

INTENSIFICATION OF A BRINE PURIFICATION PROCESS IN THE OF SODA ASH PRODUCTION BY THE INTRODUCTION OF FLOCCULANTS

Yeskendirov M.Z., Yeskendirova M.M.*

M. Auezov South Kazakhstan University, Shymkent, Kazakhstan

***Corresponding author's e-mail:** yesmm12@mail.ru

ABSTRACT

This article considers the results of studying the purification of the sodium chloride brine used for manufacturing soda ash by the ammonia method. The purpose of the study was to develop a purification method involving coagulation and flocculation processes using polyacrylamide flocculants in the presence of surface-active substances as crystallization modifiers. A complex technology for purification of the brine from magnesium and calcium compounds and sulfate ions is proposed, which includes three stages for sodium chloride solutions with a high Mg^{2+} content and two stages for the brines with a low Mg^{2+} content. The article contains the results of experiments to investigate the effect of the concentration of anionic polyacrylamide flocculants on the height of the clarified layer when removal of calcium and magnesium ions. The best result was achieved at using an anionic polyacrylamide flocculant Flopam AN 934 PWG at its concentration of 0.004% wt. The introduction of sodium tripolyphosphate improves the flocculating effect of the anionic polyacrylamide flocculant and increases the suspension clarification rate. The best indicators were obtained at 0.05% wt of sodium tripolyphosphate. With the simultaneous use of a cationic polyacrylamide additive Superfloc C-498 ($4 \cdot 10^{-4}$ % wt.) and sodium tripolyphosphate (0.05% wt.), the concentration of sulfate ions in the purified brine was 0.016 g/l; this corresponds to the purification efficiency of 99.75%. It has also been established that the use of surface-active substances in combination with polyacrylamide flocculants makes it possible not only to increase the suspension clarification rate, but also to obtain the cleaner brine.

Keywords: technology, soda ash, purification, brine, polyacrylamide flocculant, surface-active substance, sodium tripolyphosphate, suspension.

INTRODUCTION

Soda ash is one of the most important products of inorganic synthesis, which is widely used in various industries: metallurgical, chemical, glass and detergent production, mining, textile, etc. [1-4].

The Republic of Kazakhstan does not have its own soda ash production, and the total demand for this product exceeds 400 thousand tonnes per year. In addition, there is a trend of annual stable growth of this demand [5]. In this regard, the implementation of the investment project "Construction of a soda ash production plant in the Kyzylorda Oblast with a capacity of 300 thousand tonnes per year" has begun in Kazakhstan [6].

Soda ash can be produced by various ways. About 26% of its world production is produced from a natural mineral (trona), and 74% is synthetic soda manufactured by the ammonia method [1-3].

The Aral Sea region is characterized by the presence of both carbonate minerals and sodium chloride, which are the main raw materials for the manufacturing soda ash in accordance with the ammonia method. Kazakhstan has the richest reserves of halite and

sulfate salts (thenardite, mirabilite, astrakhanite) on Zhaksyklysh Lake located in the Aral Sea area. This deposit is characterized by a combination of chloride and sulfate salts of sodium. Such a combination, especially in large quantities, is rarely found anywhere. In this regard, there is a need to create technologies for the effective use of these salts [5].

The main raw material component of soda ash production by the ammonia method is sodium chloride. The efficiency and reliability of the ammonia method of producing soda ash largely depends on the purity of a sodium chloride solution (brine).

The traditional technology for purifying a sodium chloride solution has significant disadvantages.

This is, first of all, the low efficiency of removing magnesium and calcium salts from the brine. If magnesium and calcium salts are not previously removed, then at the next stages – ammonization and carbonization of a sodium chloride solution (absorption of ammonia and carbon dioxide) – poorly soluble compounds will precipitate from the brine: CaCO_3 , $\text{Mg}(\text{OH})_2$, $\text{NaCl}\cdot\text{Na}_2\text{CO}_3\cdot\text{MgCO}_3$, $(\text{NH}_4)_2\text{CO}_3\cdot\text{MgCO}_3$. Their deposition on the surface of equipment and pipelines can further cause contamination of the finished product – soda ash.

