Journal of Chemistry and Technologies

pISSN 2663-2934 (Print), ISSN 2663-2942 (Online).

journal homepage: http://chemistry.dnu.dp.ua

UDC 628.3

DESALINATION OF MINERALIZED WATERS USING REAGENT METHODS

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Received 23 Octoder 2020; accepted 13 September 2021; available online 27 October 2021

Abstract

Finding a solution to a problem of water supply and water protection within aquatic ecosystems is one of the major issues today. The present work treats and gives the solution of an important scientific and technical problem of developing highly efficient methods of water treatment and wastewater treatment from pollutants, which allows creating low-waste technologies for demineralization. Nanofiltration water treatment technologies allow obtaining high-quality drinking water and water with the necessary indicators. Concentrates formed during nanofiltration purification of highly mineralized natural and mine waters are characterized with high content of hardness ions and sulfates. Effective purification of water from sulfates can be achieved by using synthesized sodium aluminate and lime. The degree of softening and purification of concentrates from sulfates depends on the dose of lime and sodium aluminate, the ratio of reagents and the reaction of medium. The efficiency of the extraction of sulfates from water increases with increasing dose of lime at a constant dose of coagulant and with increasing dose of sodium hydroxyaluminate at a constant dose of lime. Exceeding the dose of lime by 20 % more than the stoichiometric ratio is inappropriate, and it only leads to slight increase in the efficiency of extracted sulfates from water. The efficiency of sulfate extraction at constant doses of lime increases with increasing dose of coagulant to 20–60% of the stoichiometric quantity of sulfates. By adjusting the pH of the medium to 7–7.5 with the help of carbon dioxide, an increase in the efficiency of extraction of hardness ions and sulfates was achieved. During desalination of highly mineralized waters at the optimal dose of reagents, the concentration of sulfates decreased to 69–89 mg/dm^3 and hardness ions to 0.44–1.15 mg-eq/dm^3. The regression equations were calculated for the dependence of residual concentrations of sulfates and hardness ions in water depending on the dose of lime and sodium hydroxyaluminate.

Keywords: highly mineralized waters; sodium aluminate; lime; carbon dioxide; hardness ions; sulfates.

ЗНЕСОЛЕННЯ МІНЕРАЛІЗОВАНИХ ВОД ПРИ ВИКОРИСТАННІ РЕАГЕНТНИХ МЕТОДІВ

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Анотація

Вирішення проблем водозабезпечення та охорони вод в рамках водних екосистем є актуальним питанням сьогодення. В роботі вирішено важливу науково-технічну проблему розробки високоефективних методів водопідготовки та очищення стічних вод від забруднень, що дозволяє створити маловідходні технології демінералізації. Нанофільтраційні технології водопідготовки дозволяють отримувати високоякісну питну воду та технологічну воду з необхідними показниками. Концентрати, які утворюються при нанофільтраційному очищенні високомінералізованих природних та шахтних вод, характеризуються підвищеним вмістом іонів жорсткості і сульфатів. Ефективного очищення води від сульфатів можна досягти при застосуванні синтезованого алюмінату натрію та вапна. Ступінь пом'якшення та очищення концентратів від сульфатів залежить від дози вапна та алюмінату натрію, співвідношення реагентів, реакції середовища. Ефективність вилучення сульфатів з води зростає з підвищенням дози вапна при постійній дозі коагулянту та з підвищенням дози гідроксоалюмінату натрію при постійній дозі вапна. Перевищення дози вапна на 20 % більше від стехіометричного співвідношення є недоречним, оскільки призводить до незначного підвищення ефективності вилучених сульфатів з води. Ефективність вилучення сульфатів за постійних доз вапна зростає з підвищенням дози коагулянту до 20–60 % від стехіометричної кількості сульфатів. При доведенні pH середовища до 7–8 за допомогою вуглекислого газу досягнуто підвищення ефективності вилучення іонів жорсткості та сульфатів. При знесоленні високомінералізованих вод при оптимальній дозі реагентів концентрація сульфатів знизилась до 69–89 мг/дм^3 та іонів жорсткості – до 0.44–1.15 мг-екв/дм^3. В роботі були розраховані рівняння регресії для залежності залишкових концентрацій сульфатів і іонів жорсткості у воді в залежності від дози вапна і алюмінату натрію.

