Production of Water with Reduced Content of Deuterium for Water Supply System with Desalination Installation

A Yu Smirnov, G A Sulaberidze

National Research Nuclear University MEPhI
31 Kashirskoe Shosse, Moscow 115409, Russian Federation

E-mail: a.y.smirnov@rambler.ru

Abstract. Industrial methods for obtaining light water have been analyzed in order to find an optimal variant of a separation plant for reducing deuterium content in desalinated sea water for its further use in various applications (domestic needs, medicine, nuclear energy). It is assumed that the installation should ensure the reduction of deuterium content to the level of the cleanest freshwater ponds, working as an integral part of the water supply system based on the nuclear desalination complex.

It was shown that the most promising option for a deuterium content reduction in desalinated water is an installation based on the distillation method. Analysis of the results of the study allows us to formulate proposals and recommendations for the implementation of a subsequent scientific research and feasibility study to assess the key characteristics of nuclear desalination plants and make decisions about their implementation.

1. Introduction

Over the last years the mankind has faced an ever-growing problem involving the deficiency of freshwater suitable for drinking as well as domestic and hygienic applications. Many experts note that clean water becomes more and more significant strategic reserve for the development and safety of particular countries and the mankind in whole. This fact makes them regard the world ocean as a potential source of water. However, the high content of salts in sea water makes it unsuitable for water supply and drinking needs. The solution to this problem is possible with desalination techniques [1, 2].

Under the project being implemented in the RF on creation of a nuclear desalination complex a scientific basis is assumed to be developed for water desalination technique environmentally-friendly and involving the development of a water-supply hybrid system based on the up-to-date low-power nuclear reactors in order to solve the water deficiency problem, mitigate the ecological impact on the environment and provide the water-deficient regions with fresh water. The plant being developed, as compared with the ones already implemented, involves the combination of the desalination complex with a mobile nuclear power plant that may be developed based on the Russian KLT-40S and RITM-200 reactors (designer: JSC AKBM Africantov). The said power plants are designed based on the naval reactors and may be installed on an offshore platform, which ensures their mobility. They can also operate in self-contained mode for a long time (up to 7 years) on single fueling. Thus, the complex being developed is simultaneously both a mobile electric power station capable to feed relatively small communities (up to 100 thousand people) and a desalination plant using not only the electric power generated in the reactor, but also its “exhaust” heat (waste steam heat).

The complex being developed has one more specific feature, i.e. a plant available therein for reducing deuterium content in water. As a matter of fact, the desalinated water thus obtained may be unrestrictedly used for only technical use. It is a problem to use it for drinking due to a higher total...
deuterium content therein as compared with freshwater ponds. For example, according to the ocean water standard (VSMOW) the deuterium content in ocean water amounts to approximately 155 ppm which is in about 10% excess over the deuterium average content in freshwater. In some experts’ opinion, using such water for drinking is not advisable since the results of studies concerning the effect of the deuterium contained in water on vital processes of some animals and insects show that an increase of its content has a negative impact on metabolic processes and immune activity of organisms [3-5].

Thus, to obtain drinking water in the nuclear desalination complex, it is necessary to correct its isotopic composition in order to reduce the deuterium content therein to the average level for freshwater (120-130 ppm) and less.

To reduce the deuterium concentration in desalinated water means to separate the hydrogen isotopes. The solution to this problem demands appropriate separation techniques to be applied. To separate isotopes of the biogenic elements including hydrogen, the so-called two-phase separation methods have gained widespread use [6-10] including distillation, chemical isotope exchange, et al [10]. It should be stressed that the problem to obtain water with a reduced deuterium content (or “light” water) is not typical for the separation of hydrogen isotopes since the major studies in this respect are aimed at heavy water (D$_2$O) [6-10] to be obtained or cleared from protium and tritium isotopes [11-14]. The said factors impose particular conditions on the process of protium and deuterium separation since, unlike the case of deuterium enrichment and heavy water production, this task implies that the above process runs mainly in the H$_2$O-HDO, but not in the H$_2$O-D$_2$O system, which affects the values of separation coefficients. In addition, in view of the low content of deuterium in water, it is actually about further depletion of water over a given isotope.

