Combined Scheme of Permafrost Water Purification in Central Yakutia

S Fedorova and A Kryzhanovsky

1Melnikov Permafrost Institute of Siberian Branch of the Russian Academy of Sciences, 36, St., Merzlotnaya, Yakutsk, 677010, Russia
2Novosibirsk State University of Architecture and Civil Engineering, 630099 Novosibirsk, Russia
E-mail: *veta_f@mail.ru

Abstract. The problem of providing the of the Sakha (Yakutia) Republic population with drinking water, taking into account severe climatic conditions, is extremely urgent. The uneven distribution of the population over the republic vast territory dictates special requirements for the water supply organization. One of the solutions may be the partial involvement of sub-permafrost waters in the local systems of drinking water supply for the population of Central Yakutia. They contain increased concentrations of lithium, fluorine and sodium and can be used for drinking water supply only after preliminary water treatment, despite the significant reserves of subpermafrost waters and their undoubted advantages. The choice complexity of the water treatment technological scheme is due to the lack of approved methods for purifying drinking water from lithium. The authors carried out an experimental-industrial approbation of the ion-exchange method for removing lithium from the subpermafrost waters of the Yakutsk artesian basin. On the basis of the results obtained, a comprehensive scheme for the purification of Central Yakutia subpermafrost waters for drinking water supply was developed, which provided for a decrease in the concentrations of lithium, fluorine and sodium to standard requirements.

1. Introduction

The problem of providing the population with drinking water is especially acute, despite a huge reserve of water resources in the Republic of Sakha (Yakutia). According to statistics, centralized water supply covers about 62% of the republic's population, 96% in urban and 4% in rural settlements. Only 7% of settlements are provided with water treatment facilities, in connection with, the population is forced to use water without preliminary purification. Traditional sources of water supply, confined to surface water bodies and streams, have a number of disadvantages, such as non-observance of sanitary protection zones and insufficient efficiency of treatment facilities, especially during the flood period. In addition, the organization of water supply from surface sources is impossible due to their insignificant water availability or remote location in a number of Yakutia settlements.

Therefore, the issue of organizing water supply to the Central Yakutia population with the help of subpermafrost waters use of the Yakut artesian basin is very promising. These waters have a stable chemical composition that does not undergo seasonal changes. They are reliably protected from technogenic impact and are safe in radiological and bacteriological terms. The use of regionally widespread groundwater will make it possible to bring water supply sources as close as possible to specific water consumers, which will significantly reduce of organizing and operating systems' cost of
domestic and drinking water supply. A characteristic feature of the permafrost waters chemical composition, which significantly complicates their widespread use for household and drinking purposes, is the increased content of lithium, fluorine and sodium [1, 2]. Thus, the concentration of lithium in fresh subpermafrost waters of Central Yakutia reaches 25-35 maximum permissible concentrations (MPC), fluorine concentration reaches 8-10 MPC, sodium concentration - 2-2.5 MPC. The deviation from the norms for the content of the listed elements is caused by the geological structure, permafrost-hydrogeological conditions and the lithological composition of the water-bearing rocks [3].

The choice complexity of the water treatment technological scheme is due to natural lithium presence in the water, which content significantly exceeds the maximum permissible concentration for household and drinking water supply. Mica and clays can serve as sources of lithium in subpermafrost waters, so leaching of lithium is enhanced by the presence of elevated chloride concentrations in the water. It is known that the sorption capacity of alkaline elements form the geochemical series K \textsuperscript{+} > Na \textsuperscript{+} > Li \textsuperscript{+}. This means that, when groundwater interacts with aquifers, dissolved potassium (K) passes into the solid phase, displacing water Li from it [4, 5, 6].

In accordance with the current regulatory documents, lithium belongs to the second hazard class with a sanitary and toxicological indicator of harmfulness, its maximum permissible concentration in drinking water is 0.03 mg / l. Lithium is carcinogenic, it has a toxic effect in the suppression form of renal function and disorders of the cardiovascular and central nervous system. The main places of its accumulation in the human body are the thyroid gland and bone tissue [7].