The second negative factor is that the purified brine contains dissolved sulfate compounds in the form of highly soluble sodium sulfate. The presence of sulphate ions in the brine complicates the flow of technological processes at almost all production stages. This is especially true for the stage of ammonia regeneration [4].

In addition, disadvantages of the traditional brine purification technology include the considerable time spent on the settling and separating the resulting suspension leading to the significant loss of the brine (up to 13.5% wt.) [3].

MATERIALS AND METHODS

To intensify the sedimentation process of the sludge suspension, without resorting to high temperatures, we propose the use of the flocculation process in the presence of surface-active substances as crystallization modifiers [7-8]. Flocculation is the most expedient way of coarsening fine particles, the essence of which is their aggregation into larger complexes, which leads to an increase in the settling rate by dozens of times [9-10]. The separation rate of the brine suspension when using the flocculation process may depend on the chemical composition of the precipitate, on the physical structure of the initial raw materials, on the conditions of precipitation, and on the nature of the flocculant. Therefore, the search for new and effective flocculants is one of the main tasks for intensifying the suspension separation process.

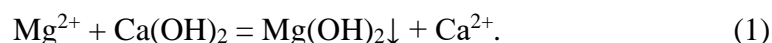
The aim of the study was to develop a method for purifying the brine, used for the production of soda ash, based on coagulation and flocculation processes using polyacrylamide flocculants in the presence of low molecular weight salts as surface-active substances.

A prototype of the proposed integrated brine purification technology is the technology proposed in the monograph [4]. In [4], the purification process is carried out in three stages and involves elevated temperatures (up to 90 °C), which is necessary to accelerate the formation of Ca^{2+} and Mg^{2+} salt precipitates and increase the purification efficiency. The disadvantages of this technology include the high temperatures of the brine purification regimes, which leads to significant costs, because it is necessary to heat large volumes of the brine and to install refrigerators before the absorption section to reduce the temperature of the brine to 20-22 °C.

To reduce the temperature of the brine purification process without reducing its quality and intensity, we propose the following integrated technology using polymeric flocculants

(PF) and surface-active substances (SAS). The purpose of using PF is to increase the efficiency of the purifying and accelerate the sludge sedimentation process, and the purpose of adding SAS is to reduce the solubility of CaSO_4 [3] to remove sulfate ions.

Initially (at the first stage) it is proposed to carry out the removal of magnesium salts from the brine. For this, a lime suspension prepared on the basis of the purified brine and containing up to 5% of magnesium hydroxide as seed is used. The brine before the treatment is pre-mixed with a flocculant. The interaction of substances occurs according to the following reaction:



The magnesium hydroxide seed must be added to intensify the coagulation and precipitation of magnesium salts [3, 4], since the presence of crystallization nuclei in the solution increases the growth rate of $\text{Mg}(\text{OH})_2$ crystals.

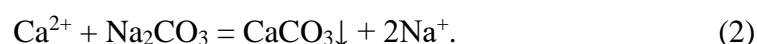
When the crystallization centers are introduced into the solution, the crystallization process is accelerated [12-14]. This is because the work required to form a crystal is proportional to its surface. Therefore, the work expended for crystallization on an already existing surface is less than the work demanded for formation of a crystal in a free volume [13]. The role of crystallization centers can be performed by mechanical impurities; and the greater the similarity between the crystalline structures of the seed and the precipitated compound, the stronger their influence on the course of the crystallization process. It should be noted that on the curvilinear surface of the seed, especially in recesses, the crystallization occurs faster than on flat surfaces [11].