To create the nuclear desalination complex, it is necessary to consider the following criteria for choosing the method of water isotopic composition correction for deuterium:

- Using water as working agent
- Possibility to utilize energy of reactor coolant
- Relatively easy implementation and availability of techniques
- Fire and explosion safety
- Possibility to integrate the plant into the water desalination scheme with minimum of additional components.

In this article the industrial methods for separation of hydrogen isotopes have been analyzed in order to find an optimal variant of a separation plant for reducing deuterium content in desalinated sea water. It is shown that the water rectification allowing utilizing the exhaust heat of nuclear power plant directly is the most promising method to implement the deuterium separation plant. Specific energy consumption to obtain the product of required quality by this method has been assessed in terms of drinking water supply to a community with a population of 100 thousand people. Aspects of further efforts to create the deuterium separation plant within the nuclear desalination complex have been formulated.

2. Choice of Hydrogen Isotope Separation Method

The problem of the hydrogen isotope separation occurred to appear at different times and for different purposes. For instance, at the rise of nuclear power industry and military programs the main interest was to obtain heavy water, but several decades later the major problem became to clear hydrogen isotope mixtures from tritium [11-14]. The versatility of the problems gave rise to various techniques for their solutions. To separate the hydrogen isotopes at industrial level, such methods have been applied as water electrolysis [11], rectification of various hydrogen-containing compounds (ammonia, water, molecular hydrogen) [6-11], chemical isotope exchange [11]. Hereinafter find a brief critical analysis of the hydrogen isotope separation methods in
terms of their applicability to implement the deuterium separation plant within the nuclear desalination complex.

2.1 Electrolytic Method
The method means the following: at water decomposition into hydrogen and oxygen under electric current the isotope separation effect appears. To multiply the single separation effect, the electrolyzers are connected in series thereby implementing the cascading principle.

The main advantage of electrolysis, as compared with other methods, are rather high (1.5-10) separation coefficients. However, this gain is negated several times (or even by orders) due to high energy consumption of the traditional electrolysis relative to other methods of hydrogen isotope separation, e.g. when heavy water is obtained [11]. One more major shortcoming of the electrolysis is its fire and explosion hazard due to the generation of hydrogen and oxygen in one apparatus, which imposes strict demands on electrolyzer design.

It should also be stressed that the electrolytic method can be implemented subject to direct use of electric power and thus makes it difficult to utilize the waste steam energy in turbine of the mobile NPP. This means that such installation will be capable of full power operation during only power plant “off-peak” hours. However, this may prove to be insufficient to ensure the required water volumes with reduced deuterium content.

Summarizing the above, it should be noted that this method is not advisable to be considered as a key one to obtain water with reduced deuterium content within the nuclear desalination complex for the following major reasons:

- High energy consumption
- Failure to directly use nuclear reactor exhaust heat.

2.2 Chemical Isotope Exchange Method
Chemical isotope exchange (CIE) method [10, 11] is another method applicable for the hydrogen isotope separation. The method is based on the fact that in a system of two chemically not interacting substances an isotope exchange reaction may run with equilibrium constant differing from the value corresponding to distribution of isotopes with equal probability between the molecules involved in the reaction [10]. The process of separation (isotope exchange) may run in the water-hydrogen system:

\[ \text{H}_2\text{O} + \text{HD} \leftrightarrow \text{HDO} + \text{H}_2. \]  

The characteristic values of separation coefficients for the chemical isotope exchange reactions in such system are approximately 3-3.5 [11], therefore the CIE processes have become dominant in the up-to-date techniques of heavy water production.

In practice the CIE may be implemented in column-type separation device. Reactions of chemical isotope exchange between molecules incessantly run in the volume of the column. Flow conversion nodes are the major parts of the vessel (column): upper flow node and lower flow node. The function of the lower flow node is to quantitatively convert the total liquid flow leaving the column into a gaseous working agent of the chemical exchange system (water into hydrogen for the above reaction). In the upper flow node this process needs to be conducted in the opposite direction (hydrogen into water).

For the water-hydrogen system the flow conversion nodes can be implemented as follows: the lower flow node is meant for water electrolysis, while the upper one – for burning or hydrogen catalytic oxidation [11]. This system has a “weak point” which is the necessity to use a hydrogen-activating catalyst capable of working effectively in a system with liquid water [11].

