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EFFICIENCY OF REDUCING GROUNDWATER HARDNESS BY ION EXCHANGE METHOD

Zokhidjon Abdulkhaev[1], Shoirakhon Abdujalilova[1,*] and Xurshida Raxmatullayeva[2]

[1]Fergana State Technical University, Feragana, Uzbekistan
[2]Tashkent University of Architecture and Civil Engineering, Tashkent, Uzbekistan
*Correspondence: shoiraxon.abdujalilova@fstu.uz

Abstract

High hardness of drinking and process water leads to the formation of deposits in heat exchange equipment, increased energy consumption, and rapid wear of equipment. Various water softening methods are used to solve this problem. Among them, the Na-cation exchange method is characterized by high efficiency, stable operation, and simplicity of the operation process. This method improves water quality by exchanging Ca and Mg ions with sodium ions. Samples were taken from 6 underground wells in the Fergana Valley, covering a total area of 0.72 thousand km^2 in the Fergana city, Toshlok district, Qoshtepa district, and Yozyavon district, and the hardness of drinking water was determined using the titration method in laboratory conditions. Based on the results obtained, boiling, filtration (ion exchange), chemical, reverse osmosis, and distillation methods of water softening were compared. The water softening method for each region was selected using scientific principles. It was found that the most optimal method for reducing groundwater of different hardness to a uniform hardness is the ion exchange method. The amount of NaCl was determined for each well to reduce water hardness.

Keywords: Total hardness, calcium ions, magnesium ions, water softening, filtration, ion exchange, sodium chloride.

1. Introduction

Providing the population with drinking water is a very complex and important engineering system. The rational use of water, ensuring its quality and safety, is one of the most pressing global issues.

When selecting sources for a water supply system, it is necessary to study sanitary, hydrological, hydrogeological, and topographical conditions. The water supply system uses groundwater and surface water as sources. Groundwater is characterized by a high content of dissolved substances, and the most common ions are calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^{+}), potassium (K^{+}), and iron (Fe^{2+}, Fe^{3+}). Calcium (Ca^{2+}) and magnesium (Mg^{2+}) ions in groundwater cause the overall hardness of the water.

Scientific research into water hardness and methods for softening it is essential for ensuring the efficiency and safety of water supply systems. Abramova et al. [1] conducted a comprehensive analysis of existing water softening methods and proposed an algorithm for selecting the most optimal technology for production processes. The study compared ion exchange, chemical precipitation, and other methods and evaluated them based on the criteria of technological efficiency, economic performance, and operational convenience. This approach demonstrates the need to optimize the water softening process.

Campanile et al. [2] studied the potential of water softening through ion exchange and precipitation processes using zeolite-based monolithic materials. The results of the study showed that Ca^{2+} and Mg^{2+} ions can be effectively reduced, and this method is considered a promising technology for industrial application. This work scientifically substantiates the high efficiency of ion-exchange processes in water softening.

The effect of water hardness on human health has also been scientifically studied. Jabbar-Lopez et al. analyzed the relationship between drinking water hardness and adverse health effects based on long-term observation [3]. The results of the study indicate that there is a gene-environment interaction between water hardness levels and skin diseases. This justifies the need to establish regulatory limits for Ca and Mg ions in drinking water.

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However, there are also negative aspects of very soft water. Water quality criteria developed by the US Environmental Protection Agency (EPA) assess metal ions in water and their effects on aquatic organisms [4]. This document demonstrates the ecological and technical importance of the chemical composition of water and confirms the role of metals in corrosion processes.

Vazdirvanidis et al. studied the corrosion phenomenon in copper pipes and showed that corrosion processes can be enhanced in soft water conditions [5]. The results of the study confirm that the chemical composition of the water, especially the low mineralization level and the aggressive environment, lead to rapid corrosion of the pipes.

The above studies show that the issue of water hardness requires a two-pronged approach: on the one hand, high hardness is harmful to industrial equipment and pipes, and on the other hand, extremely soft water can also cause corrosion and health problems. Therefore, maintaining the hardness of drinking water within the optimal range and choosing a suitable softening method for technological processes is scientifically and practically relevant.

2. Materials and Methods

The overall hardness of water varies in different regions. The reason for this is related to the composition of the rocks in the area, the amount of rainwater, climatic conditions, and the level of industrialization. The population of the Fergana Valley mainly uses groundwater for drinking and domestic needs. Groundwater is characterized by its colorlessness, clarity, absence of bacteria, high salt content, as well as the presence of iron, fluorine, and dissolved gases.There are soda-lime method, soap determination, atomic absorption spectrometry, and rapid express methods for determining water hardness.

