Criteria for the Choice of the Optimal Desalination Systems of Sea Water for the Crimean Region

G. A. Sigora1,a, L. A. Nichkova1,b, T. Y. Khomenko1,c, S.V. Lukachev2

1 Federal State Autonomous Educational Institution of Higher Education "Sevastopol State University", Sevastopol, Russian Federation
2 Federal State Autonomous Educational Institution of Higher Education "The Samara National Research University named after the academic S. P. Korolev", Samara, Russian Federation

Email: a sigoral@yandex.ru; b prohvatalov12@mail.ru; c tamara_homenko93@mail.ru

Abstract. The article deals with the problem of choosing the optimum desalination system for seawater for the Crimean region. Criteria are proposed for choosing the optimal method of desalination - "study and reliability", "geographic", "industrial application", "economic", "electricity consumption", "environmental safety" and others. Criterion "study and authenticity" means that the method must be well studied and applied in practice (therefore, the methods of desalination not introduced in production are not accepted). Criterion "geographical" takes into account the climatic features of the regions. Criterion "industrial application" analyses the industrial application of the method. The criterion of "economic" takes into account the costs of water preparation, reagents, additional treatment facilities and the like. The criterion of "limitation" takes into account the limitation of the initial level of salt content of the cultivated water for desalination. The criterion of "temporal" takes into account the period of possible operation of desalination plants. The criterion of "electricity consumption" takes into account the energy consumption for desalination of sea water. Criterion of "ecological safety" takes into account the physicochemical properties of water after desalination. Based on these criteria, a choice of 12 alternatives was made. It was found out that the most suitable method of desalination in this region is vacuum distillation.

1. Introduction
According to the UN, more than 40 percent of the world's population suffers from water shortages and this figure is constantly growing. According to experts, access to clean water deprived 783 million people on the planet and more than 1.7 billion people living in the river basin, need additional sources of fresh water [1].

Until 2014, water from the Dnieper, flowing through the North-Crimean Canal, provided about 84% of all water use needs. More than half of the territory of the Crimea is desert steppe. In the north of the Crimea, where the channel was the only source of water supply, there is a threat of soil degradation. According to some geologists, the solonchak soils of the Crimea have been saturated with water from the North Crimean Canal for billions of tons of water per year for decades, without proper irrigation, these soils can again come to a state unfit for agricultural purposes, or even completely degrade. Agriculture, industry of the Crimea is under threat in general.
For today it is necessary to search for alternative ways of the decision. It is necessary to find a way to replenish fresh water. Since the Crimea is washed by the Black and Azov seas, this geographical feature of the region makes it possible to widely apply the methods of sea water desalination.

There are a large number of methods for desalination of sea water, among them: distillation, freezing, helio-desalination, ion exchange, precipitation of salts with reagents, electrolysis, electrodialysis, reverse osmosis, extraction with organic solvents, gas hydrate extraction, adsorption on porous electrolytes, biological desalination methods using algae, living organisms, bacteria [2].

To choose the most optimal, we will use a systematic approach and define criteria that will significantly help to understand, determine priority indicators and narrow the range of diversity of world and domestic methods of desalination.

2. Suggested criteria

Such criteria, in our opinion, are the following [3].

1. Criterion "study and authenticity". This means that the method must be well studied and applied in practice (therefore, the methods of desalination not introduced in production are not accepted).
2. Criterion "geographical" - takes into account the climatic features of the regions.
3. Criterion "industrial application". The volumes of fresh water to be used for solving the problem are large, therefore, it is necessary to analyze the industrial application of the method.
4. The criterion of "economic". This criterion takes into account the costs of water preparation, reagents, additional treatment facilities and the like.
5. The criterion of "limitation". It takes into account the limitation of the initial level of salt content of the cultivated water for desalination.
6. The criterion is "temporal". It takes into account the period of possible operation of desalination plants.
7. The criterion of "electricity consumption". It takes into account the energy consumption for desalination of sea water.
8. Criterion of "ecological safety". It takes into account the physicochemical properties of water after desalination.