Many biochemists believe that lithium is the most toxic to the body of all the alkali metals, due to its ability to replace sodium and potassium ions. Lithium is reabsorbed and replaced in the tissues with a deficiency of potassium and sodium. In addition, lithium ions affect the operation of the sodium-potassium pump, which ensures the ionic balance of cells, including brain cells. The ability of lithium in the body to release magnesium from cell stores inhibits the transmission of nerve impulses, thereby reducing the excitability of the nervous system [8]. On the other hand, the skeleton becomes one of the target organs, since more than half of the magnesium ions are concentrated in the bone tissue. This is due to the fact that lithium and magnesium are linked by the so-called diagonal analogy, largely due to the practical equality of their ionic radii. Since lithium, on the one hand, and potassium, sodium and magnesium, on the other, are antagonists, metabolic processes involving the disrupted latter, which can affect the central nervous and cardiovascular systems.

The elimination system comes to be active with an excess intake of a trace element. In particular, the processes of microelement absorption in the gastrointestinal tract can be blocked, leading to its deposition in the depot. A defect in a certain link in the system, providing microelement homeostasis, leads to the fact that an excess of a microelement may appear in the body, accompanied by appropriate clinical symptoms and the development of the disease [9].

The literature sources analysis does not give an idea of the water treatment systems for household and drinking purposes, which allow reducing the lithium content. The published materials contain information on the extraction of lithium from natural solutions and technological brines for industrial purposes. The known methods for extracting lithium from solutions of various origins belong to the field of hydrometallurgy and inorganic chemistry and are not suitable for household and drinking systems. Basically, the extraction of lithium from aqueous media is carried out by methods of reverse osmosis, sorption and electrodialysis [10, 11, 12]. They have a number of significant disadvantages, such as low manufacturability, multistage, insufficient degree of purification, complexity of sorbents preparation, their limited capacity, need for sorption at elevated temperatures, an increased content of residual concentrations of some elements in water, complexity of the sorbent regeneration process, all this does not allow using these methods in the processes of water treatment for household and drinking purposes [13, 14]. Thus, the absence of approved methods for purifying drinking water from lithium compounds determines the high relevance of this study.

Earlier, laboratory experimental studies were carried out to study the sorption of lithium from model solutions and natural subpermafrost waters by various filtering materials on the basis of the
underground waters laboratory and permafrost zone geochemistry of P.I. Melnikov of the Siberian Branch of the Sciences Russian Academy. As a result of the work carried out, a high efficiency of the ion exchange method with respect to lithium ions was established [15]. The degree of lithium extraction from natural sub-permafrost waters was 90% under static conditions and 99.3% under dynamic conditions [16].

Thus, the research aim was to test the ion exchange method for removing lithium from subpermafrost waters in industrial conditions, as well as to develop an integrated technological scheme for the purification of subpermafrost waters in Central Yakutia, which made it possible to ensure the water quality according to the content of lithium, sodium and fluorine.

Figures and tables, as originals of good quality and well contrasted, are to be in their final form, ready for reproduction, pasted in the appropriate place in the text. Try to ensure that the size of the text in your figures is approximately the same size as the main text (10 point). Try to ensure that lines are no thinner than 0.25 point.

2. Materials and Methods

Experimental-industrial approbation of the ion exchange method for removing lithium from subpermafrost waters was carried out at well No. 1-Ya (Permafrost Institute SB RAS, Yakutsk). The study object was the subpermafrost waters of the Lower Jurassic aquifer under a layer of permafrost rocks with a thickness of 320 m. The water-bearing rocks are represented by various-grained sandstones with interlayers of siltstones and clays. According to the data of long-term hydrochemical testing of subpermafrost waters from well No. 1-Ya, their chemical composition is sodium chloride-hydrocarbonate with a mineralization of 780-1000 mg/l (MPC 1000 mg/l), lithium content is 0.12-0.21 mg/l (MPC 0.03 mg/l), fluorine - 3.7-5.4 mg/l (MPC 1.5 mg/l), sodium - 220-250 mg/l (MPC 200 mg/l).

Standard pressure filter 325 mm in diameter and 1700 mm in height was installed in the well to establish the main technological parameters of removing lithium process from subpermafrost waters, using the ion exchange method. A commercially available strongly acidic Na-cation exchange resin containing active sulfo groups was used as an ion exchanger. The total exchange capacity of the cation exchanger was 2.0 g-equiv/l. The granulometric composition was characterized by grains of a monospheric type with a size of 0.6-0.8 mm. The volume of the cation exchanger was 70 liters.