Ключові слова: високомінералізовані води; алюмінат натрію; вапно; вуглекислий газ; іони жорсткості; сульфати.

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doi: 10.15421/jchemtech.v29i3.214939

Journal of Chemistry and Technologies, 2021, *29*(3), 417-424

ОБЕССОЛИВАНИЕ МИНЕРАЛИЗОВАННЫХ ВОД ПРИ ИСПОЛЬЗОВАНИИ РЕАГЕНТНЫХ МЕТОДОВ

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Аннотация

Решение проблем водообеспечения и охраны вод в рамках водных экосистем является актуальным вопросом современности. В работе решена важная научно-техническая проблема разработки высокоэффективных методов водоподготовки и очистки сточных вод от загрязнителей, что позволяет создать малоотходные технологии деминерализации. Нанофильтрационные технологии водоподготовки позволяют получить высококачественную питьевую воду и технологическую воду с необходимыми показателями. Концентраты, образующиеся при нанофильтрационной очистке высокоминерализованных природных и шахтных вод, характеризуются повышенным содержанием ионов жесткости и сульфатов. Эффективной очистки воды от сульфатов можно достичь при применении синтезированного алюмината натрия и извести. Степень умягчения и очистки концентратов от сульфатов зависит от дозы извести и алюмината натрия, соотношения реагентов, реакции среды. Эффективность извлечения сульфатов из воды возрастает с повышением дозы извести при постоянной дозе коагулянта и с повышением дозы гидроксоалюмината натрия при постоянной дозе извести. Превышение дозы извести на 20 % больше стехиометрического соотношения неуместно, так как приводит к незначительному повышению эффективности изъятия сульфатов из воды. Эффективность извлечения сульфатов при постоянной дозе извести возрастает с повышением дозы коагулянта до 20–60 % от стехиометрического количества сульфатов. При доведении pH среды до 7–8 с помощью углекислого газа достигнуто повышение эффективности извлечения ионов жесткости и сульфатов. При обессоливании высокоминерализованных вод при оптимальной дозе реагентов концентрация сульфатов снизилась до 69–89 мг/дм^3 и ионов жесткости – до 0.44–1.15 мг-экв/дм^3. В работе были рассчитаны уравнения регрессии для зависимости остаточных концентраций сульфатов и ионов жесткости в воде в зависимости от дозы извести и алюмината натрия.

Keywords: высокоминерализованные воды; алюминат натрия; известь; двуокись углерода; ионы жесткости; сульфаты.

Introduction

In many parts of the world, especially in the industrialized areas, excessive pollution has a negative impact on the human health and efficiency. One of the main problems of environmental pollution is the surface water pollution. Intensive mining leads to changes in the regime and balance of groundwater, the transformation of the chemical composition of natural waters with the formation of mineralized mine water, pollution of surface watercourses, the development of consolidation and compaction of rocks and many other phenomena and processes [1–4]. The chemical composition and general mineralization differ from the groundwater surrounding the mine workings, which is associated with the oxidation of mine water, increased leaching of rocks, changes in bacterial and gaseous composition, as well as their contamination by petroleum products, oils, etc. [5; 6]. Discharge of mineralized mine water into the river network worsens the environmental situation even further. It also leads to siltation and acidification of surface watercourses, which are often sources of drinking and industrial water consumption. Many large and medium-sized rivers have almost lost their water management value and recreational value. The water stocks have decreased, the quality has deteriorated, and the shortage of drinking and industrial water has increased. This situation is typical for the majority of coal basins around the world [7; 8]. The problem can be solved by effective treatment of mineralized wastewater, including mine water.

To ensure environmental safety all mineralized water must be desalinated before being discharged into open water. Processing of mineralized mines will help solve the problem of water supply in the regions where the water is scarce [9; 10].

High pollution of water bodies with mineralized waters and toxic substances requires the development of effective measures to reduce this impact, so the problem of environmental management and the transition to the use of environmentally friendly energy efficient technologies is acute [11; 12].