Thus, despite the proved effectiveness of the CIE method for hydrogen isotope separation, this method is not the best choice to implement the deuterium separation plant in the desalination complex. The major reasons: failure to directly use nuclear reactor exhaust heat as well as additional catalysts to be used for the separation in the water-hydrogen system.

2.3 Rectification Method
The rectification method was widely used for the hydrogen isotope separation at different times [6-11]. In terms of this method the separation occurs in the volume of a column-type separation device at redistribution of isotopes between liquid and gaseous phases of the working substance, which may be hydrogen, water or ammonia [6-11]. In the nuclear desalination complex water is the only acceptable option. In this case the following reaction is running [11]:

$$H_2O_{\text{liquid}} + HDO_{\text{steam}} \leftrightarrow HDO_{\text{liquid}} + H_2O_{\text{steam}}$$

(2)

At water rectification protium and deuterium concentrate in gaseous and liquid phases, respectively. Thus, there is a counterflow of two phases (liquid-steam) occurring in the column with the incessant isotope exchange between them.

Among all the above methods of hydrogen isotope separation the water rectification is least effective as for separation coefficients. Thus, depending on separation process conditions (operating pressures and temperatures) the characteristic values of protium-deuterium separation coefficients may fall in a range of 1.022-1.069 [10]. However, unlike the previous methods, the water rectification allows direct utilization of the turbine waste steam energy to heat up the water evaporators.

For contact interface buildup and, hence, separation process intensification there are various contact devices used in columns. At water rectification the so-called tray-type and packing-type contact devices are used [6-11].

Packing that fill the column volume is the most effective contact device. The packing is known to be preformed, i.e. forming regular-shaped channels for steam passage, and random (or dumped), when the packing elements being positioned in a random way form curved channels of arbitrary shape [11]. The random packing has, as a rule, better mass-exchange characteristics (height of equivalent theoretical separation stage, etc.) and ensures the best separation conditions. However, its cost is in excess to the preformed option, which can impede its use in the large-scale industrial production of the isotope product required.

The preformed packing is inferior to the random one for mass-exchange characteristics, but demonstrates higher throughput and lower cost. The preformed roll-type helical band packing offered by D.I. Mendeleev RHTU [15] is one of the promising domestic options. This packing may be made of stainless steel gauze by winding either corrugated bands only or, in turn, corrugated and flat bands at an angle to each other. The advantages of this packing are as follows: (a) relatively easy production, (b) the roll can be made in size to column shell. This makes this packing accessible, effective and easily adaptable to columns of various diameters According to the data in [15] such packing is competitive with known foreign analogs for a number of characteristics and, hence, may be used to implement the deuterium separation plant with rectification.

Summarizing the above, it should be noted that the water rectification is one of the most suitable methods to obtain water with reduced deuterium content based on the nuclear desalination complex. The major reasons of this are as follows:

- Using water as working agent
- Developed and proved at industrial level the RF-located manufacturing processes for columns themselves and packing to them
- Relative safety of the method.

However, its major shortcoming is tangible energy consumption due to heating and evaporation of water. This problem can be solved by utilizing the nuclear reactor exhaust heat as well as applying the effective schemes of energy recuperation allowing the energy of steam condensation in the condenser to be returned to heat up the evaporator. To implement such conditions, it is necessary to subsequently choose an optimal heat balance scheme for such installation. To find a heat balance scheme for the installation considering its “coupling” with the reactor on one side and desalination plant on other side is the key stage of the work being done and its main feature as compared with the already implemented desalination plants or rectification cascades for hydrogen isotope separation. When choosing the optimal heat balance scheme, it is necessary to consider, as inlet conditions, the parameters of the turbine waste heat (mass flow, temperature, etc.) and the temperature of the desalinated water inlet flow from the desalination plant. Based on the heat balance scheme found, it
will become possible to work out proposals on design features of the flow conversion nodes, which will be conditioned by heat balance between the amount of heat necessary for functioning of the evaporators providing the specified steam flow in the columns and the energy of the steam having passed through the turbine.

