of finished TEG; 4) as simple as possible technology for processing raw materials and manufacturing TEG (without vacuum or inert atmosphere); 5) high values of $T_H$, $S$, $\sigma$ and low $\kappa$ to provide $ZT > 2$ or $\eta_{el} > 20\%$; 5) a wide range of operating temperatures (large difference $T_H - T_C$).

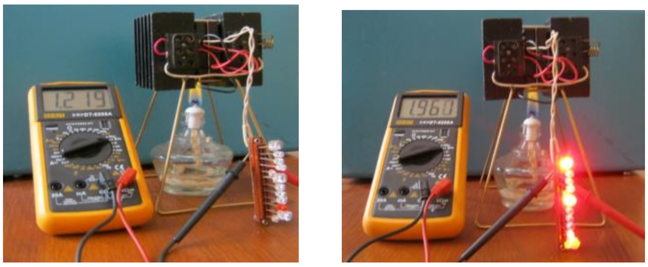
Here we note that multistage TEGs, on which a record value of $\eta_{el} = 20\%$ has achieved (see above), is made from compounds of antimony, selenium and tellurium - rare and expensive substances, poisonous and with complex technology (Fig. 6). Therefore, such structures will be even more expensive than the currently widespread TEG based on $Bi_2Te_3$, PbTe and Si-Ge solid solutions. Added to this are geopolitical risks due to the fact that the deposits of these elements are distributed extremely unevenly, and the export of this raw material at any time can be severely limited by the states on whose territory the deposits are located. For example, more than 80% of the explored deposits of rare earth metals and rare elements are located in China, which owns more than 90% of their world production [26]. Therefore, the introduction of export quotas (export reduction by 72%) of these elements in 2009 [27] forced the United States to apply to the WTO with a claim against China.

In the above formula for $\eta_{el}$, not all parameters can be changed arbitrarily. Namely, for $\kappa$, there is a fundamental lower limit of about 0.1-0.15 W · $m^{-1}K^{-1}$, attainable in glassy (amorphous) materials. For $\sigma$, the upper limit is determined by the Wiedemann-Franz law $\sigma / \kappa_e = LT$ - with increasing $\sigma$, the electronic thermal conductivity $\kappa_e$ also increases, and the moment comes when $\kappa_e \geq \kappa_{ph}$, and then $ZT$ stops growing. Most of the studies performed over the past 20 years have been aimed at increasing $ZT$ through a decrease in $\kappa_{ph}$ (skutteridites, clathrates, superlattices, and other nanoscale inhomogeneities that enhance phonon scattering). In this case, the main idea was Slack's formula "electronic crystal, phonon glass" [28]. In this way, ZT > 3 were achieved.

At the same time, it can be seen from the formula for $\eta_{el}$ (1) that the influence of $S$ on ZT can be more significant than the influence of $\sigma$ and $\kappa$. However, the existing physical theories describe the relationship between the $S$ value and the composition and structure of materials only in general terms, and the search for new materials with high $S$ values is carried out in a purely empirical way, various oxide compounds, natural minerals (manganates, cobaltates, tetrahedrite, etc.) are being investigated. It should be noted that materials with $S$ = 45 mV / K at a temperature of 10 K [29], and even 10 V / K near room temperature [30] have been discovered in this way. Unfortunately, in the first case, the high thermal conductivity negates the effect of $S$, and in the second case, the values of $\sigma$ and $\kappa$ are not given, which does not allow us to estimate *ZT*.

The authors of this report investigated the thermoelectric properties of one of the most widespread and cheapest available materials - silicate glass doped by transition metal oxides (Fe, Mb, Cu, V, Ru, etc.), and showed that it can be a fairly effective thermoelectric material [31] with *ZT* > 2 made fron simple technology (all technological operations are performed in air). This allows us to talk about the possibility of creating cheap TEG from local raw materials for wide use in various sectors of the national economy of Uzbekistan, including for the utilization of APG, FG and waste heat from compressor stations. In fig. 7 shows a layout of a TEG based on doped silicate glass.

After the technology of doped silicate glass and the design of a TEG made of it are finalized, it will be possible to create a TEG for specific requirements (power, heat source, additional effects).



*a* *b*

Fig. 7. TEG model made of doped silicate glass. *a* - in the process of warming up, *b* - in the operating mode

**CONCLUSION:**

The most promising method of generating electricity from waste heat of various technological equipment, APG and FG is the thermoelectric method. The modern level of understanding of the physics of thermoelectric phenomena in various materials and the achieved parameters of thermoelectric materials allow us to speak about the possibility of widespread use of TEG for these purposes. In Uzbekistan, only from APG it is possible to receive up to 2.4 billion kWh of electricity per year in the amount of 1.1 trillion Uzbek sums. The unit price of a TEG based on the materials created is estimated as $1,500-2,000 and the payback period is 6-7 years.

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