Baromembrane water treatment techno-logies allow obtaining high-quality drinking water and water with the necessary indicators [13; 14]. This produces concentrates with high mineralization (above 4 g/dm^3), which require further processing [10; 15]. When using nanofiltration membranes, the degree of extraction of sulfates is 97 %, for reverse osmosis membranes, this value reaches 99 % [16]. When choosing a method of baromembrane cleaning, it is important to assess the environmental and economic components of the process [17]. Nanofiltration desalination concentrates are characterized with high hardness, sulfates and alkalinity, chloride concentration does not exceed 100 mg/dm^3. Discharge of mineralized solutions into water bodies is prohibited according to the existing environmental legislation. Therefore, when processing concentrates, it is advisable to soften them and remove sulfate ions, which will reduce the level of their mineralization to acceptable values. Purified concentrates can be discharged into reservoirs or reused in the process of water treatment [2].

The removal of sulfate ions is one of the main problems in the mining, metallurgical and other industries [18]. Due to the high solubility and stability of sulfates, their extraction from mine waters is a challenge. Methods of electro-coagulation [19; 20], ion exchange [21; 22], and adsorption [23–26] are used to extract sulfate ions from mine waters. Many methods have not been widely used due to the low productivity, high process costs, the use of hazardous chemicals and waste generation [27; 28].

The main advantages of the method of reagent water softening are its cheapness and simplicity of hardware design as well as the possibility of hardness salts separation in the form of non-toxic sediments that can be disposed [29].

The removal of sulfates from acidic mine waters is quite effective during precipitation with barium compounds [30]. But when using barium salts, toxic precipitates are formed, which are difficult to dispose of. Magnesium was used to remove sulfate from mine water. At pH = 12.5, sulfate is extracted, but at pH = 9.6, the sulfate is in the soluble state in the form of magnesium sulfate [31]. The lime is used to soften the water, which is considered to be a highly eco-friendly and a very cost effective technique for softening process [32]. At one-stage treatment of mine waters by lime it is possible to remove effectively a considerable quantity of metals (99.4 % for Al, % for Cd, 99.6 % for Co, 99.7 % for Cu, 98.5 % for Mn, 99.7 % for Ni, 99 % for U, and 99.5 % for Zn) [33]. However, the residual concentrations of sulfates are quite high. A coagulant was used to increase the effectiveness of the reagent softening. Sodium aluminate is characterized with high efficiency of pollution removal, it does not oxidize the cleared water. The coagulant is easy to dispense and does not contain heavy metals. Lime and sodium hydroxyaluminate were used as reagents in the studies. The dose of reagents was calculated based on the composition of the precipitate formed during the co-precipitation of calcium aluminate and gypsum – $3CaO \cdot Al_2O_3 \cdot 3CaSO_4$. In addition, the consumption of lime to soften the water was taken into account.

The aim of the work is to develop effective methods of reagent desalination of highly mineralized waters and water purification from sulfates without increasing the concentration of chloride ions in purified water.

Materials and methods

Synthesis of sodium hydroxyaluminate. 100 g of a 70 % solution of NaOH was added to a three-necked reactor with a stirrer and a condenser. The temperature of the solution was raised to 70–80 °C with the help of an oil bath. At this temperature, while constantly stirring, 122 g of technical amorphous $Al(OH)_3$ was added in parts (TU 48–5–128–89, containing 52.5–53.7 % Al_2O_3, 0.017 % SiO_2, 0.029 % Fe_2O_3, 0.3 % (Na_2O + K_2O) (in terms of Na_2O) and 10.27 % water). Each subsequent portion of $Al(OH)_3$ was added after dissolving the previous one. After dissolving all $Al(OH)_3$, the solution was cooled, 50 cm^3 of water were added. The volume of the solution was determined and the concentration of $Na[Al(OH)_4]$ in g/dm$_3$ and g-eq/dm^3 was calculated based on the amount of $Al(OH)_3$.

In the case when the content of free alkali in the coagulant was 25 %, in order to reduce the content of free alkali, 2 g of Al were added to 20 cm^3 of solution. The solution was heated until complete dissolution of Al. The concentration was calculated based on the determined concentration of aluminum by $NaAl(OH)_4$ in g/dm^3 and g-eq/dm^3.