3. Optimization method

Using these restriction criteria, we will create a model of the system "the optimal method of sea water desalination" (Figure 1).

![Figure 1. The system "the optimal method of sea water desalination"](image)
The criterion "geographical" excludes freezing methods and gas hydrate extraction, for which the field of practical application is limited to completely defined climatic zones. The method of freezing requires complex equipment and energy-intensive. Therefore, in practice it is used extremely rarely.

Possessing all the advantages of contact freezing, the gas hydrate method is also excluded, since in its basic principle there is freezing.

The criterion "industrial application" excludes extraction and the method of biological desalination of sea waters.

The criterion "economic" excludes at once a number of methods of desalination with the use of reagents. Because:
- the method of chemical deposition uses expensive reagents;
- the precipitation reaction with barium salts proceeds slowly, as barium salts are toxic (the criterion "ecological safety" is also excluded by this method);
- for each of the individual dissolved salts in seawater, the selection of certain reagents is required;
- as a rule, the reagents are not amenable to regeneration, which increases the cost of this desalination method.

Therefore, chemical deposition in desalination of water is used very rarely.

4. Methods comparison

The method of electrodialysis involves the use of expensive membranes, and for desalination it is possible to use water with a salt content of not more than 10,000 mg/l, (the average salinity of the Black Sea is 17,000 mg/l).

In the ion exchange method, membranes are very sensitive to the slightest scale deposits, especially magnesium hydroxide, which falls out even at low temperatures due to an increase in the concentration of ions at the membrane surface in the brine chambers. Viruses and bacteria that are not sensitive to the electric field will remain in the water, so the criterion of "environmental safety" would also not miss this method.

For consideration are the two most commonly used methods of desalination - distillation and reverse osmosis.

Let's compare these methods by the criteria of "limitation", "temporal" and "electricity consumption".

Advantages of reverse osmosis [4]:
- high water quality by suspensions, biological and organic pollution;
- the minimum amount of reagents and total discharge of salts into the environment;
- the possibility of discharging concentrate without treatment into the sewage system;
- relatively low operating costs;
- absence of aggressive reagents and the need for their processing.

Disadvantages of reverse osmosis:
- organization of a complex technology of preliminary treatment of initial water, the cost of which is sometimes two to three times higher than the cost of the reverse osmosis unit itself and the availability of which doubles energy consumption;
- requires a large number of chemical reagents, which reduces the ecological component of the desalination process;
- the actual service life of membranes is sometimes three to four years;
- desirability of continuous operation of the reverse osmosis unit;
- the reverse osmosis method entails a high dependence on membrane manufacturers.

Advantages of the distillation method:
- the minimum number of chemical reagents used and the minimum discharge of salts into the environment;
- low operating costs;
- long service life - about 20 years;
- the thermal method allows desalting water with virtually any type of pollution and with any salt content;
- high water quality by suspensions;
- possibility to receive waste of minimum volume, up to dry salts;
- ability to use excess heat;
- removal of dissolved gases from the water.

Disadvantages of distillation:
- high unit capital costs;
- a significant specific energy consumption. Therefore, it is economically expedient to build these facilities in the presence of a cheap heat source, for example, at sites of operating or under construction thermal and nuclear power plants.

Now in the world for desalination, either heat generation (TPP or CHPP with combined generation of electricity and heat) or "impersonal" electricity from the grid, or even renewable energy sources, is mainly used.

The criterion of "environmental safety", taking into account the physical and chemical properties of water after desalination of sea water, is probably the most important final criterion when choosing a desalination method for the Crimean region. Fresh water obtained by almost any method of desalination, for its use for drinking purposes needs to be corrected composition. In addition to the generally accepted criteria for assessing the quality of drinking water in accordance with GOST R 51232-98 "Drinking Water. General requirements to the organization and methods of quality control" [5] – favorable organoleptic properties, harmlessness of chemical composition and safety in epidemic (infectious) relation, for desalinated water additional criteria – physiological fullness and stability of quality are defined [6].

