

Vertical temperature gradient of the ocean as perspective source of renewable energy

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Abstract. In our research we studied the efficiency of converting low-grade heat into electrical energy. The studied cycle is based on sulphuric acid solutions separation in temperature gradient and further electricity generation in concentration galvanic cell. In our calculations we used combined method. To calculate obtained electrical energy we used experimental data, because it is rather difficult to predict electrodes overpotential. The heat, consumed in distilling process, was calculated in theory. As the result of calculations it was shown that if temperature difference is 20 K ($T_1=300\text{K}$ and $T_2=280\text{K}$) the efficiency of the cycle is about 1.5 percent (about 23% of Carnot cycle efficiency). Such temperature difference could be provided, for example, by vertical thermal gradient of the ocean.

1 Introduction

Ocean is perspective source of renewable energy. Ocean energy – it is not only the energy of waves and currents [1-6], but also the energy of vertical thermal gradient [7-10]. In some areas of the ocean temperature difference between the surface of the deep layers of the water could reach 20-25 °C. Vertical thermal gradient of the ocean does not depend on weather or season. The energy of vertical thermal gradient could be used in such countries and regions as Cuba, Haiti, Dominican Republic and some other countries of Caribbean Sea, Venezuela, Ecuador, Costa Rica, Mexico, Panama, Brazil, Philippines, Indonesia, Malaysia, Papua New Guinea, Thailand, Vietnam, Australia, Nigeria and also in southern regions of China.

There are several ways of converting low-grade heat into other types of energy, such as mechanical energy or electrical energy. The pure mechanical way of converting low-grade heat into work is most popular and well developed [11-13]. Mechanical generators work as classical vapour turbines. High price, technical complexity and low efficiency are the main disadvantages of such devices. Earlier we described the cycle, where vapour pressure difference was used not for turbine rotation, but for charged droplets growth [14]. Further coalescence of charged droplets increases their electrical energy, and the total efficiency of such cycle is expected to be higher than the efficiency of mechanical devices.

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Unfortunately, the technical complicity of suggested device is high and this concept is far from practical application.

The second way is electrochemical converting of low-grade heat. An example of electrochemical devices for converting low-grade heat into electrical energy are thermogalvanic cells [15-18]. Low-temperature thermogalvanic cells consist of two identical electrodes immersed in vessels with identical electrolyte solutions. These vessels have different temperatures, and this is the reason for the potential difference between the electrodes. But chemical thermocouples of this design are not as effective as semiconductor thermocouples.

More promising is the method described in [19-20]. It is based on the separation of electrolyte solutions by distillation. At low atmospheric pressure, this is rather fast process, even if the temperature difference is low. The second stage of the process is the generation of electrical energy in a concentration galvanic cell. The authors conducted a series of experiments and recommended a zinc chloride solution as the optimal electrolyte for such a cycle.

A few words about the advantages of this cycle. As we know, the efficiency of semiconductor thermocouples and thermogalvanic cells is rather low due to their high thermal conductivity. In the proposed device there is no direct thermal contact between the heater and the cooler. Heat transfer occurs due to the evaporation of water from a more concentrated solution and its condensation into a less concentrated solution. Thus, by transferring heat, we carry out a useful reaction.

We suggested to use sulphuric acid solution instead of a zinc chloride solution in the cycle, described in [19,20].

In contrast with traditional concentration galvanic cells, where the electromotive force could be calculated as

$$EMF = \frac{RT}{zF} \ln \frac{c_1}{c_2} \quad (1)$$

In solutions of sulphuric acid (approximately starting from a concentration of 1 mol per liter) the dependence of the electrode potential on the concentration of sulphuric acid is practically linear. This effect is consequence of exothermic reaction of dissolving sulphuric acid in water. Another advantage of the proposed electrolyte is that special electrodes are not required. Electrodes for lead cells are suitable for these purposes.

2 Materials and methods

The aim of our work was to calculate the efficiency of converting low-grade thermal energy into electrical energy in suggested cycle.

The efficiency was calculated as

$$\eta = \frac{A}{Q} \quad (2)$$

Where A is the electrical energy produced in the concentration galvanic cell, and Q is the amount of heat required to distill the solution.

The generated electrical energy was calculated using the equation:

$$A = U_{av} z F \Delta v \quad (3)$$

Where Δv is the amount of sulphuric acid, transferred in electrochemical processes, z is the number of electrons, participating in reaction, and F is a Faraday constant. The average value of voltage was calculated as

$$U_{av} = \frac{U_{initial} + U_{final}}{2} \quad (4)$$

Where $U_{initial}$ and U_{final} is the voltage on resistance R at the initial and final stage of the process. This values were determined in experiment, because it is difficult to predict the electrochemical overvoltage of the electrodes in theoretical calculations.