Reagent water softening using synthesized sodium and lime aluminate. Concentrates formed during the nanofiltration purification of highly mineralized natural and mine waters are characterized by high content of hardness ions and sulfates. The concentration of sulfates in concentrates at a degree of permeate selection of 70 % ranges from 1200–3000 mg/dm^3, the hardness exceeds 20–40 mg-eq/dm^3. Therefore, in the research process a model solution similar in composition to real mine waters and nanofiltration desalination concentrates was used, with the content of sulfates 32.0 mg-eq/dm^3, chlorides 3.0 mg-eq/dm^3, hardness 58.9 mg-eq/dm^3, alkalinity 18.7 mg-eq/dm^3, pH 6.5.

Lime and sodium hydroxyaluminate synthesized in the laboratory, were used as reagents for softening high-hardness water while removing sulfates.

The calculated amount of lime was added to the water while stirring, followed by sodium hydroxoaluminate. The solution was stirred for 2 hours. The precipitate was separated by settling and filtration. Carbon dioxide was being passed through clarified water with a pH of 12.0–12.5 until a pH of 7.0–7.5 was reached. The treated water was clarified by filtration. The residual hardness, alkalinity, concentration of sulfate anions were determined afterwards.

Water hardness was determined by trilonometry with eriochrome black T indicator, alkalinity was measured by acid-base titrimetric method in the presence of phenolphthalein and methyl orange indicators. Sulfates were determined by spectrophotometric method with barium ions, while the argentometric method of Moore was used for chlorides determination, pH was measured with a pH meter pHTestr 30 (Eutech Inst., USA).

The degree of softening (Z) and the degree of extraction of sulfates from water (A) was calculated by the formulas:

$$Z = (1 - \frac{H_i}{H_p}) \cdot 100 \quad ; \quad A = (1 - \frac{C_{SO_4^{2-}i}}{C_{SO_4^{2-}p}}) \cdot 100$$

where H_i – initial hardness; H_p – hardness in the purified water; $C_{SO_4^{2-}i}$ – is the initial concentration of sulfates; $C_{SO_4^{2-}p}$ – concentration of sulfates in purified water.

Results and Discussion

One of the most important factors in the coagulation process is the amount of reagent that determines the efficiency of water purification [34]. When using iron coagulants there is a secondary contamination of water with iron ions and chlorides [35].

Sodium hydroxaluminate additionally introduces sodium ions and alkali into the water, the 10 % excess of which is always present in the solution of this reagent. Therefore, when using lime and sodium hydroxyaluminate, the alkalinity of water reaches high values. When treating water with lime and sodium hydroxyaluminate, carbon dioxide was used to neutralize the solution. This has significantly increased the efficiency of water purification from sulfates with high water softening efficiency. When water is treated with carbon dioxide, its pH decreases from 12–12.5 to 7–7.5. In a number of experiments, the sulfate content decreased to 69–103 mg/dm^3, the hardness decreased to 0.44–5.30 mg-eq/dm^3. Hydrate alkalinity in most cases was zero, the total alkalinity was 23–25 mg-eq/dm^3. Effective extraction of sulfates occurs when using lime and sodium hydroxyaluminate in a stoichiometric amount or in excess of 20 %. Reducing the dose of aluminum coagulant leads to a decrease in the efficiency of extraction of sulfates and hardness ions from the solution (table 1).

Table 1

The effect of the dose of reagents on the efficiency of extraction of sulfates and hardness ions during treatment of the solution with lime, sodium hydroxyaluminate (I) and lime, sodium hydroxyaluminate and carbon dioxide (II)

