Ion-exchange separation of anions for the development of low-waste technologies for water demineralization

Inna Trus

Candidate of Technical Sciences, senior lecturer
National Technical University of Ukraine «Igor Sikorsky Kyiv Polytechnic Institute»
Kyiv, Ukraine
E-mail: inna.trus.m@gmail.com

Hanna Fleisher

Candidate of Technical Sciences,assistant
National Technical University of Ukraine «Igor Sikorsky Kyiv Polytechnic Institute»
Kyiv, Ukraine

Viktoria Vorobyova

Candidate of Technical Sciences, assistant
National Technical University of Ukraine «Igor Sikorsky Kyiv Polytechnic Institute»
Kyiv, Ukraine

Olena Hlushko

Candidate of Technical Sciences, associate professor
National Technical University of Ukraine «Igor Sikorsky Kyiv Polytechnic Institute»
Kyiv, Ukraine

Mukola Gomelia

Doctor of Technical Sciences, professor
National Technical University of Ukraine «Igor Sikorsky Kyiv Polytechnic Institute»
Kyiv, Ukraine

Abstract
Discharges of a huge amount of insufficiently purified mine waters lead to a significant deterioration of the ecological situation, as a result of which, there is a quantitative and qualitative depletion of water resources. Therefore, the most rational solution to this problem is the creation of low-waste technologies for the purification of mineralized waters.This will increase the efficiency of using local water resources and also solve the problem of providing enterprises and the population with qualitative water. The objective of the work was to study the processes of ion-exchange separation of chlorides and sulfates on a highly basic anion AB-17-8 in Cl^-form. The carried-out researches have shown that efficiency of separation of chlorides and sulfates increases with increase in height of an ion exchangerlayer and decrease in water salt content. The processes of regeneration of anion exchanger have been studied and a method of their recovery for reusing has been developed.A principal technological scheme for the demineralization of mine and sewage water is proposed, which allows obtaining water with mineralization< 1 g/dm^3, hardness < 2.3 mg-eq/dm^{3}for complete recycling of generated wastes.

Key words: ION-EXCHANGE SEPARATION, ANION EXCHANGER, CHLORIDES, SULFATES, REGENERATION

Introduction

Recently in the southern and eastern regions of Ukraine, there is an acute shortage of clean fresh water for drinking water supply. The need for drinking water of good quality is not provided by local sources of water supplyin these regions.The salt content of water in the rivers flowing on the territory of the Donbas has risen to such an extent that the water in these rivers is already unsuitable for use in drinking-water supply systems.In work [1], it is shown that increase of economic efficiency of the mining enterprises of Ukraine and improvement of the environment condition are possible by expansion of their activity in directions which are problems for the whole world and Ukraine.The situation is complicated by the excessive discharge of highly mineralized (up to20 g/dm^3) acidic (pH 5-6) mine waters with high sulfate content (up to 5000 mg/dm^3)and iron (up to 1500 mg/dm^3) [2]. In 2010, the volume of mine waters in the Eastern Donbass, despite the closure of most of the mines, amounted to 78 million m^3/year and the removal of dissolved substances amounted to 411 thousand tons (SO_4^{2-} – 211 andFe – 6.5) [3].

To solve this problem, it is necessary to develop a technology for demineralization of mine waters with simultaneous solution of the problem of utilization of concentrated salt brines formed during desalting.In works [4, 5], reviews of various methods of purification from sulphates of mining enterprisessewage waters are presented on the basis of domestic and foreign experience. Mine waters have a very diverse chemical composition, there are sulfate-hydrocarbonate and hydrocarbonate-sulphate waters with different cation composition in the Donbass [6, 7].

Combined cleaning methods such as mechanical, reagent, sorption, electrochemical and other physical and chemical methodsare usedfor mineralized mine waters. To date, when cleaning water with a high content of chlorides and sulphates, preference is given to reverse osmosis.At the same time in the concentrate, there is an accumulation of sulfates and chlorides, which complicates their further processing. The methods of processing sulfate-containing concentrates by electrodialysis methods are presented in [8], which allow obtaining desalted concentrate and sulfuric acid.If there are anions and carbonates chloride in the concentrate it can be processed by electrolysis methods to produce such commodity products as alkali, hydrochloric acid and hypochlorite. Therefore, solving the problem of separation of chlorides and sulfates is an importantissue.

The objective of this work is to study the processes of ion-exchange separation of chlorides and sulfates on the highly basic anion exchangerAB-17-8 in Cl^-form, to determine the efficiency of sorption and regeneration depending on the height of the ion exchanger ball.