The process is performed at a temperature of 12-22 °C with stirring and an excess of $\text{Ca}(\text{OH})_2$ (0.05 n.d.). An increase in temperature reduces the viscosity of the solution and thereby increases the brine's clarification (precipitation) rate [1,3]. However, a significant increase or fluctuation in the temperature of the brine can lead to disruption of the consolidated settled layer. In addition, it is unprofitable to carry out the process at high temperatures, because in real production it is difficult to heat large volumes of the brine to be purified. According to [3], the more magnesium salts contain in the brine, the looser the flakes become and the slower they settle. Therefore, at high concentrations of magnesium salts, the brine must be purified at a temperature not lower than 12 °C.

Settling of the suspension is carried out at the same temperature.

This stage makes it possible to obtain the brine with a concentration of magnesium ions not higher than the regulated ones – 0.007 n.d. [3].

The second stage is the conversion of calcium salts (CaCl_2 , CaSO_4 and $\text{Ca}(\text{OH})_2$ residues) into insoluble CaCO_3 . The fed brine, as at the first stage, must first be mixed with a flocculant. The purification is carried out with a soda solution at a temperature of 25-33 °C with an excess of Na_2CO_3 (0.2 n.d.) at stirring. The interaction of substances occurs according to the following reaction:



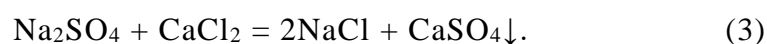
After separation of the suspension, the concentration of Ca^{2+} ions in the brine should not exceed 0.01 n.d., which is 2 times less than in the existing technology.

Sulfates in the NaCl solution are mainly in the form of highly soluble Na_2SO_4 and are removed from the brine as CaSO_4 at the third stage.

The CaSO₄ solubility in sodium chloride solutions is much higher than in water. For example, at 25 °C, the solubility of CaSO₄ in water is 2.08 g/l, and in a solution containing 181 g/l of NaCl, the solubility of CaSO₄ is 7.06 g/l [11]. In more concentrated NaCl solutions, the solubility of CaSO₄ decreases, but still remains much higher than in water.

To reduce the concentration of sulphate ions in the brine to a level that excludes the formation of gypsum encrustations in a distiller, it is recommended in [3] to use surface-active substances that can be selectively adsorbed on the surface of CaSO₄ particles and thereby to reduce their solubility. Authors [3] recommend using sodium tripolyphosphate (STPP) for this purpose.

The precipitation of sulfate impurities is carried out with a calcium chloride solution at agitation and the molar ratios [SO₄]:[Ca] ≥ 0.25, CaSO₄:Na₂SO₄ = 0.2. The interaction of substances occurs according to the following scheme:



As a result, the content of sulphate ions does not exceed 0.01 n.d.

The three-stage brine purification technology described above should be used with a high content of Mg²⁺ ions (compared to Ca²⁺ ions). This technology makes it possible to obtain, in addition to pure NaCl brine, relatively pure precipitates of Mg(OH)₂, CaCO₃, CaSO₄. These sediments can be processed into very valuable products: MgO, CaO, Ca(OH)₂, CaCO₃, CaSO₄·2H₂O, concentrated Na₂SO₄ solution (or solid salt).

In the case of purification of NaCl brines with a low content of Mg²⁺ ions, it is proposed to purify the brine in two stages. A block diagram of the brine purification technology in the case of a low content of Mg²⁺ ions is shown in Fig. 1.