№	Dose CaO, mmol/dm^3	Dose Na[Al(OH)$_4$], mmol/dm^3	SO_4^{2-} mg-eq/dm^3		H, mg-eq/dm^3		Alkalinity, mg-eq/dm^3 (OH$^-$; total)	
			I	II	I	II	I	II
1	116.0	4.50	12.87	11.45	5.90	4.50	8.0; 20.5	0.0; 22.7
2	116.0	4.75	10.32	9.14	6.10	3.52	9.3; 21.4	0.0; 23.9
3	116.0	5.00	8.13	6.81	6.30	2.63	12.0; 22.5	0.0; 23.4
4	116.0	5.25	6.22	4.45	8.70	1.69	15.3; 27.0	0.0; 23.6
5	116.0	5.50	5.11	2.06	10.20	0.8	17.8; 29.3	0.0; 23.9
6	121.0	4.50	10.15	7.96	6.90	4.91	8.9; 21.8	0.0; 23.9
7	121.0	4.75	8.45	6.45	7.30	3.93	10.3; 26.8	0.0; 24.2
8	121.0	5.00	7.10	4.97	8.20	3.03	11.4; 28.2	0.0; 24.3
9	121.0	5.25	5.85	3.49	10.20	2.01	15.7; 31.7	0.0; 24.7
10	121.0	5.50	3.95	1.98	12.40	1.11	19.2; 35.4	0.0; 24.9
11	126.0	4.50	7.12	4.38	12.70	5.30	9.6; 22.3	0.0; 24.5
12	126.0	4.75	4.95	3.77	13.00	4.35	13.2; 29.6	0.0; 24.7
13	126.0	5,00	4.70	3.15	15.20	3.33	21.2; 39.0	0.0; 24.8
14	126.0	5.25	3.25	2.48	16.40	2.36	24.4; 42.1	0.0; 25.1
15	126.0	5.50	2.60	1.89	17.20	1.40	27.1; 47.3	0.0; 25.3

Figure 1 shows the dependence of the degree of extraction of sulfates and the degree of softening of the solution on the dose of sodium hydroxyaluminate. At a dose of 120 mg-eq/dm^3 of lime, increasing the dose of sodium hydroxyaluminate from 4.5 to 5.5 mmol/dm^3 increases the rate of extraction of sulfates from 87.3 to 95.5 % and the degree of softening from 90.2 to 98.0 %.

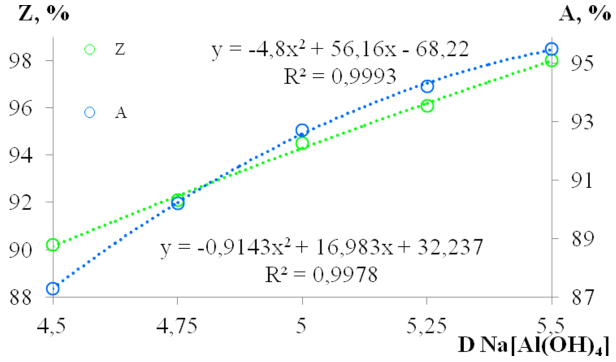

Fig. 1. Dependence of the degree of softening (Z) and degree of extraction of sulfates (A) on the dose of sodium hydroxyaluminate at a dose of lime 120 mg-eq/dm^3

To implement the method of reagent treatment of mineralized mine waters it is necessary to have dependencies that show the main parameters of the process in optimal conditions. Therefore, regression equations were calculated for the dependence of residual concentrations of sulfates and hardness ions in water depending on the dose of lime and sodium hydroxyaluminate.

The calculation was based on a complete factor plan (CFP) of type 2^2 [36]. The plan-matrix of CFP 2^2 and the results of the experiment of residual concentrations of sulfates in water depending on the dose of lime and sodium aluminate are shown in table 2.

Table 2

Plan-matrix CFP 2^2 and the results of studies on the extraction of sulfates from aqueous solutions using lime and sodium hydroxyaluminate

№	Planning matrix		Natural value of factors		Value of parameters
	x_1	x_2	Dose CaO, mmol/dm^3	Dose Na[Al(OH)$_4$], mmol/dm^3	C (SO_4^{2-}), mg-eq/dm^3
1	−1	−1	116.00	4.50	11.45
2	+1	−1	126.00	4.50	4.38
3	−1	+1	116.00	5.50	2.06
4	+1	+1	126.00	5.50	1.89