To determine the values of $U_{initial}$ and U_{final} a model of this device was made. It consisted on two lead batteries with different electrolyte concentrations. We used standard lead batteries "6MTS-9", made in Russia. With a standard electrolyte concentration of 40%, the electromotive force of both batteries was the same. Then the standard electrolyte was removed, and solutions of sulphuric acid of the studied concentrations were poured into the batteries. The "plus" of one battery was connected to the "plus" of the other one. As a result the battery with a higher electrolyte concentration was discharged and the density of its electrolyte decreased. A battery with a lower electrolyte concentration is charged, and the density of its electrolyte increases.

The calculation was carried out under the assumption that the process of operation of the concentration galvanic element will continue until the initial concentration difference is halved. In this case, the amount of substance in equation (2) can be calculated using the equation:

$$\Delta v = \frac{(c_1 - c_2)V}{4} \quad (5)$$

Where c_1 and c_2 are the initial electrolyte concentrations and V is the volume of the cell. To repeat the cycle, it is necessary to return the same amount of sulphuric acid to the first cell.

The processes of sulphuric acid solutions of distillation are well studied and described. To predict the possibility of water transfer from acid solution with concentration c_1 to acid solution with concentration c_2 , it is necessary to have information about the vapour pressure above the acid solutions at different temperatures. This data could be taken from literature sources. For example, the vapour pressure above the solution of fifty percent sulphuric acid at 300 K is about 130 Pa and the vapour pressure above the ten percent solution of sulphuric acid at 280 is about 116 Pa. It means that this temperature difference is enough to perform water transfer from 10% to 50% solution of sulphuric acid.

The amount of consumed heat (denominator in equation 2) was calculated as:

$$Q = \lambda \Delta v_{water} + \Delta Q_{solvation} \quad (6)$$

Where λ is the molar heat of water vaporization at temperature T_1 ; Δv_{water} is the number of moles of evaporated water; $\Delta Q_{solvation}$ is the heat released when the corresponding volume of sulphuric acid solution is diluted from the concentration c_1 to concentration c_2 .

In its equation 6 the amount of evaporated water could be calculated as

$$\Delta v_{water} = v_{water} \frac{\Delta v}{\Delta v + v_2} \quad (7)$$

Where v_{water} is the total number of moles of water in cell 2, and the initial number of moles of sulphuric acid in cell 2 was calculated as

$$v_2 = c_2V \quad (8)$$

3 Results and Discussion

The results of our modelling are presented in Table 1. It was necessary to find out optimal initial concentrations of solution 1 and solution 2. High initial concentration difference leads to increasing the electromotive force of concentration galvanic cell, and, as a consequence, increasing numerator in equation (2). Low concentration difference decreases the amount of evaporated water, and decreases the denominator in equation (2).

Table 1. The efficiency of converting heat energy into electrical energy in the case if $T_1=300\text{K}$, $T_2=280\text{ K}$ and $I=0.25\text{ A}$.

$C_{1\text{ initial}}$	$C_{2\text{ initial}}$	Efficiency, %
10	50	1.35
20	50	1.4
25	50	1.4
30	50	1.41
30	55	1.45
35	55	1.5

Thus, we see that when the battery under study is discharged with a current of 0.25 A, the efficiency of the device is practically does not depend on concentration difference. As we can see in Table 1, the efficiency of converting heat into electrical energy in suggested cycle is 1.35-1.5 percent. The efficiency of Carnot cycle at this temperatures is 6.66 percent. So, the efficiency of studied cycle is only about 20-23 percent of Carnot efficiency. It is necessary to add that we made the same calculations with the current $I=0.01\text{ A}$. In this case the dependence between the efficiency and concentration difference was more clear, and optimal initial concentrations of solutions 1 and were 55 and 35 percent. In this case the efficiency of the cycle will be about 2.7 percent (about 40 percent of Carnot efficiency), but the device with such a low ratio current/mass can not have any practical application. All these data are given for a single-cascade distiller. Using a multi-cascade distiller, where the refrigerator of one cascade is a heater for another, it is possible to increase the efficiency of converting thermal energy into electrical energy.

4 Conclusions

- An electrochemical way of converting low-grade heat into electricity, based on the reversible reaction of dissolving sulphuric acid in water, could be rather effective.
- Taking into account the overpotential of the electrodes, if $T_1=300\text{ K}$ and $T_2=280\text{ K}$ the efficiency of converting thermal energy into electrical energy in the proposed cycle is 1.35-1.5 percent (about 0.2-0.23 of Carnot cycle efficiency).

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