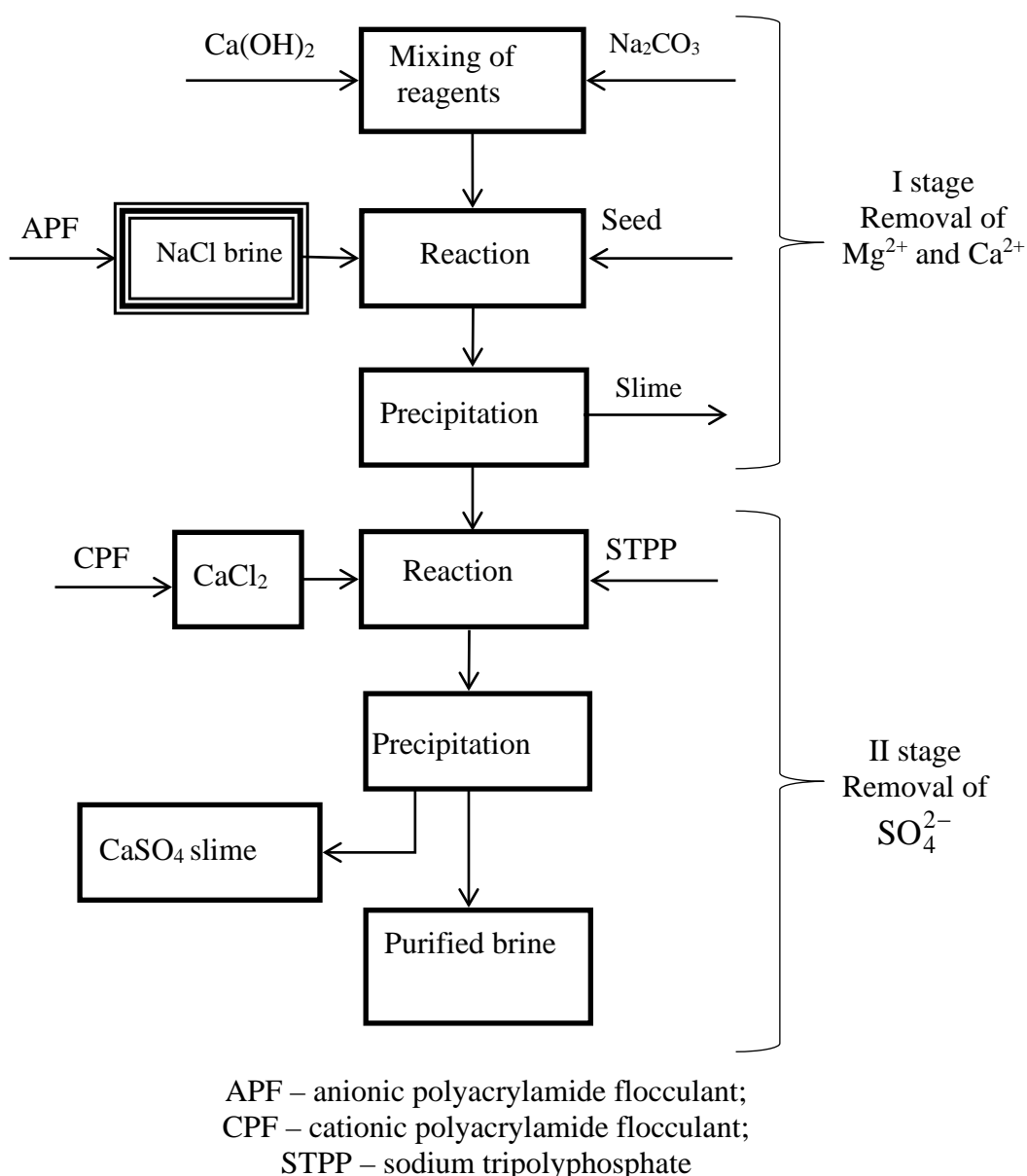


Fig. 1. A block-diagram of the brine purification technology (a low content of Mg^{2+} ions)

RESULTS AND DISCUSSION

Laboratory studies of the proposed method for purifying sodium chloride brine from magnesium, calcium and sulfate compounds using flocculants and surface-active substances were carried out.

We used the Lake Zhaksyklysh brine (Kazakhstan, Aral Sea region) with the following composition: sodium chloride - from 91.5 to 99.3%; anhydrite - from 0.3 to 4.3%; magnesium sulfate - from 0.07 to 3.26%; magnesium chloride - up to 1.1%; sodium sulfate - up to 1.6%; clay sludge - up to 1.4%

The brine, prepared on the basis of this salt, contained: 308 g/l of NaCl; 1.1 g/l of Ca^{2+} , 0.14 g/l of Mg^{2+} and 6.5 g/l of SO_4 .