The hardness of groundwater in various regions of the Fergana region was determined using the titration method. The following equipment and reagents were required to carry out the measurements.

Laboratory glassware, pipettes, burettes for measurements.

Conical flasks with a capacity of 250–300 cm^3.

Dropper.

Trilon B 0.01 H

Ammonium chloride.

Aqueous ammonia — 25% solution

Special chromogen ET-00 (indicator).

Chromium-red acid indicator.

Conducting the study. 100 cm^3 of the water being analyzed is taken into a conical flask. Then the following is added to the flask:

5 cm^3 buffer solution,

5–7 drops of indicator,

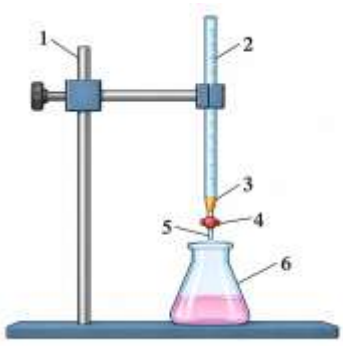
Then, with vigorous shaking, it is titrated with Trilon B 0.01 H solution until the color change at the equivalence point. At the equivalence point, the solution should turn from purple to blue.

If no clear color change is observed at the equivalence point, it is assumed that copper and zinc are present in the water. In this case, to eliminate the effect of interfering substances, 1–2 cm^3 of sodium sulfide solution is added to the water sample taken for titration and the analysis is continued as described above.

If, after adding the buffer solution and indicator, the solution gradually discolors and turns gray, this indicates the presence of manganese in the water. In such cases, five drops of a 1% hydroxylamine hydrochloride solution should be added to the water sample taken for titration before adding the reagents, and the hardness is determined as described above.

If the titration process is too long and the color at the equivalence point is unstable or unclear, which occurs when the water is highly alkaline, then the effect of alkalinity can be eliminated as follows.

Before adding reagents to the water sample to be titrated, 0.1 normal hydrochloric acid is added in the amount necessary to neutralize the alkalinity of the water. After that, the solution is boiled for 5 minutes or treated by spraying and blowing with air. After that, a buffer solution and an indicator are added and the total hardness of the water is determined according to the procedure described above.



1. Stand (retort stand)
2. Burette
3. Rubber tubing
4. Bulb (ball valve)
5. Glass tip
6. Titration flask

Figure 1. Titration device.

A sample of groundwater was taken from a depth of 300 meters in the Konizar neighborhood, Tashlok district, Fergana region.

1. A 100 ml water sample was taken into a conical flask.

2. 5 ml of ammonium buffer solution was added to the conical flask.

3. 5-7 drops of indicator solution were added, and the liquid in the flask turned purple.

4. The burette was filled with Trilon B – 0.01 H solution.

5. The Trilon B solution was titrated into a conical flask using a burette until the color changed.

6. The mixing of Trilon B was stopped when the liquid in the conical container turned an inky color.

7. The volume of the trilon mixed from the burette showed 1.8.



Figure 2. Color change of water during titration.

Based on the results obtained, the total hardness of the water was determined.

$$T = \frac{0{,}1 \cdot v \cdot K \cdot 1000 \cdot 1000}{V}, \quad mg\frac{eq}{l}$$

$$T = \frac{0{,}1 \cdot 1{,}8 \cdot 0{,}01 \cdot 1000 \cdot 1000}{100} = 18\ mg\ eq/l9 \quad (1)$$

The total hardness of groundwater at a depth of 300 meters in the Konizar MFY of the Tashlok district of the Fergana region is 18 $mg\ eq/dm^3$.

If the total hardness of groundwater at a depth of 300 meters in the Konizar MFY area of Tashlok district is 18 $mg\ eq/dm^3$, the titrant volume for a 100 ml sample is $\vartheta = 1{,}8\ ml$. Let's look at the measurement errors for these results. Typically, the accuracy of readings on a burette is ±0.05 ml. So the relative error is as follows:

$$\delta = \frac{0{,}05}{1{,}8} \cdot 100 \approx 2{,}77\ \%;$$

Absolute error

$$\Delta T = 18 \cdot \frac{2{,}77}{100} \approx 0{,}5\ \frac{mg\ eq}{\text{l}};$$

If additional factors, indicator error, reagent concentration, and pH factor are also taken into account, the total probable error is:

$$\pm 3 - 5\ \%$$

namely:

$$18 \pm (0{,}5 - 0{,}9)\frac{mg\ eq}{l}$$

Samples were also taken from wells of various depths located in other regions of the Fergana Valley and the hardness level was determined using the titration method (Table 1).