The study of reducing the fluorine and sodium concentration in subpermafrost waters was carried out, using a reverse osmosis unit with a permeate capacity of up to 2 m³/h.

Chemical analyzes of water samples before and after purification were carried out in the laboratory of underground waters and permafrost zone geochemistry in P.I. Melnikov of the Siberian Branch of the Sciences Russian Academy by the capillary electrophoresis method on a Kapel-104T device.

The degree of lithium S(%) extraction from the subpermafrost waters at each specific time moment t was found by the formula:

\[ S = \left( \frac{C_0 - C_t}{C_0} \right) \times 100\% \]

where \( C_0 \) – initial concentration of lithium ions, mg/l; \( C_t \) – concentration of lithium ions at time t, mg/l.

In order to intensify the process of subpermafrost waters delithiation, attempts were made to study the influence of external factors on the filtration cycle duration. Experimental studies were carried out with a change in the filtration rate and temperature of the source water (Figure 2, 3).

Comprehensive technological scheme for the subpermafrost waters purification from lithium, fluorine and sodium was developed and implemented, based on the experimental-industrial testing results of the ion exchange method in well No. 1-Ya, (Figure 4). The complex scheme provides for three main stages of water purification and conditioning. The initial water after coarse and fine filters enters the first stage - a reverse osmosis unit, which is configured to yield 70% permeate. At this stage, there is a decrease in the content of sodium and fluorine to the established maximum permissible
concentrations, as well as a partial decrease in the content of lithium (Table 1). Further, the water enters the second stage - an ion exchange unit, where additional purification of water from lithium ions takes place. During the purification process, a significant decrease in the total hardness of the water is observed. Therefore, the purified water is supplied to the third stage - the water conditioning station according to the content of calcium and magnesium ions.

**Figure 1.** The degree of lithium extraction from the permafrost waters of well No. 1-Ya during the filtration cycle.

**Figure 2.** Dependence of the residual concentration of lithium on the filtration rate.
Figure 3. Dependence of the residual concentration of lithium on the source water temperature.

Figure 4. Integrated technological scheme for the subpermafrost waters treatment in Central Yakutia: 1 - coarse mechanical filter; 2 - fine mechanical filter; 3 - reverse osmosis unit; 4 - ion exchange filter with a regeneration tank; 5 - station for dosing hardness salts; 6 - sampling of permeate and concentrate after the installation of reverse osmosis; 7 - water sampling after installing ion exchange.
Table 1. Chemical composition of subpermafrost waters in natural state and after treatment.

| Indicators of chemical composition | Units | Maximum allowable concentration | Source water | The first stage water | The second stage water | The third stage water |
|-----------------------------------|-------|---------------------------------|--------------|-----------------------|------------------------|-----------------------|
| Mineralization                    | mg/l  | 1000                            | 870.0        | 420.0                 | 421.0                  | 470.0                 |
| Rigidity                          | meq/l | 7                               | 0.8          | 0.15                  | <0.05                  | 4.5                   |
| pH                                | -     | 6.5-8.5                         | 7.2          | 6.9                   | 7.0                    | 7.1                   |
| Sodium (Na⁺)                      | mg/l  | 200                             | 245.0        | 140.0                 | 143.0                  | 143.0                 |
| Calcium (Ca²⁺)                    | mg/l  | 80                              | 12.0         | 0.9                   | 0.15                   | 28.0                  |
| Magnesium (Mg²⁺)                  | mg/l  | 50                              | 2.4          | 0.5                   | 0.1                    | 22.0                  |
| Bicarbonates (HCO₃⁻)              | mg/l  | -                               | 500.0        | 215.0                 | 215.0                  | 215.0                 |
| Chlorides (Cl⁻)                   | mg/l  | 350                             | 104.0        | 48.0                  | 49.0                   | 49.0                  |
| Sulfates (SO₄²⁻)                  | mg/l  | 500                             | 2.0          | <0.5                  | <0.5                   | <0.5                  |
| Fluorine (F⁻)                     | mg/l  | 1.5                             | 5.1          | 1.2                   | 1.2                    | 1.2                   |
| Lithium (Li⁺)                     | mg/l  | 0.03                            | 0.13         | 0.07                  | <0.03                  | <0.03                 |

Experimental studies, carried out during commissioning, have shown that the preliminary treatment of water by the reverse osmosis method made it possible to increase the filtration cycle of the ion exchange unit by 4-5 times (Figure 5). As a result, the number of regenerations and, consequently, operating costs were reduced.