Calcium and magnesium ions were removed using anionic polyacrylamide flocculants (APF): Superfloc A-100 PWG, Flopam AN 934 PWG, Praestol 2530 TR. In addition, in all experiments, a seed was crystals of $Mg(OH)_2$ in quantity of 5%.

To remove SO_4 ions, we studied the effect of cationic polyacrylamide flocculants (CPF): Superfloc C-498, Flopam FO 4190 PWG, Praestol 610 TR.

All the experiments were carried out using 1% solutions of the flocculants, which were then diluted with the brine to the desired concentration.

The studies have found that the addition of flocculants increases the suspension separation efficiency (Table 1). The best results were shown by Praestol and Flopam at a concentration of 0.0004% wt. The flocculants should be added to the sodium chloride solution before the introduction of the reagents, because in this case, the separation rate is higher than when flocculants are added to the soda-lime solution. Particularly, the separation rate is high at the initial settling time.

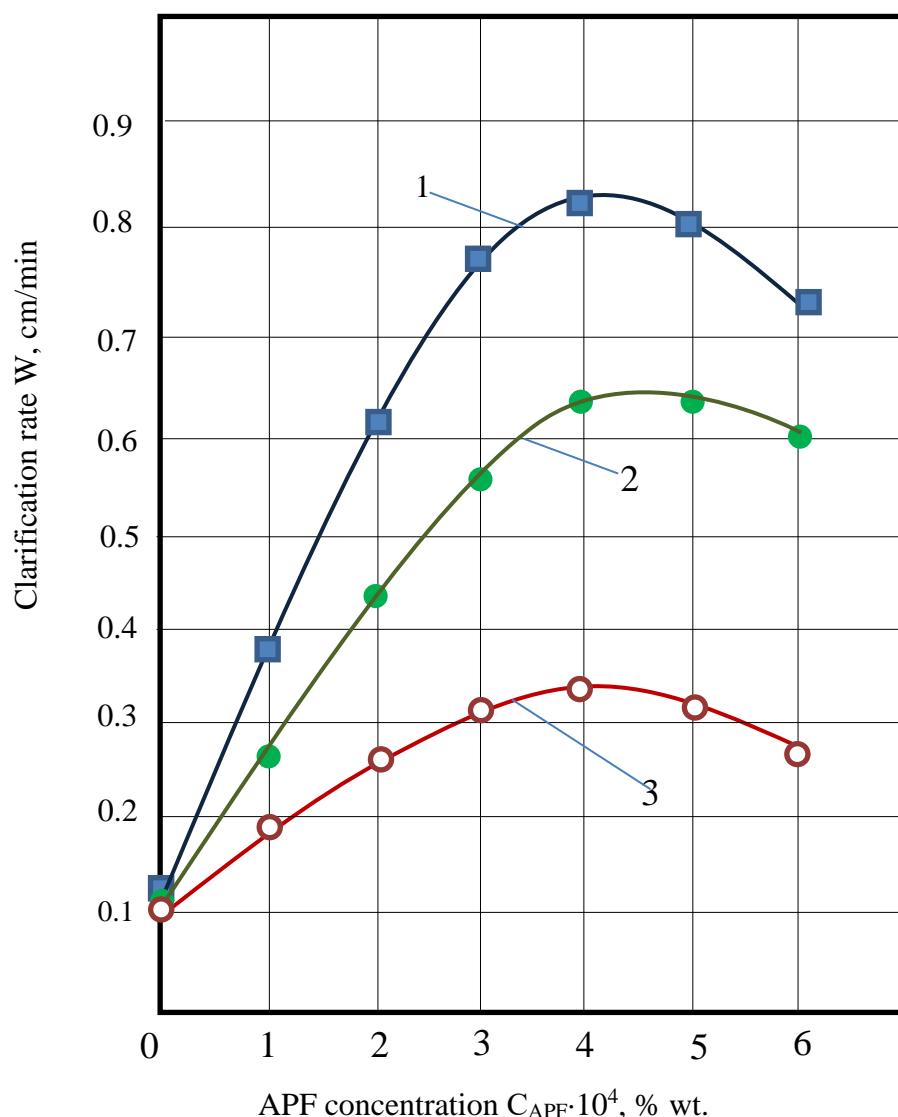
Table 1 presents the experimental results about the effect of the APF concentration on the height of the clarified layer of the suspension for I purification stage (removal of calcium and magnesium ions). As it follows from the table, the best result was achieved in a case of application of APF “Flopam AN 934 PWG” at a concentration of 0.004% wt. However, with a further increase in the APF concentration, the height of the clarified layer slightly decreases. This is apparently due to the fact that an increase in the flocculant concentration above a certain threshold one leads to the formation of a flocculant film on the crystal surface and the coagulation process slows down.