Table 1. The hardness level of groundwater supplied to the population in different regions of the Fergana Valley.

№	Region name	Well depth, m	Total hardness mg eq/l
1.	Fergana State Technical University	60	13,8
2.	Toshlok district Konizar neighborhood	300	18,0
3.	Borot neighborhood, Kushtepa district	407,33	26,1
4.	Shahartepa neighborhood, Kushtepa district	447.0	25,2
5.	Sample neighborhood of Kushtepa district	8	21,1
6.	Istiqlol neighborhood, Yozyavon district	431	27,8

As can be seen from Table 1 above, the population of Fergana region uses groundwater at different depths. The hardness of groundwater varies from region to region. It was determined that the hardness of water at a depth of 8 meters in the Namuna neighborhood area of Kushtepa district is 21.1 mg eq/l, and the hardness of groundwater at a depth of 447 meters in the Shakhartepa neighborhood area of Kushtepa district is 25.2 mg eq/l. However, it was determined that the greatest hardness was found in groundwater in the Istiqlol neighborhood area of Yozyavon district, at a depth of 431 meters. Based on the results obtained, it can be concluded that the level of water hardness does not depend on depth.

3. Results

Based on the data in Table 1, we can conclude that the groundwater in the Fergana Valley is much higher than the standard level. The problem to be solved here is to what level should drinking water be reduced. Different countries have different limits and standards for the hardness of drinking water. In order to solve the issues of human health, technological safety and efficiency, it is necessary to determine what the optimal hardness level is and to what level water should be softened. To solve this problem, we implemented an

approach based on the relationship between the daily intake of calcium and magnesium per person, the amount obtained from drinking water and the level of water hardness.

The average daily calcium intake is 1000 mg/day and the magnesium intake is 420 mg/day, with humans absorbing this intake through food and water [10-11].

Depending on the calcium concentration in mineral water, it can provide up to a quarter of the total daily calcium intake, or 25%. Depending on the magnesium concentration in mineral water, it can provide between 6% and 17% of the daily magnesium intake [12].

Table 2. Amount of calcium and magnesium extracted from drinking water.

Mineral name	Daily norm, mg	Standard for drinking water, %	Required amount, mg
Calcium (Ca)	1000	25	250
Magnesium (Mg)	420	17	71,4

Assuming a daily water consumption rate of 3 liters/day for 1 person, drinking water with a hardness of 1 mg eq/liter contains 20.04 mg/L of calcium (Ca^{2+}) and 12.15 mg/L of magnesium (Mg^{2+}) [13]. Based on the calcium and magnesium content of drinking water, we determine the optimal hardness level.

Optimal water hardness in terms of calcium content

$$j_{Ca} = Ca \div V \div eq_{Ca} = 250 \div 3 \div 20{,}04 = \\ = 4{,}19\ mg\ eq/l$$

Optimal water hardness by magnesium content

$$j_{mg} = Mg \div V \div q = 71{,}4 \div 3 \div 12{,}15 = \\ = 1{,}96\ mg\ eq/l$$

Table 3. I optimal level of hardness of lawn water.

Standards	Calcium (Ca)	Magnesium (Mg)
Required norm, mg/day	250	71,4
Daily water consumption rate, l/day	3	3
Standard for drinking water, mg/l	20,04	12,15
Optimal hardness level, mg eq/l	4,19	1,96

As a result of the above calculations, the optimal water hardness level for the population of the Fergana region can be considered to be 4 mg eq/liter.

Based on the results obtained, we calculate the softening of drinking water supplied to the population using the Na cation method for each region.

$$m(NaCl) = V(H_2O) \cdot (j_1 - j_2) \cdot \frac{M(NaCl)}{1000} \quad (2)$$

Here: m(NaCl) – mass of NaCl, (grams)

$V(H_2O)$ – water volume, (liters)

$j_1 - j_2$ – Initial and final water hardness, $\frac{mg \cdot eq}{liter}$

M(NaCl) – equivalent weight of NaCl, 58,44 g/mol

$$M_{NaCl} = M_{Na} + M_{Cl} \quad (3)$$

$$M_{NaCl} = 22{,}99 + 35{,}45 = 58{,}44\ g/mol$$

We calculate the amount of NaCl needed to reduce the hardness of water from a well 60 meters deep at Fergana State Technical University from 13,8 mg eq/dm³ to 6 mg eq/dm³:

$$m(NaCl) = 1000 \cdot (13{,}8 - 4) \cdot \frac{58{,}44}{1000} = \\ = 572{,}71\ grams$$

