SULPHATES AND WATER HARDNESS IONS REMOVAL FROM THE WATER IN THE DEMINERALIZATION PROCESS

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ABSTRACT
The results of treatment of solutions with high sulphates concentration and the high rate of water hardness are given.
The task of reducing water salinity was solved by isolation of sulphate in the form of poorly soluble calcium hydroxsulphoaluminate and also due to its softening with lime or lime and carbon dioxide processing.
Calcium hydroxsulphoaluminate has been received during water treatment using lime and highly basic aluminium coagulants.
It is shown that the usage of aluminuim hydroxchloride can reduce sulphate concentrations from 1200-4500 to 40-500 mg/l and reduce water hardness from 10-18 mmol/l to 0,25-1,5 mmol/l. In this case the chloride content in water depends on the basicity and hydroxchloride aluminum flow.
Significant reduction of secondary pollution by chlorides achieved through an integrated use of aluminium hydroxchloride and sodium aluminate coagulants.
It was found that that the efficiency of water purification of sulphates and water softening can be increased with the carbon dioxide processing. This helps to remove the calcium ions as calcium carbonate and to increase the yield of calcium hydroxsulphoaluminate.
It is shown that the residual level of salinity and alkalinity depends on its ionic composition, in particular on the content of sodium sulphate, as well as the type and rate of aluminium coagulant. The developed method helps to solve the problems of natural water conditioning, treatment of wastewater with different concentrations.
Perspective is the process of concentrates processing produced by nanofiltration water treatment.
A slight increase in chloride concentration does not significantly influence the efficiency of water treatment in general while treated concentrates are reused in the technological process.

KEYWORDS: nanofiltration water treatment, sulphates, water hardness, aluminium coagulant

INTRODUCTION

Existing technologies of sewage purification can effectively remove organic and insoluble inorganic impurities, but these technologies have little effect on the level of mineralization in sewage waters. In fact, application of these technologies can sometimes even raise the concentration of salts in the water [Belichenko,1990]. As a result, many natural water reservoirs in the industrial regions of Ukraine are characterized by the increased levels of mineralization. This is further aggravated by dumping of mine waters into natural water reservoirs. Importantly, mine waters are dumped into the environment regardless of whether a mine is operational or not which often exacerbates the situation as it is harder to control how mine waters are dumped in inactive mines. In addition, underground water and surface water in Priazovye and in Prichernomorye, have increased levels of mineralization due to natural factors. As a result, people in many regions of Ukraine (especially the

south, the east and some areas of the central and western areas) consume drinking-water with inadmissibly high levels of hardness and mineralization. The use of such water in the industry, power and municipal services, leads to increased dumps of sewage into the environment as these dumps are necessary to maintain water-circulated systems in a satisfactory condition.

The raised level of impurity of waters of large and small rivers of Priazovye, other southeast regions of Ukraine, contributes to considerable pollution of Azov and Black seas.

Under such conditions, development and introduction of processes to demineralize and soften water become critically important. Membrane filtration technologies of water treatment represent the most popular approach among known technologies for demineralization and softening the water. The popularity of this approach is determined by the high efficiency of processes and high quality of the purified water. With this approach, one can obtain high-quality drinking water and technological water meeting the key standards. However, wide introduction of the these technological processes raises an issue of how to recycle concentrates formed at membrane filtration during water treatment. The mineralization of such concentrates exceeds 4 g/dm^3. Dump of such solutions in natural water reservoirs is forbidden by the current environmental legislation. Moreover, such concentrates are formed in territories where natural reservoirs are characterised by high levels of a background mineralization.

The existing methods of sulphate removal from the water involve using the compounds of calcium [Lebedev,2007], barium [Kubasov,2010], lime and aluminium coagulants [Berengarten,2008; Butseva, 2009; Salnikova, 1992; Salnikova 1983]. However, using calcium compounds does not reduce the concentration of sulphates below 1500 mg/dm^3. Using barium compounds is expensive and is accompanied by secondary pollution of water by highly toxic barium. Although removal of sulphates by sedimentation sulphate of calcium with calcium aluminate has been studied for solutions with concentration of sulphates of 400-1800 mg/dm^3, published works [Berengarten,2008; Butseva, 2009; Salnikova, 1992; Salnikova 1983]do not consider processes of water softening.