Figure 5. Dependence of the lithium residual concentration on the filtered water volume, processing it on an ion-exchange unit and on a combined circuit.

4. Discussions

Maximum degree of lithium removal at the initial stage of subpermafrost waters filtration through an ion-exchange unit was 97-98%, carrying out experimental studies. Further, there is a breakthrough of the lithium ion into the filtrate in a concentration exceeding the maximum permissible, caused by the exchange capacity depletion of the resin. The exchange capacity is completely restored after the regeneration of the ion exchange resin with a NaCl solution.
The reactions of lithium ions substitution for sodium ions on a Na-cation exchange resin will look like this:

- in molecular form:
  \[ \text{NaR} + \text{LiCl} \rightarrow \text{LiR} + \text{NaCl} \]
- in ionic form:
  \[ \text{Na}^+\text{R}^- + \text{Li}^+ \rightarrow \text{Li}^+\text{R}^- + \text{Na}^+ \]

where \( R^- \) is a complex radical of a cation exchanger that cannot be dissolved in an aqueous medium.

Regeneration reaction of Na-cationic ion exchange resin in molecular form:

\[ \text{LiR} + \text{NaCl} \rightarrow \text{NaR} + \text{LiCl} \]

During the experimental-industrial testing of the ion-exchange method, it was found that an increase in the temperature of the source water from 4 °C to 5 °C, as well as a decrease in the filtration rate from 15 to 8 m³/h, using a Na-cation exchange resin, allowed increasing the duration of the filtration cycle no more than 10%.

Despite the proven high efficiency of the ion exchange method with respect to lithium ions, its use does not allow solving the problem of increased concentrations of fluorine and sodium in subpermafrost waters. So, a comprehensive scheme for the treatment of subpermafrost waters in Central Yakutia, consisting of water treatment three stages, was developed, implemented and tested. Thus, a reverse osmosis unit was envisaged as the first stage, which made it possible to reduce the concentration of sodium and fluorine, as well as partially remove lithium ions. As the second stage, an ion exchange unit was used, which provided additional purification of water from lithium. The water enters the third stage - the station for dosing hardness salts, due to the absence of physiologically necessary calcium and magnesium cations in the purified water, at the final stage. The approbation of the integrated scheme showed that the permafrost waters that had been treated fully comply with the requirements established by regulatory documents. In addition, it was found that during the preliminary treatment of water by the reverse osmosis method, an increase in the filtration cycle of an ion-exchange unit was observed by 4-5 times. At the same time both, a deeper purification of water from lithium ions was achieved, and also the number of regenerations was reduced, within the operational expenses.

5. Conclusion

A literary sources review over the effect of lithium on the human body and living beings showed that lithium is was a toxic metal, which accumulated primarily in the liver with an increased intake into the body, lymph nodes, bone tissue, causing various disorders in the work of the cardiovascular and central nervous systems. ...

In the published sources, there is no information on drinking water treatment systems that can reduce the concentration of lithium and is limited to known methods for extracting lithium from various solutions for industrial purposes. These methods have several disadvantages and are not quite suitable for drinking water treatment systems.

The authors of the article developed and implemented a comprehensive technological scheme for the purification of subpermafrost waters in Central Yakutia, which provided for a decrease in the content of lithium, fluorine and sodium to the regulatory requirements. In the course of experimental work, a high efficiency of the ion exchange method for removing lithium from subpermafrost waters was established, which amounted to more than 97%. At the same time, the use of the reverse osmosis method as a preliminary preparation made it possible to increase the duration of the ion-exchange unit filtration cycle and the water purification quality from lithium ions, and also provided a decrease in the content of sodium and fluorine to the established concentrations.

The research results can be used in the design of drinking water supply systems for settlements and production facilities in Central Yakutia.
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