We calculate the amount of NaCl needed to reduce the total hardness of groundwater at a depth of 300 meters in the Konizar neighborhood of the Toshlok district from 18 mg eq/dm³ to 6 mg eq/dm³.

$$m(NaCl) = 1000 \cdot (18 - 4) \cdot \frac{58{,}44}{1000} = \\ = 818{,}16\ grams$$

We calculate the amount of NaCl needed to reduce the total hardness of groundwater at a depth of 407.33 meters in the Borot neighborhood of the Kushtepa district from 26.1 mg eq/dm³ to 6 mg eq/dm³.

$$m(NaCl) = 1000 \cdot (26{,}1 - 4) \cdot \frac{58{,}44}{1000} = \\ = 1291{,}52\ grams$$

We calculate the amount of NaCl to reduce the total hardness of groundwater at a depth of 447 meters in the Shakhartepa neighborhood of the Kushtepa district from 25.2 mg eq/dm³ to 6 mg eq/dm³.

$$m(NaCl) = 1000 \cdot (25{,}2 - 4) \cdot \frac{58{,}44}{1000} = \\ = 1238{,}928\ grams$$

We calculate the amount of NaCl needed to reduce the total hardness of groundwater at a depth of 8 meters in the Namuna neighborhood of the Kushtepa district from 21.1 mg eq/dm³ to 6 mg eq/dm³.

$$m(NaCl) = 1000 \cdot (21{,}1 - 4) \cdot \frac{58{,}44}{1000} = \\ = 999{,}324\ grams$$

We calculate the amount of NaCl to reduce the total hardness of groundwater at a depth of 431 meters in the Istiqlol neighborhood of Yozyavon district from 27.8 mg eq/dm³ to 6 mg eq/dm³.

$$m(NaCl) = 1000 \cdot (27{,}8 - 4) \cdot \frac{58{,}44}{1000} = \\ = 1390{,}872\ grams$$

As a result of the above calculations, it is enough to change the amount of NaCl to bring the water hardness to the optimal level for each region.

Table 4. The amount of NaCl for softening groundwater in the Fergana Valley using the Na cation method.

№	Region name	Overall hardness, mg eq/l	Required hardness, mg eq/l	NaCl content, mg
1.	Fergana State Technical University	13,8	4	572,71
2.	Konizar neighborhood of Toshlok district	18,0	4	818,16
3.	Borot neighborhood of Kushtepa district	26,1	4	1291,52
4.	Shahartepa neighborhood of Qoshtepa district	25,2	4	1238,928
5.	Namuna neighborhood of Kushtepa district	21,1	4	999,324
6.	Istiqlol neighborhood of Yozyavon district	27,8	4	1390,872

4. Discussion

The World Health Organization's drinking water standard adopted in Geneva in 1993 does not specify a standard for total hardness. [6]. The Chinese national drinking water standard adopted in 2022 sets a maximum limit for total hardness of 9 mg eq/l [7]. According to the Indian National Standard, the acceptable level of hardness of drinking water is 4 mg eq/l, and the permissible limit is 12 mg eq/l [8]. According to the standard for drinking water quality in Russia, the hardness level is considered to be in the range of 7-10 mg eq/l [9]. In Uzbekistan, the requirement for drinking water hardness is 7 mg eq/l and the permissible limit is 10 mg eq/l. Reducing water hardness is a complex process. There are several methods for softening water. Below are some of the advantages and disadvantages of each method.

Table 5. Analysis of methods for reducing drinking water hardness.

Softening method	Advantages	Disadvantage
Boiling	No equipment required; No chemicals used Can be used at home; Kills germs.	Only temporarily reduces hardness; Deposits form on the walls of the container; Softens small volumes of water Deposits damage containers and equipment; The taste of water changes when boiled frequently;
Filtration (ion exchange method)	Can reduce the amount of calcium (Ca^{2+}) and magnesium (Mg^{2+}) ions to the required value; also reduces the permanent hardness of the water passing through the filter; high efficiency; low cost; convenient, easy to use; can be used as drinking and technical water; automation is possible; environmental waste is minimized; local cation exchangers can be developed, good for health;	The filter must be regenerated periodically; The cation exchanger must be replaced at a certain time; Efficiency decreases in water with high iron, manganese and turbidity; The amount of Na ions in the water exceeds the norm
Chemical softening with	The cost of reagents is low; Ability to soften large amounts of water; Also precipitates iron and manganese;	Low softening efficiency; Produces large amounts of sediment; Requires large settling tanks;