Amounts of sulphates in concentrates which are formed at nanofiltration water treatment depend on the initial concentration of sulphates in natural or mine water before clearing and on the intensity of permeate intake. With permeate intake at approximately 75 %, the concentration of sulphates at the initial concentration of 400-1100 mg/dm^3 in the water will result in the concentration of sulphates of 1600-4400 mg/dm^3. In addition, resulting concentrates have high levels of hardness and alkalinity while the concentration of chlorides does not exceed 100 mg/dm^3.

In light of these results, it is potentially expedient to process concentrates with reagent softening and removing sulphatic ions. This will allow reducing the level of concentrate mineralization to permissible values. Processed concentrates can be discharged into reservoirs or can be used repeatedly in the technological process of water preparation.

The objectives of this work are to study the processes of demineralization of concentrates which appear in nanofiltration purification of mine and mineralized water withhigh sulfate concentration, to identify conditions to effectively soften these solutions and to remove sulfates with a complex treatment by lime and aluminium coagulants under minimal secondary pollution by chloride anions.

MATERIALS AND METHODS

Concentrates with sulphate concentration from 1200 to 4500 mg/dm^3 at hardness from 13 to 36 mg-eq/dm^3 were treated with lime and aluminium coagulants. We estimated the residual concentration of sulphates and chlorides, residual hardness and alkalinity of water. In some cases, we used 2/3 or 5/6 aluminium hydrochloride, sometimes used aluminium hydrochloride and sodium hydroxaluminate as coagulants. The concentration of sulphates was estimated with a photometric method, while the concentration of chlorides was estimated with the method of Mora.

RESULTS AND DISCUSSION

Efficiency of water treatment by sulphate removal, as well as the efficiency of softening, depends both on the total amounts and proportional ratio of used lime and coagulant. With low amounts of lime, increasing the dose of 2/3 aluminium hydrochloride results only in increased concentration of chlorides in water without its substantial softening and clearing from sulphates (tab. 1). As the amount of lime is increased while holding the dose of coagulant fixed (tab. 1), we observed an increase in the efficiency of sulphate removal. The effective softening of water is attained at the consumption of lime from 76 to 99 mg-eq/dm^3 at all doses of coagulant. Remaining alkalinity of water grows as the amount of lime used increase but it decreases as the amount of coagulant used increases.

Table 1. The efficiency of removal of sulphatic ions from a solution ($[SO_4^{2-}]$=29,0 mg-eq/dm^3; H=21,5 mg-eq/dm^3; $[Ca^{2+}]$=1,8 mg-eq/dm^3; $[Mg^{2+}]$=19,7 mg-eq/dm^3; $[Cl^-]$=95 mg/dm^3; A=19,0 mg-eq/dm^3) as a function of used lime and Al (OH)$_2$Cl