3. Specific Energy Consumption Estimation

To create the nuclear desalination complex with the deuterium separation plant, an integrated installation is assumed to be developed to obtain water with deuterium content reduced relative to its level in the desalinated sea water. Such plant is mainly intended to obtain water with the deuterium content at the level of freshwater ponds (~120-130 ppm) to provide the communities connected to the desalinated plant with water suitable for drinking. According to the requirements imposed such plant should cover the needs of a community with a population of up to 100 thousand citizens. At a standard consumption rate of drinking water averaged to 3 l/day per person the plant throughput should be ~12.5 t/h. It should be observed that the water must enter the deuterium separation plant as having been preliminarily cleared from salts, but being mixed up at outlet with a salted solution to provide the final product. Assuming the initial water as containing deuterium at a level of ~155 ppm, the approximate mixing proportion should be 1:1. Proceeding from this fact, the further development of the deuterium separation plant should be conducted for the following external conditions specified:

- Deuterium content in the feeding mixture is 155 ppm
- Deuterium content in the product flow is 100 ppm (so that the water to be obtained after mixing with a deuterium content of ~120-125 ppm)
- Separation plant does not have the exhausting part and the water at the waste end must be repeatedly directed into the evaporator. In this case the deuterium content in the inlet section of the column will only slightly (not more than by 5 ppm) exceed the corresponding content in the steam flow entering the column
- Product flow rate is 6.25 t/h.

Proceeding from the provided analysis of hydrogen isotope separation methods, it follows that the water rectification is the most promising method to be used for the development of the deuterium separation plant. It should be stressed, however, that its choice is dictated to a great extent by the fact that the problem set forth demands a relatively minor change in the deuterium concentration, as well as the fact that the water rectification will allow involving the waste heat of the nuclear reactor.

To proceed with the design of the deuterium separation plant, its technological analysis and feasibility study, it is necessary to receive estimates on specific energy consumption for production and material flow rates.

Let us estimate the material flow rates required to implement the above external conditions for a supposed binary separation (protium-deuterium). According to [10] the minimal liquid flow through the section of the column/columns at a specified throughput of the separation plant can be calculated as:

\[
I_{\text{min}} = \frac{P(aC_p - \varepsilon C_F C_p - C_F)}{\varepsilon C_F (1 - C_F)}
\]  

(3)

where \(C_p\) and \(C_F\) – concentrations of the component being enriched in product flow and feed flow, \(a\) – separation coefficient, \(\varepsilon\) – enrichment coefficient, \(P\) – product flow.

Let us consider the most easily implemented case of the rectification at atmospheric pressure, which runs at a temperature of 373 K and with a \(\text{H}_2\text{O} - \text{HDO}\) separation coefficient of \(a=1.026\) [10]. Subject to such assumptions and with \(P=6.25\) t/h, \(C_p=99.99\) atomic %, \(C_t=99.845\) atomic % as above specified the calculated \(I_{\text{min}}\) amounts to 91.6 t/h. The liquid flow rate in the real installation may be estimated as \(L=1.5L_{\text{min}}=137.4\) t/h. In this case the steam flow rate at column inlet \((G)\) will be \(G=L+P=143.65\) t/h. Based on the \(G\) value thus calculated, it is an easy task to estimate the power for heating and evaporation of the water mass required. Assuming the temperature of the feed water to the evaporator as 293 K, the specific energy for water heating and evaporation will be 18.74 kW·h/kg.
value of specific energy consumption thus received should be construed as “overestimate” since this calculation does not consider such factor as return of the heated liquid from the column to the evaporator. Besides, the received value may be reduced subject to application of effective manufacturing process schemes that allow utilization of the heat releasing at condensation of the working agent in the condenser to heat up the evaporator. According to the data in [14] such schemes allow reducing the energy consumption by at least 2-3 times. In addition to the above, the separation equipment as itself demands a proper heat insulation, which can allow further reduction of the specific energy consumption.