Distillation is a process almost similar to what is happening in nature. As a result of the distillation, it is possible to obtain desalted water, purified from all harmful salt elements. This can be done using the reverse osmosis method. However, the water obtained as a result of cleaning by these methods is of different quality. Let's consider the quality of desalinated water in two ways, according to three indicators - the content of boron, bromine and deuterium.

Some data on the separation of biologically active trace elements (boron and bromine) are given in [7] for various methods of desalination of mineralized water. If boron content in the initial mineralized water is 2-4 mg/l boron under experimental distillation conditions, the boron is delayed by 100 % regardless of the evaporation temperature (70-100 °C); with a content of 3-6 mg/l bromine in the initial water, bromine is delayed by 90-95 % under experimental conditions, while the retention effect decreases with a decrease in the boiling point in a vacuum. With reverse osmosis desalination, the efficiency of boron and bromine retention is practically independent of the cellulose acetate membrane type, the operating mode of the plant and the level of the initial content, and is 30-35 % boron and 70-80 % bromine.

In electrodialysis desalination, the efficiency of boron and bromine retention depends on the depth of desalination. The general pattern of the retention of trace elements, depending on the desalination method, is characterized by a decreasing series; for boron - distillation > reverse osmosis; for bromine - distillation > reverse osmosis > electrodialysis.

It is necessary to emphasize that when choosing the desalination method, attention should be paid to the presence of "heavy water" in sea water. "Heavy water" plays a significant role in various biological processes. Various studies [8-11] found that "heavy water" acts negatively on living organisms.

The content of heavy isotopes of hydrogen and oxygen in natural waters is controlled by two international standards: Standard Mean Ocean Water and Standard Light Antarctic Precipitation

Table 1 shows isotopic determinations of water samples, including a sample of the International Standard for Stable Isotopes. The International Standard for Stable Isotopes is the average sample of the water of the World Ocean, universally accepted as a zero reading.
Table 1. The content of deuterium and oxygen-18 in samples from different sources

|                      | International Standard for Stable Water Isotopes | Lake Baikal | Black Sea, Sochi, 100 m | City water supply, Moscow | Mediterranean Sea, Israel, district Ashkelon | Desalinated water after installation, Israel, Ashkelon |
|----------------------|--------------------------------------------------|-------------|-------------------------|--------------------------|---------------------------------------------|-----------------------------------------------------|
| \( \delta^D \), %/SMOW | 0,00                                             | -118        | -30                     | -90                      | +5                                          | +6                                                  |
| \( \delta^{18}O \), %/SMOW | 0,00                                             | -15,7       | -4,0                    | -7,0                     | +0,8                                        | -4,7                                                |

For the comparative analysis samples of data from Lake Baikal, the Black Sea, the water of the city water pipe of the city of Moscow, the Mediterranean Sea, water after the desalination plant of reverse osmosis of the city of Ashkelon (Israel) are involved.

As can be seen from Table 1, the deuterium content in the Mediterranean Sea is much higher than in the Black Sea. The concentration of deuterium does not decrease, when sea water passes through the reverse osmosis unit. The isotopes in the original water are not filtered out, but are completely passed to the desalinated water, a number of highly toxic and radioactive impurities of water are also not retained by the filters and completely, partially or as a part of the compounds newly formed when water is pushed through the filters, also falls into the desalinated water.