№	Dose CaO, mg-eq/dm^3	Dose Al(OH)$_2$Cl (by Al$_2$O$_3$), mmol/dm^3	pH	$[SO_4^{2-}]$ mg/dm^3	H, mg-eq/dm^3	A, mg-eq/dm^3 (OH$^-$; the general)	$[Cl^-]$, mg/dm^3	Degree of removal of ions SO$_4^{2-}$ %	Degree of soft-ening, Z %
1	47,19	4,5	7,4	1120	7,5	0; 4,4	417	13,6	68,8
2	47,19	6,8	7,5	600	18,0	0; 6,7	579	53,7	25,0
3	76,05	4,83	7,5	800,0	3,4	0,0; 9,5	435	42,5	84,2
4	87,65	4,83	7,7	578,0	2,2	0,0; 12,5	447	58,5	89,8
5	99,25	4,83	8,9	433,0	2,4	0,0; 17,0	453	68,8	88,8
6	110,85	4,83	9,7	480,0	11,7	4,8; 21,5	446	65,5	45,6
7	122,45	4,83	11,3	515,0	20,0	5,8; 34,0	424	63,0	7,0
8	134,05	4,83	11,4	425,0	27,0	11,0; 37,0	419	69,5	0,0
9	99,25	5,32	9,1	481,0	2,8	0,0; 16,5	470	65,4	87,0
10	99,25	5,80	8,7	330,0	3,0	0,0; 17,0	485	76,3	86,0
11	99,25	6,28	7,9	385,0	3,7	0,0; 11,0	546	72,3	82,8
12	99,25	6,77	7,8	500,0	4,5	0,0; 7,0	551	64,1	79,1
13	99,25	7,25	7,6	340,0	6,0	0,0; 8,5	610	75,6	72,1
14	76,05	7,25	7,9	476,0	5,0	0,0; 9,0	625	21,0	76,7
15	87,65	7,25	7,8	512,5	6,0	0,0; 9,0	630	63,2	72,1
16	99,25	7,25	7,7	328,5	8,0	0,0; 8,0	627	76,4	62,8
17	110,85	7,25	7,8	195,0	11,0	0,0; 9,0	619	86,0	48,8
18	122,45	7,25	7,9	130,0	12,0	0,0; 9,0	622	90,7	44,2
19	134,05	7,25	7,9	164,0	15,0	0,0; 10,0	623	88,2	30,2

Although $Al_2(OH)_5Cl$ is a more expensive coagulant than commonly used chloride aluminium and sulphate aluminium, $AlCl_2(OH)$ and $Al(OH)_2Cl$, $Al_2(OH)_5Cl$ introduces fewer anions that cause secondary pollution in water.

The use of $Al_2(OH)_5Cl$ provides high efficiency of sulphate removal, and it uses smaller concentrations of chlorides in comparison with $Al(OH)_2Cl$. However, as a result of lower acidity of aluminium hydrochloride with high alkalinity , treated solutions still have high alkalinity of solutions, especially at low doses of coagulant.
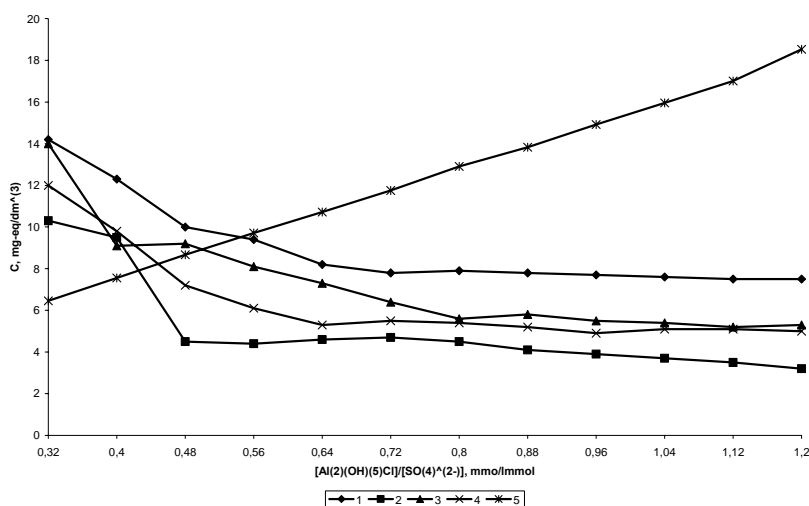

Figure 1. Residual concentration of sulphates (1,2,3,4) and chlorides (5) as a function of $Al_2(OH)_5Cl$ relative to SO_4^{2-} ($[Al_2(OH)_5Cl]$ / $[SO_4^{2-}]$) for a given amount of lime (mg-eq/dm^3): 82 (1,5), 93 (2), 108 (3) and 124 (4) at softening of solution ($[SO_4^{2-}]$=26,0 mg-eq/dm^3; H=16,0 mg-eq/dm^3; $[Ca^{2+}]$=1,6 mg-eq/dm^3; $[Mg^{2+}]$=14,4 mg-eq/dm^3; $[Cl^-]$=2,3 mg-eq/dm^3; A=16,0 mg-eq/dm^3)