As a result of the appropriate calculations after checking the compliance of the results of the study, assessing the significance of the obtained coefficients and checking the regression equation for adequacy, the dependence is as follows:

$$y = 4.945 - 1.810 \cdot X_1 - 2.970 \cdot X_2 + 1.725 \cdot X_1 \cdot X_2 \qquad (1)$$

Code values:

$$X_1 = \frac{D(\text{CaO} - 121.0)}{5.0} \qquad (2)$$

$$X_2 = \frac{D(\text{Na[Al(OH)}_4]) - 5.0)}{0.5} \qquad (3)$$

After replacing the code values with natural ones, the following regression equations were obtained:

$$y = 495.897 - 3.812 \cdot D\,(\text{CaO}) - 89.430 \cdot \cdot D\,(\text{NaAl(OH)}_4) + 0.690 \cdot D\,(\text{CaO})\,D(\text{NaAl(OH)}_4) \qquad (4)$$

Cochren's criterion is: G_p = 0.5384. The limit value of the Cochren's criterion (G) for f = 2 and N = 4 is G = 0.768. The experiments are reproducible, as the requirement $G_p \leq G$ is satisfied.

The obtained dependence is presented in Figure 2 in the form of a plane on which lies the solution of the given equation. The figure shows the dependence of sulfates concentration in aqueous solutions on the concentration of reagents.

During the purification of the model solution, the consumption of reagents was 4.0–5.5 mmol/dm^3 for sodium hydroxoaluminate and 110–130 mg-eq/dm^3 for lime. The efficiency of water purification from sulfates increased with increasing the dose of sodium hydroxyaluminate and lime.

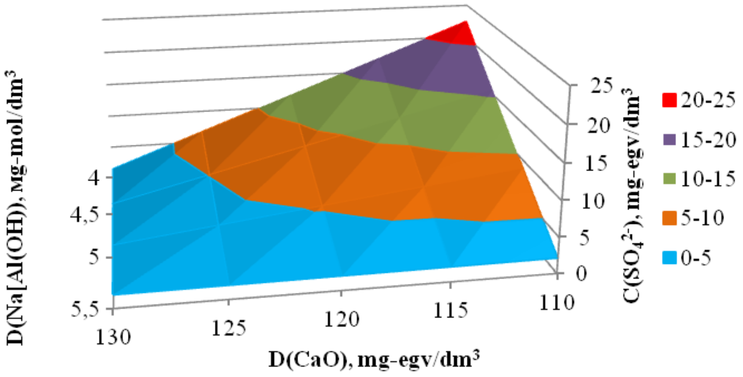

Fig. 2. Graphic representation of the results of CFP type 2^2 when removing sulfates from the aqueous solutions while using lime and sodium hydroxyaluminate

Table 3

Plan-matrix CFP 2^2 and the results of studies on the extraction of hardness ions from aqueous solutions using lime and sodium hydroxyaluminate

№	Planning matrix		Natural value of factors		Value of parameters
	x_1	x_2	Dose CaO, mmol/dm^3	Dose Na[Al(OH)$_4$], mmol/dm^3	Hardness, mg-eq/dm^3
1	−1	−1	116.00	4.50	4.50
2	+1	−1	126.00	4.50	5.30
3	−1	+1	116.00	5.50	0.80
4	+1	+1	126.00	5.50	1.40

The conformity of the research results was checked, the significance of the obtained coefficients was assessed and the regression equation was checked for adequacy. As a result of the corresponding calculations the unknown dependence looks in the following way:

$$У = 3.000 + 0.350·X_1 - 1.900·X_2 - 0.050·X_1·X_2 \qquad (5)$$

After replacing the code values in the obtained equation with natural ones

$$X_1 = \frac{D(\mathrm{CaO} - 121.0)}{50.} \qquad (6)$$

$$X_2 = \frac{D(\mathrm{Na[Al(OH)_4]}) - 5.0)}{0.5} \qquad (7)$$

the following regression equation was received:

$$У = 1.430 + 0.170·D\,(CaO) - 1.380·D\,(NaAl(OH)_4) - 0{,}020·D\,(CaO)\,D\,(NaAl(OH)_4) \qquad (8)$$

Cochren's criterion is: G_p = 0.3265. The limit value of the Cochren's criterion (G) for f = 2 and N = 4 is G = 0.768. The experiments are reproducible, as the requirement $G_p \le G$ is satisfied.