Table 1 – Effect of APF concentration on the height of the clarified suspension layer (I purification stage)

№	Flocculant	Height of the clarified layer, mm					
		Flocculant concentration, % wt.					
		0,0001	0,0002	0,0003	0,0004	0,0005	0,0006
1	Praestol 2530 TR	100	130	155	185	160	140
2	Flopam AN 934 PWG	120	160	190	215	180	150
3	Superfloc A-100 PWG	75	90	105	120	95	85

Without APF additives, the height of the clarified suspension layer was 60 mm.

The experiments have shown that the addition of PF leads to almost instantaneous flocculation, increase in the settling rate and good compaction of the deposit.



1 – Flopam AN 934 PW; 2 – Praestol 2530 TR; 3 – Superfloc A-100 PWG;

Fig. 2. The suspension clarification rate – APF concentration curve (I stage)

The results of studying the effect of the CPF concentration on the height of the clarified layer of the suspension containing sodium tripolyphosphate during the II purification stage (precipitation of SO_4 ions) are presented in Table 2.

Table 2 – Effect of CPF and STPP concentrations on the height of the clarified suspension layer

No.	CPF	STPP concentration, % wt.	Height of the clarified layer, mm					
			CPF concentration, % wt.					
			0.0001	0.0002	0.0003	0.0004	0.0005	0.0006
1	Praestol 610 TR	0.01	103	112	124	130	125	117
2	Flopam FO 4190 PWG		100	113	127	157	132	115

Table 2 continuation

3	Superfloc C-498		74	78	83	92	85	78
1	Praestol 610 TR	0.02	112	120	131	144	133	123
2	Flopam FO 4190 PWG		110	119	130	142	133	120
3	Superfloc C-498		77	84	93	100	95	88
1	Praestol 610 TR	0.03	121	130	142	153	140	131
2	Flopam FO 4190 PWG		118	128	141	150	137	129
3	Superfloc C-498		85	92	100	111	105	97
1	Praestol 610 TR	0.04	130	141	150	162	152	139
2	Flopam FO 4190 PWG		128	139	147	160	148	135
3	Superfloc C-498		92	99	106	118	112	105
1	Praestol 610 TR	0.05	132	143	151	162	150	137
2	Flopam FO 4190 PWG		128	138	145	156	143	129
3	Superfloc C-498		90	97	103	115	110	100
1	Praestol 610 TR	0.06	125	133	140	149	138	128
2	Flopam FO 4190 PWG		121	133	138	145	135	126
3	Superfloc C-498		88	94	101	108	105	97

The addition of SAS increases the efficiency of separation and the settling rate of the slime. The best results were obtained in a case of 0.05% wt. of sodium tripolyphosphate.

At the simultaneous use of Superfloc C-498 ($4 \cdot 10^{-4}$ % wt.) and STPP (0.05% wt.), the sulfate ion concentration in the purified brine was 0.016 g/l; the purification efficiency in this case is 99.75%.