As coagulant's dose increases, the efficiency of removal of sulphates grows. However, raising lime's dose above 93 mg-eq/dm^3 does not increase the efficiency of sulphate removal from a solution. Furthermore, residual concentration of sulphates can increase in some cases. The same results apply to the efficiency of softening of water (fig. 2). Note that as coagulant's dose increases, the efficiency of softening of water grows while the residual alkalinity of waters decreases. The best results for alkalinity are obtained at the maximum usage of coagulant when lime doses are at 82-108 mg-eq/dm^3.

However, solving the problems of purification of concentrates only at the expense of increasing the coagulant's dose is not always expedient because in such a case the residual concentration of chlorides in the water increases.

The addition of anions into the water with coagulant can be prevented by using sodium hydroxaluminate as aluminium coagulant (fig. 3)

Efficiency of water treatment from sulphates increases with using lime and aluminium coagulant by 100-150 % compared to stoichiometry-based estimates. The concentration of sulphates can reach 137-350 mg/dm^3. However, the residual alkalinity of water grows as the usage of reagents increases. Mineralization rises with greater usage of sodium hydroxaluminate, because with the latter, sodium ions and alkali (always present in solutions as 10-20% excess) are also added into the water.
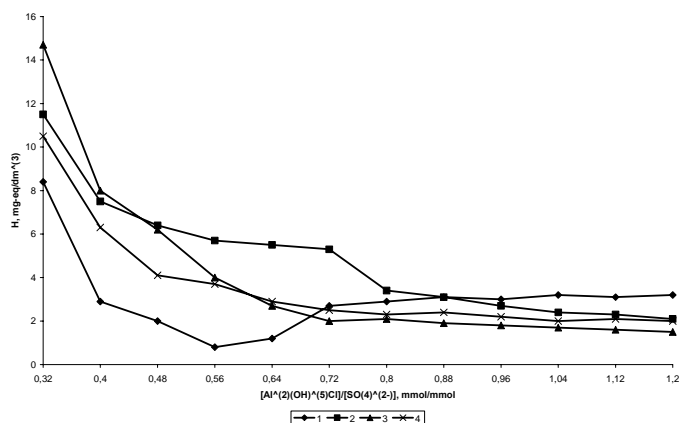
Figure 2. Relative usage of coagulant per amount of the sulphates ($[Al_2(OH)_5Cl]$ / $[SO_4^{2-}]$) in the solution ($[SO_4^{2-}]$=26,0 mg-eq/dm^3; H=16,0 mg-eq/dm^3; $[Ca^{2+}]$=1,6 mg-eq/dm^3; $[Mg^{2+}]$=14,4 mg-eq/dm^3; $[Cl^-]$=2,3 mg-eq/dm^3; A=16,0 mg-eq/dm^3) as a function residual hardness of water (1,2,3,4) at the lime dose (mg-eq/dm^3): 82 (1), 93 (2), 108 (3) and 124 (4)
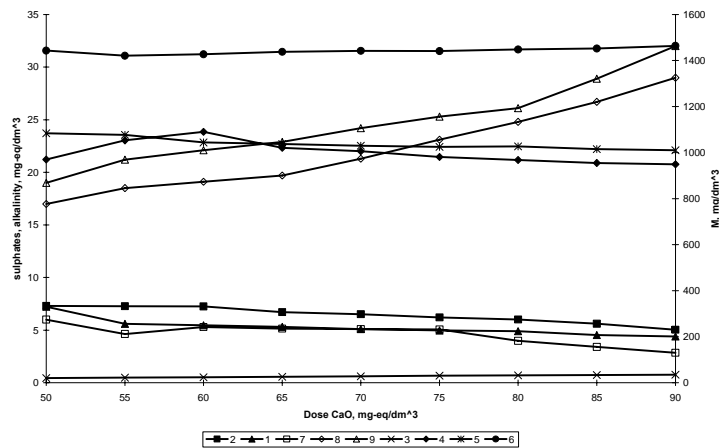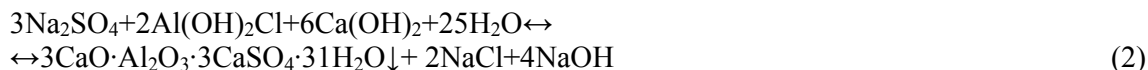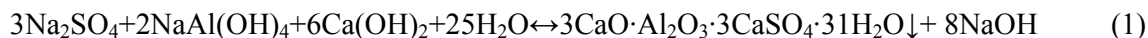