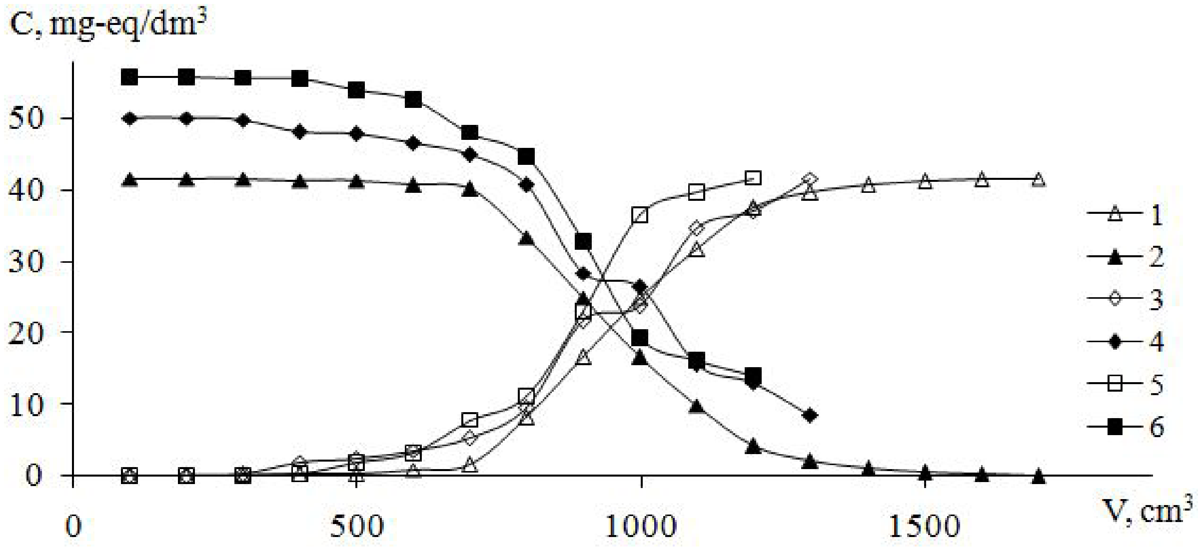
Methods of the study

The processes of ion-exchange separation of chlorides and sulfates were studied using a highly basic anion exchanger AB-17-8 in Cl^-form. Since, when water is pretreated on the cation exchanger, it may be softened and for sorption on the anion exchanger, model solutions of chloride and sodium sulfate with a sulfate concentration of 2000 mg/dm^{3}and chlorides 0.300 and 500 mg/dm^3. These solutions were passed through the anion exchanger AB-17-8 in Cl^-form with volume 20 cm^3. The consumption of the solution during sorption was 10-15 cm^3/min. Samples were taken with a volume of 100 or 200 cm^3, after which they were analyzed for the content of chlorides and sulfates. During the regeneration, samples of 20 cm^3 were taken. The consumption of the regeneration solution was 1-2 cm^3/min. The content of chlorides and sulfates was determinedin each sample.

Exchange dynamic capacity before channeling ($EDC_{bef.ch.}$) and the total exchange dynamic capacity (TEDC) of the ion exchanger was calculated from the mass of sorbed ions on the anion exchanger. The degree of regeneration of ion exchanger after passing through *n* samples of the regeneration solution was calculated as the ratio of the mass of desorbed and sorbed ions.

Research results

When processing mine waters with reagent methods using lime and aluminum-containing reagents, it is possible to reduce the residual sulfate content to 135-250 mg/dm^3 [9]. The main disadvantage in using these methods is the high cost of coagulants and secondary water contamination with chlorides. When treating water with a high content of sulphates, only lime is able to reduce their concentration to 20-30 mg-eq/dm^3 [10]. Therefore, for research, it was expedient to study the separation of solutions with the concentration of sulfates up to 2000 mg/dm^3. The concentration of chloride in the mine waters ranges from 500 mg/dm^3. On the efficiency of ion-exchange separation of chlorides and sulfates on a highly basic anion exchanger in Cl^-formcan be judged from the sorption curves, which are shown in Fig. 1.