soda (Na_2CO_3) or lime ($Ca(OH)_2$)	Does not require complex technical equipment; The precipitate can be reused; Can be combined with other treatment methods.	Slow process; Water is not completely softened; Requires precise dosage control; Increased pH can change the taste of water; Disposal of chemical residues is problematic; Poor quality of soda or lime negatively affects the process.
Reverse osmosis	Very high efficiency Stable water quality No additional chemical reagents required; Allows for high-quality drinking water with minimal energy consumption; Possibility of removing salt, magnesium, calcium from wastewater.	Very high cost; Operates at very high pressure; Membranes are prone to clogging; Requires pre-treatment of water; Removes all minerals from water; Requires constant electricity; High iron, manganese, or turbidity in water negatively affects membrane life.
Distillation (evaporation and condensation)	It removes all substances from water; No chemical reaction required; Completely removes water hardness; Widely used in industry;	Energy consumption is very high; Slow processing speed; Equipment is expensive and complex; Cannot be used as drinking water; Completely destroys the healing properties of water.

According to the above analysis, it can be concluded that the most optimal method for reducing the hardness of drinking water in the Fergana region is the filtration (ion exchange) method. There are two ion exchange methods: Na cation and H cation. The most effective, simple and convenient method is the Na cation method.

When softening water with Na-form cationite, the cationite is regenerated beforehand with table salt (NaCl). The following reactions occur during Na-cationization:

$$2NaR + Ca(HCO_3)_2 \rightleftarrows CaR_3 + 2NaHCO_3; \quad (4)$$

$$2NaR + Mg(HCO_3)_2 \rightleftarrows MgR_3 + 2NaHCO_3; \quad (5)$$

$$2NaR + CaCl_2 \rightleftarrows CaR_2 + 2NaCl; \quad (6)$$

$$2NaR + CaSO_4 \rightleftarrows CaR_2 + Na_2SO_4; \quad (7)$$

$$2NaR + MgCl_2 \rightleftarrows MgR_2 + 2NaCl \quad (8)$$

$$2NaR + MgSO_4 \rightleftarrows MgR_2 + Na_2SO_4 \quad (9)$$

Here, NaR, CaR_2, MgR_2 are salt forms of cationite. As can be seen from the above reactions, Ca^{2+} and Mg^{2+} cations are removed from the treated water, and Na^+ ions enter the water instead, but the anion composition of the water does not change.

5. Conclusions

In conclusion, water hardness levels that exceed the norm, as well as very soft water, have a negative impact on human health, networks, and technological equipment. The hardness level of groundwater supplied to the population in various regions of the Fergana Valley has been determined. The total hardness of groundwater taken from a 60-meter deep well in the Fergana State Technical University was determined using the titration method to be 13.8 mg eq/l, the hardness of water taken from a 300-meter well in the Konizar mahalla of Toshlok district was 18 mg eq/l, the hardness of water taken from a 407.33-meter deep well in the Borot mahalla of Qoshtepa district was 26.1 mg eq/l, the hardness of water taken from a 447-meter deep well in the Shakhartepa mahalla of Qoshtepa district was 25.2 mg eq/l, the hardness of water taken from an 8-meter deep well in the Namuna mahalla of Qoshtepa district was 21.1 mg eq/l, and the hardness of water taken from a 431-meter deep well in the Istiqlol mahalla of Yozyavon district was 27.8 mg eq/l.

Studies have shown that each water softening method has its advantages and disadvantages. Softening methods directly affect the quality of water, both positively and negatively. Therefore, it is necessary to design and implement drinking water softening processes taking into account the negative effects.

The study proposes a scientific and practical approach to determining the optimal water hardness level based on the daily intake standards of calcium

and magnesium in drinking water necessary for the human body. According to calculations, based on the fact that 25% of the daily calcium requirement and 17% of the magnesium requirement are obtained through drinking water, the optimal water hardness level is justified as 4 mg eq/l.

Based on the initial and required hardness values for each region, a methodology was used to calculate the amount of NaCl required in the Na-cationization process, and practical calculation results were obtained.

It is substantiated that the ion-exchange (Na-cation) method is the most technologically optimal method for groundwater in the Fergana Valley, and the possibility of controlling hardness by adjusting the amount of NaCl to achieve optimal hardness is shown.

It has been scientifically proven that excessive or excessively low hardness of drinking water can have negative consequences for human health and engineering systems, based on comprehensive approaches, and the need to establish optimal standards based on regional conditions.

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