The obtained dependence is presented in Figure 3 in the form of a plane on which lies the solution of the given equation. The figure shows the dependence of hardness ions' concentration from aqueous solutions on the concentration of lime and sodium hydroxyaluminate.

The analysis of the presented results shows that the residual stiffness decreases from 8 to the values of ≈ 1 mg-eq/dm^3 with a decrease in lime consumption from 130 to 115–110 mg-eq/dm^3. As the consumption of sodium hydroxyaluminate increases from 4.0 to 5.5 mmol/dm^3, the water softening efficiency increases.

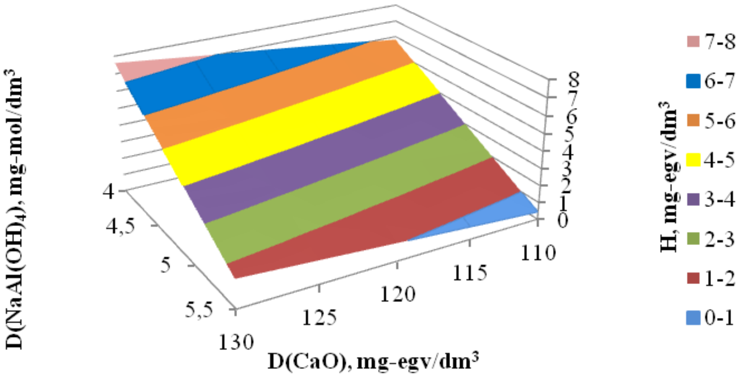

Fig. 3. Graphic representation of the results of CFP type 2^2 when removing hardness ions from the aqueous solutions while using lime and sodium hydroxyaluminate

The maximum concentration limit for sulfates in drinking water bodies is 500 mg/dm^3, and for fishery purposes it is 100 mg/dm^3. In the demineralization of wastewater, the vast majority of which in one way or another enters surface water, it is important to reduce the concentration of sulfates to values < 100 mg/dm^3 with total mineralization < 1000 mg/dm^3. As can be seen from Fig. 2, Fig.3 and table. 1 effective softening of the solution occurs at a 5.00-5.50 mg-mol/dm^3 dose of sodium hydroxyaluminate and when a dose of lime is 110-130 mg/dm^3. When doses of sodium hydroxyaluminate and lime of are equal to 4.50-5.00 mg/dm^3 and 110-115 mg/dm^3 respectively, mineralized water is also softened, but the efficiency of sulfate extraction at such doses is insufficient. To reduce the concentration of sulfates to values less than the MPC, the dose of sodium hydroxyaluminate should be 5.25 mg-mol/dm^3 at a dose of lime 128-130 mg/dm^3 and 5.50 mg-mol/dm^3 at a dose of lime 110-130 mg/dm^3.

Using the data of the regression equation, it is quite easy to calculate the doses of reagents for the extraction of sulfates and stiffening ions when used as an aluminum coagulant sodium hydroxyaluminate.

Conclusions

1. The efficiency of extraction of sulfate anions from model solution similar in composition to

real mine waters and nanofiltration desalination concentrates and softening efficiency depending on doses of lime and sodium hydroxyaluminate were determined. It was shown that the efficiency of purification of model solutions from sulfates depends on the doses of lime and aluminum coagulant. When the pH of the medium is adjusted to 7–7.5 with the help of CO_2, an increase in the effective extraction of hardness ions and sulfates is achieved. During desalination of highly mineralized waters at the optimal dose of reagents, the concentration of sulfates decreased to 69–89 mg/dm^3 and hardness ions to 0.44–1.15 mg-eq/dm^3.

2. On the basis of the complete factor plan the regression equation which has linear character is received. The equation allows optimizing the calculation of the dose of sodium and liming aluminate. When using sodium aluminate in the amount of 5.5 mmol/dm^3 and at a dose of lime 110–115 mg-eq/dm^3, the residual stiffness does not exceed 1 mg-eq/dm^3 at a sulfate concentration of ~ 73.5 mg/dm^3.

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