CONCLUSION

Thus, to increase the clarification rate of the suspension, formed during the brine treatment, it is proposed to use alkali metal phosphates. The introduction of sodium tripolyphosphate into the suspension improves the APF flocculating effect and increases the clarification rate of the suspension. The combination of alkali metal phosphates and

polyacryamide flocculants at the sedimentation of brine purification slimes allows not only to increase the rate of suspension clarification, but also to obtain a cleaner brine.

REFERENCES

- 1 Krasheninnikov S.A. *Tekhnologiya kal'tsinirovannoy sody i ochishchennogo bikarbonata natriya. 3-ye izd.* [Technology of soda ash and purified sodium bicarbonate. 3rd ed.]. Moscow, Vysshaya shkola, 1985. 287 p.
- 2 Zaitsev I.D., Tkach G.A., Stoyev N.D. *Proizvodstvo sody* [Production of soda]. Moscow, Khimiya, 1986. 312 p.
- 3 Shokin I.N., Krasheninnikov S.A. *Tekhnologiya sody* [Technology of soda]. Moscow, Khimiya, 1975. 288 p.
- 4 Tkach G.A., Shaporev V.P., Titov V.M. *Proizvodstvo sody po malootkhodnoy tekhnologii: Monografiya* [Production of soda according to a low-waste technology: Monograph]. Kharkov: Kharkov State Polytechnic University, 1998. 429 p.
- 5 Bishimbayev V.K., Mukashev D.R. Innovative approaches in a soda ash production technology // Materials of Round Table “Innovative technologies and approaches in metallurgy and chemical industry of the Republic of Kazakhstan”. Almaty, 2016, pp.84-90.
- 6 *V Kazakhstane postroyat pervyy zavod po proizvodstvu kal'tsinirovannoy sody* [The first plant for the production of soda ash will be built in Kazakhstan]. Available at: <https://www.zakon.kz/4858989-v-kazahstane-postroyat-pervyy-zavod-po.html> (14 May 2022).
- 7 Absatov M.M., Yeskendirov M.Z. Studying a brine purification process from magnesium and calcium compounds and sulfate ions. South Kazakhstan Science Herald, 2018, no. 1, pp. 6-9.
- 8 Yeskendirov M.Z., Absatov M.M. A new brine purification technology in soda ash production. South Kazakhstan Science Herald, 2018, no. 1, pp.610-13.
- 9 *Poliakrilamid / Pod redaktsiyey V.F. Kurenkova* [Polyacrylamide / Edited by V.F. Kurenkov]. Moscow, Khimiya, 1992. 192 p.
- 10 Nebera V.P. *Flokulyatsiya mineral'nykh suspenziy* [Flocculation of mineral suspensions]. Moscow, Nedra, 1983. 288 p.
- 11 Veitser Yu.I., Mints D.M. *Vysokomolekulyarnyye flokulyanty v protsessakh ochistki prirodnykh i stochnykh vod* [High molecular flocculants in natural and waste water treatment processes]. Moscow, Stroyizdat, 1984. – 202 p.
- 12 Postoronko A.Y., Marchenko Y.L. *Primeneniye vysokomolekulyarnykh flokulyantov v tekhnologii prigotovleniya rassolov* [Use of high molecular flocculants in a brine preparation technology]. Naukovi pratsi Donets'koho natsional'noho tekhnichnoho universytetu. Seriya : Khimiya i khimichna tekhnolohiya - Scientific works of Donetsk National Technical University. Series: Chemistry and chemical technology, 2012, no. 18, pp. 147-151.
- 13 Postoronko A.I., Popov V.V., Lebedev A.T., Gayvoronskiy V.F. Effect of polyelectrolytes on suspension separation at purification of natural brines. Scientific works of Donetsk National Technical University. Series: Chemistry and chemical technology. 2003. – № 61, pp. 58-61.
- 14 Kurbangaleyeva M.X., Pergushova L.R., Khassanova A.A. Studying the effect of flocculants on settling a brine purification slime. Bashkir Chemical Journal, 2016, V.23, no. 3, pp. 68-70.