Figure 3. Residual concentration of sulphates (1,2,3), alkalinity (4,5,6) and mineralizations (7,8,9) as a function of lime usage at solution purification (pH=7,8; $[SO_4^{2-}]$=mg-eq/dm^3; H=24,0 mg-eq/dm^3; $[Ca^{2+}]$=7,0 mg-eq/dm^3; $[Mg^{2+}]$=17,0 mg-eq/dm^3; A=3,75 mg-eq/dm^3; $[Cl^-]$=73 mg/dm^3) at given doses of sodium hydroxaluminate (mg-eq/dm^3): 17,5 (1,4,7); 18,4 (2,5,8); 21,0 (3,6,9)

Thus, using lime and sodium hydroxaluminate can lead to high alkalinity of water. In addition, due to solubility of lime excess, water hardness is also very high. With water treatment by carbon dioxide, pH decreases from 12 to 7-8. Under these conditions, calcium ions become separated as the insoluble calcium carbonate. Residual hardness of water does not exceed 1 mg-eq/dm^3, although alkalinity is high. This is observed because sodium hydroxide is separated during the formation of calcium aluminate from sodium hydroxaluminate. When sodium sulphate is present in the water, sodium hydroxide also is formed at sedimentation gypsum with sodium

hydroxaluminate. When water is treated with carbon dioxide, sodium hydroxide becomes soda, which explains the anomalously high water alkalinity.

The formation of alkali with sedimentation of calcium sulphoaluminate during lime and aluminum coagulant water treatment can be described with the equations:

$$3Na_2SO_4+2NaAl(OH)_4+6Ca(OH)_2+25H_2O\leftrightarrow3CaO\cdot Al_2O_3\cdot3CaSO_4\cdot31H_2O\downarrow+ 8NaOH \qquad (1)$$

$$3Na_2SO_4+2Al(OH)_2Cl+6Ca(OH)_2+25H_2O\leftrightarrow$$
$$\leftrightarrow3CaO\cdot Al_2O_3\cdot3CaSO_4\cdot31H_2O\downarrow+ 2NaCl+4NaOH \qquad (2)$$

$$3Na_2SO_4+Al_2(OH)_5Cl+6Ca(OH)_2+25H_2O$$
$$\leftrightarrow3CaO\cdot Al_2O_3\cdot3CaSO_4\cdot31H_2O\downarrow+ NaCl+5NaOH \qquad (3)$$

When sulphates of calcium and magnesium are present, alkali is formed only if sodium hydroxaluminate is used:

$$3MgSO_4+2NaAl(OH)_4+6Ca(OH)_2+25H_2O\leftrightarrow$$
$$\leftrightarrow3CaO\cdot Al_2O_3\cdot3CaSO_4\cdot31H_2O\downarrow+2NaOH+3Mg(OH)_2\downarrow \qquad (4)$$

$$3CaSO_4+2NaAl(OH)_4+3Ca(OH)_2+25H_2O\leftrightarrow3CaO\cdot Al_2O_3\cdot3CaSO_4\cdot31H_2O\downarrow+2NaOH \, (5)$$
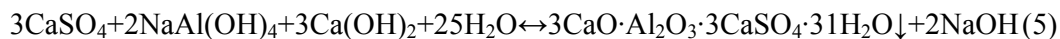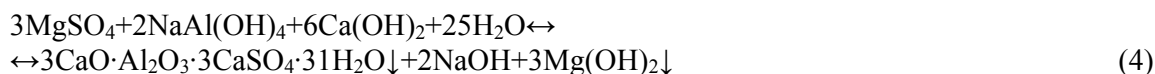
Composition of a sediment of calcium sulphoaluminate was measured according to data available in the literature [Salnikova,1983].