Disadvantages of the method of desalination by reverse osmosis taking into account the criterion for limiting "ecological safety" [11]:
- does not remove heavy stable isotopes;
- the possibility of removal of bromine and boron has certain limitations - for example, the content of boron in desalinated water should be reduced by an order of magnitude to achieve the normative value - not more than 0.5 mg / l, and this for membrane methods presents certain difficulties, during distillation there are no such difficulties;
- membrane methods involve the use in large quantities of various synthetic and polymeric materials. Cellulose, polyamide and other types of membranes have two hygienically important properties. First, non-polymerized monomers can be washed out of these polymeric materials and fed into desalinated water. Secondly, over time, under the influence of various environmental factors, the transformation of polymeric materials can occur with the formation of by-products of organic origin.

Advantages of distillation:
- in the distillation methods of desalination, polymeric materials are practically not used, and the threat of pollution by substances of artificial origin practically does not exist;
- the introduction of "heavy water" into the distillate is excluded in principle at vacuum distillation plants, since the boiling point of heavy water over the entire pressure range is several degrees higher than the boiling point of "heavy water", the water structure changes during distillation and the retires heavy stable isotopes.

Thus, according to the proposed criteria of restriction, the distillation method of seawater desalination with vacuum adiabatic installations is most suitable for the replenishment of fresh water in the needs of the Crimea.

5. Conclusion
The decision on the large-scale construction of desalination plants in the Crimea should be taken after all the necessary research and a clear understanding that, firstly, fresh water, obtained by almost any desalination method, needs to be corrected for salt in drinking purposes, and secondly, what to do with the brines that remain as a result of desalination.
Acknowledgments
This work was carried out by lead performer of research and development effort with financial support of Russian Federation Ministry of Science and Education with the realization of Government decree № 218 according to contract about providing and using subsidy № 02.G25.31.0150 from 01.12.2015.

References
[1] United Nations [An electronic resource]. – Access mode: http://www.un.org/ru/sections/issues-depth/water/index.html (date of the address 10.08.17).
[2] Slesarenko V.N. Desalination installations. / V.N. Slesarenko. - Vladivostok: DVGMA, 1999. - 244 pages.
[3] Panasyuk E.S. Search of the most optimum method of desalting of sea waters / E.S. Panasyuk, G.A. Sigora // 2nd All-Russian conference "Technosphere of the 21st Century": materials of the All-Russian conference of young scientists. - Sevastopol, on April 17 - 20, 2017 – Page 118-120.
[4] Ryabchikov B.E. Modern methods of preparation of water for industrial and household use / B.E. Ryabchikov. - M.: Have put a print, 2004. – 328 pages.
[5] Drinking GOST 2874-82 Water. Hygienic requirements and control of quality. – Vved. 1999-01-07. M.: Publishing house of standards, 1999. – 3-8 pages.
[6] Methodical instructions on sanitary control of application and operation of distillation desalination installations. – M.: Ministry of Health of CCCP, 1998. - 6-17 pages.
[7] Egorov A.I. Preparation of artificial drinking water / A.I. Egorov. – M.: Stroyizdat, 1988. – 112 pages silt.
[8] Toroptsev I.V. A biological role of heavy water in live organisms. / I.V. Toroptsev, B.N. Rodimov, A.M. Marshunina, I.O. Yafarova, V.I. Sadovnikova, I.G. Lobin // Questions of radiobiology and hematology. – Tomsk: Prod. Tomsk un-that, 1966. - 118-126 pages.
[9] Mosin O.V. Isotope effects of a deuterium in cages of bacteria and microseaweed with a growth on heavy water (D2O) / O.V. Mosin, I.A. Ignatov // Water: chemistry and ecology, 2012. No. 3. - C. 83-94.
[10] Lobyshev V.I. The abnormal activating influence of heavy water of small concentration on regeneration the gidroidnykh of polyps / V.I. Lobyshev // Biophysics, 1983. No. 4. - Page 666-668.
[11] Denko E.I. Influence of heavy D2O water on cages of animals, plants and microorganisms / E.I. Denko // Progress совр. биол., 1970. t. 20. - No. 1 (4). - Page 41 - 85.