In the context with the above the said value of the specific energy consumption for production undoubtedly demands its verification in the course of the further project implementation. Nevertheless, based on the data received, it is necessary to assess the possibility to satisfy the energy consumption as specified for the installation by utilizing the turbine waste steam of the mobile NPP providing the needs of the desalination plant itself are taken into consideration as well. The schematic diagram of the deuterium separation plant and options of its implementation will demand further development and analysis in order to find the final solution most effective. The steps to conduct the work are as follows:

- Verify the process parameters (initial temperature of the feedwater, characteristics of the turbine waste steam, etc.)
- Choose the options for implementation of separation equipment and the materials used (packing type and size, etc.)
- Define the design parameters of the separation equipment and its operating characteristics (diameters and number of the columns, height of equivalent theoretical stage and other mass-exchange characteristics, options of columns commutation, etc.)
- Make a detail thermo-fluid calculation for parameters of the evaporators and condensers, piping, as well as heat pumps suitable for energy recuperation
- Work out a schematic diagram for commutation of the plant components and its provision with automatic control systems.

4. Conclusion
Critical analysis on industrial methods of hydrogen isotope separation has been conducted. As a basic method to create the deuterium separation plant the water rectification method has been preliminarily chosen. This choice is conditioned by using water as working substance, relative easiness of its implementation, possibility to utilize the NPP turbine waste steam energy in order to heat up the evaporator. Specific energy consumption to obtain the required product by water rectification at atmospheric pressure has been estimated as 18.74 kW·h/kg.

Further efforts will be directed toward elaboration and analysis of the plant schematic diagram, options of its implementation and “interfacing” with the mobile nuclear power plant so that to find the heat balance and manufacturing process schemes most effective.

The accomplishment of the above efforts will enable a feasibility study to be conducted allowing estimates on the specific consumption for production.

Acknowledgments
The work was financially supported by the Ministry of Education and Science, agreement № 14.575.21.0159. Unique project identifier RFMEFI57517X0159.

References
[1] Obraztsov S V 2011 Complex processing of sea, reservoir, surface and waste waters: textbook (Tomsk Polytechnic University. - Tomsk: Publishing house of Tomsk Polytechnic University) p. 83 (in Russian)
[2] Mosin O V 2012 Consciousness and physical reality 1 19 (in Russian)
[3] Barishev M G, Bolotin S N, Frolov V Yu, Dzhimak S S, Pikula A A, Dolgov M A, Shashkov D I, Petriev I S 2013 Ecol. Bull. of Res. Cent. Black Sea Econom. Cooper. 1 I 13 (in Russian)

[4] Samkov A A, Dzhimak S S, Barishev M G, Volchenko N N, Khudokormov A A, Samkova S M, Karaseva E V 2015 Biophysics 60(1) 107

[5] Dzhimak S S, Barishev M G, Basov A A, Timakov A A 2014 Biophysics 59(4) 614

[6] Andreev B M, Zelvensky Ya D, Katalnikov S G 1982 Separation of stable isotopes by physicochemical methods (Moscow: Energoatomizdat) 208 p. (in Russian)

[7] Rosen A M 1960 The theory of isotope separation in columns (Moscow: Atomizdat) (in Russian)

[8] Andreev B M, Zelvensky Ya D, Katalnikov S G Heavy isotopes of hydrogen in nuclear engineering (Moscow: Energoatomizdat) 456 p. (in Russian)

[9] Isotopes: Properties. Receiving. Application 2005 ed. V Yu Baranov (Moscow: Fizmatlit) (in Russian)

[10] Andreev B M, Magomedbekov E P, Reitman A A et al. Separation of isotopes of biogenic elements in two-phase systems (Moscow: Izdat) 376 p.

[11] Magomedbekov E P, Rastunova I L, Rozenkevich M B 2014 Issues At. Sci. Technol. Ser.: Mater. Sci. New Mater. 3(78) 70 (in Russian)

[12] Magomedbekov E P, Belkin D Yu, Rastunova I L, Sazonov A B, Selivanenko I L, Kulov N N 2017 Theor. Found. Chem. Engng. 51(4) 384

[13] Magomedbekov E P, Belkin D Yu, Rastunova I L, Sazonov A B, Selivanenko I L, Kulov N N 2017 Theor. Found. Chem. Engng. 51(2) 133

[14] Niculescu A, Constantin T, Ana G, Draghia M. 2017 Fus. Engng. and Des. 124 752

[15] Magomedbekov E P, Belkin D Yu, Selivanenko I L, Rastunova I L 2016 Theor. Found. Chem. Engng. 50(4) 398