The efficiency of sulphate removal was high at considerable concentration of sulphates, including sodium sulphate, in the water (tab. 2, fig. 4). However, alkalinity of solutions was high even after the water was treated with carbon dioxide because of high doses of sodium hydroxaluminate and high concentration of sodium sulphate in the water.

The best results were obtained by using sodium hydroxaluminate and 5/6 aluminium hydroxchloride in equimolar ratio (tab. 3).

In this case, solutions were not treated with carbon dioxide after treatment with lime and aluminium coagulant. The treatment was shortened by at least to 2 stages (sparging and filtering). During this procedure, we observed the neutralisation of alkali formed at the hydrolysis of sodium hydroxaluminate by hydrochloric acid produced in the hydrolysis of aluminium hydrochloride. We found that in addition to sulphate removal, general mineralization decreased from about 2200 mg/dm^3 to less than 1000 mg/dm^3. The softening of water was effective, too. Softening efficiency increased as the usage of line increased. Alkalinity also was within the permitted levels.

Table 2. The effect of lime and sodium hydroxaluminate dosage on the efficiency of removal of sulphates and hardness at solution treatment ($[SO_4^{2-}]$=65,0 mg-eq/dm^3; H=36,0 mg-eq/dm^3; $[Ca^{2+}]$=3,2 mg-eq/dm^3; $[Mg^{2+}]$=32,8 mg-eq/dm^3; A=2,9 mg-eq/dm^3) by lime, sodium hydroxaluminate and carbon dioxide

№	Dose CaO, mg-eq/dm^3	Dose NaAl(OH)$_4$ (by Al$_2$O$_3$) mmol/dm^3	SO$_4^{2-}$		H* mg-eq/dm^3	A, mg-eq/dm^3 (OH$^-$; in general)	Degree of removal of ions SO$_4^{2-}$ %	Degree of softe-ning, Z %
			mg-eq/dm^3	mg/dm^3				
1	166	10,83	14,4	690	5,7	0,0; 46,0	77,8	84,2
2	166	13,00	13,3	640	5,2	0,0; 57,0	79,5	85,6
3	166	16,25	8,4	405	3,0	0,0; 63,5	87,1	91,7
4	192	10,83	10,8	518	3,0	0,0; 47,5	83,4	91,7
5	231	10,83	8,7	418	9,0	0,0; 60,5	86,6	75,0
6	231	13,00	8,9	427	3,2	0,0; 49,0	86,3	91,1
7	231	16,25	8,2	395	2,9	0,0; 61,0	87,4	91,9
8	130	10,83	15,6	749	6,3	0,0; 27,1	76,0	82,5
9	156	10,83	14,7	706	4,9	0,0; 31,2	77,4	86,4
10	195	10,83	7,8	374	5,1	0,0; 34,6	88,0	85,8
11	221	10,83	6,4	307	7,6	0,0; 38,5	90,2	78,9

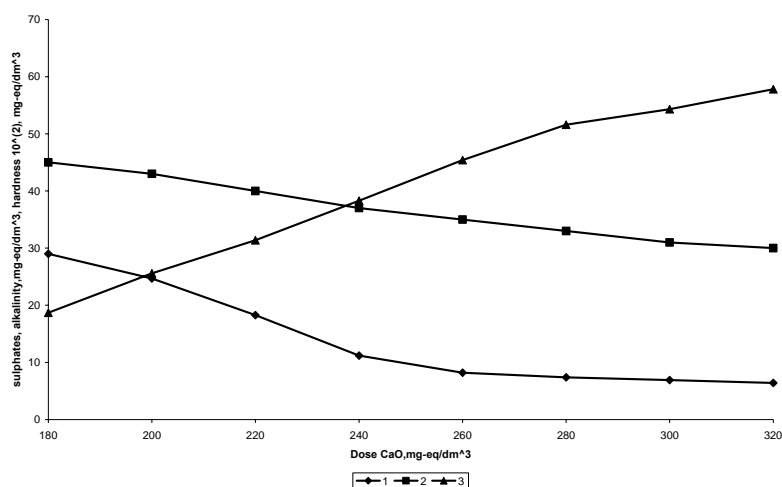● - hardness defined before the treatment of water by CO_2

Figure 4. The effect of lime usage at the dose of sodium hydroxaluminate of 15,6 mg-eq/dm^{3}on residual concentration of sulphates (1), hardness (2), alkalinity (3) solutions ($[SO_4^{2-}]$=93,8 mg-eq/dm^3; H=14,6 mg-eq/dm^3; $[Ca^{2+}]$=1,6 mg-eq/dm^3; $[Mg^{2+}]$=13,0mg-eq/dm^3; A=5,0 mg-eq/dm^3)

Table 3. Influence of dose of lime, sodium hydroxaluminate and 5/6 aluminium hydrochloride on efficiency of demineralization of solution ($[SO_4^{2-}]$=26,2 mg-eq/dm^3; H=24,0 mg-eq/dm^3; [Cl$^-$]=73 mg/dm^3; A=3,75 mg-eq/dm^3; a mineralization (=2200 mg/dm^3)

№	Dose mmol/dm^3			SO_4^{2-}		H, mg-eq/dm^3	A, mg-eq/dm^3	M, mg/dm^3	Degree of softe-ning, Z %
	CaO	NaAl(OH)$_4$	Al$_2$(OH)$_5$Cl	mg-eq/dm^3	mg/dm^3				
1	52,40	5,83	5,83	7,30	350	4,32	3,00	860	82
2	62,88	5,83	5,83	7,26	348	5,41	4,11	857	77,5
3	78,60	5,83	5,83	6,02	288	9,42	8,31	859	60,8
4	89,08	5,83	5,83	5,04	242	10,94	10,52	851	54,4
5	52,40	6,13	6,13	7,23	347	4,15	4,22	929	82,7
6	55,02	6,13	6,13	5,73	275	4,11	4,87	937	82,9
7	57,64	6,13	6,13	5,60	269	4,84	6,93	925	79,8
8	62,88	6,13	6,13	5,47	263	5,12	7,84	927	78,7
9	78,60	6,13	6,13	4,90	235	8,13	9,15	947	66,1
10	89,08	6,13	6,13	4,40	211	9,18	10,31	965	61,8
11	52,40	7,00	7,00	6,00	288	3,21	3,01	968	86,6
12	55,02	7,00	7,00	4,64	223	3,85	4,07	957	84,0
13	57,64	7,00	7,00	5,30	254	4,07	6,73	963	83,0
14	62,88	7,00	7,00	5,10	245	4,49	6,64	948	81,3
15	78,60	7,00	7,00	3,20	154	6,44	8,96	971	73,2
16	89,09	7,00	7,00	2,85	137	8,85	10,12	1009	63,1

CONCLUSIONS

We established how the usage and relative amounts of lime and 5/6 aluminium hydrochloride affect the effectiveness of sulphate removal from water and the efficiency of water softening. We showed that the efficiency of water treatment grows with increasing dose of coagulant when lime is used in stoichiometric quantities and with lime excess up to 50 %.

We established the relationship between the initial concentration of sulphates in water, water hardness, alkalinity, and both total and relative amounts of lime and coagulant. This allowed us to identify the conditions of the effective water treatment from sulphates at permissible concentration of chlorides in water.

We found that by using lime, sodium hydroxaluminate and carbonic gas, one can achieve effective water treatment from sulphates and effective softening of water at high values of alkalinity of water. The effectiveness of these treatments depends on the overall concentration of sulphates, the amount of used sodium hydroxaluminate, and concentration of sodium sulphate in water.

We showed that with combined usage of 5/6 aluminium hydrochloride and sodium hydroxaluminate in water liming one can achieve high degree of water softening and deep purification from sulphates with reduced residual concentration of chlorides in water.

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