C(Cl^-) = 0 mg/dm^3 – 1, 2; C(Cl^-) = 300 mg/dm^3 – 3, 4; C(Cl^-) = 500 mg/dm^3 – 5, 6;

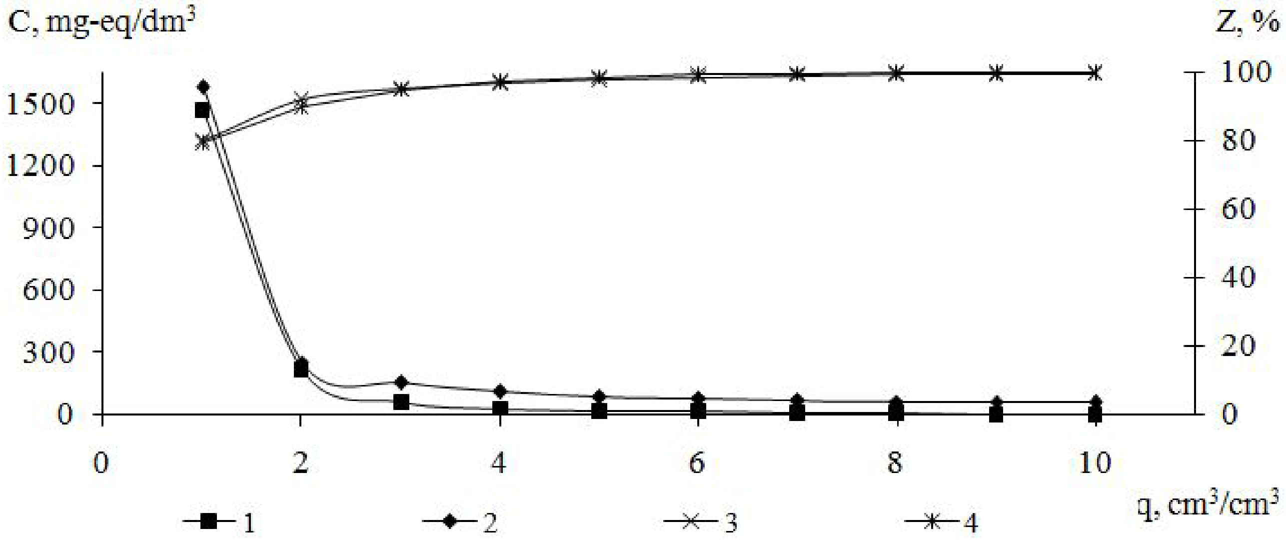
Figure 1. Dependence of the concentration of sulfates (1, 3, 5) and chlorides (2, 4, 6) on the volume of the passedsolution (C (SO_4^{2}) = 2000 mg/dm^3) through the anion exchanger AB-17-8 inCl^-form

When sorption of sulfates from the solution (C(SO_4^{2}) = 2000mg/dm^3, C(Cl^-) = 0 mg/dm^3) on the anion exchanger AB-17-8 in Cl^-formwith a volume of 20 cm^3 $EDC_{bef.ch.}$ for sulfates is 0.63 g-eq/dm^3 (Table1). With an increase in the amount of chloride up to300 mg/dm^3 $EDC_{bef.ch.}$ decreased to0.42 g-eq/dm^3. A further increase in the chloride concentration to 500 mg/dm^3 led to a decrease in chlorides to 0.21 g-eq/dm^3, which indicates a decrease in separation efficiency during sorption with an increase in the chloride concentration. Total exchange dynamic capacity is 1.91; 1.80; 1.6842 g-eq/dm^{3}at a chloride concentration of 0.300 and 500 mg/dm^3, respectively.

Table 1. Change in exchange capacity of anion exchanger AB-17-8 inCl^- formdepending on the ratio of the concentrations of sulfates and chlorides in solution

$C(Cl^-)$, mg/dm^3	0	300	500
$EDC_{bef.ch.}$, mg-eq/dm^3	630	420	210
TEDC, mg-eq/dm^3	1910	1800	1680

A 10% solution of sodium chloride was used to regenerate the anion exchangers. As can be seen from Fig. 2, the regeneration efficiency depends on the specific consumption of the NaCl solution. At a specific consumption of sodium chloride of2 cm^3/cm^3, it is possible to achieve a degree of regeneration of 87%, which is a fairly good indicator.



Freshly prepared NaCl solution (1; 3); the spent regeneration solution was restored by treatment of $CaCl_2$ – 2, 4 $C(SO_4^{2-})$ = 2000 mg/dm^3; $C(Cl^-)$ = 0 mg/dm^3

Figure 2. Dependence of the concentration of sulfates (1, 2) and the degree of their desorption (3, 4) on the consumption of a solution of sodium chloride through ion exchanger AB-17-8 inCl^-, SO_4^{2-}form

A drawback of ion-exchange technology is the need to use a significant amount of reagents to regenerate the filters and discharge of a large amount of saline sewage waters into surface water bodies.Therefore, it was necessary to develop a method for reusing regeneration solutions after their reduction. For this purpose, the regeneration solutions were treated with calcium chloride in a stoichiometric amount from the sodium sulfate content. The degree of regeneration and the sorption capacity of the anion exchanger after treatment with such solutions remains sufficiently high.

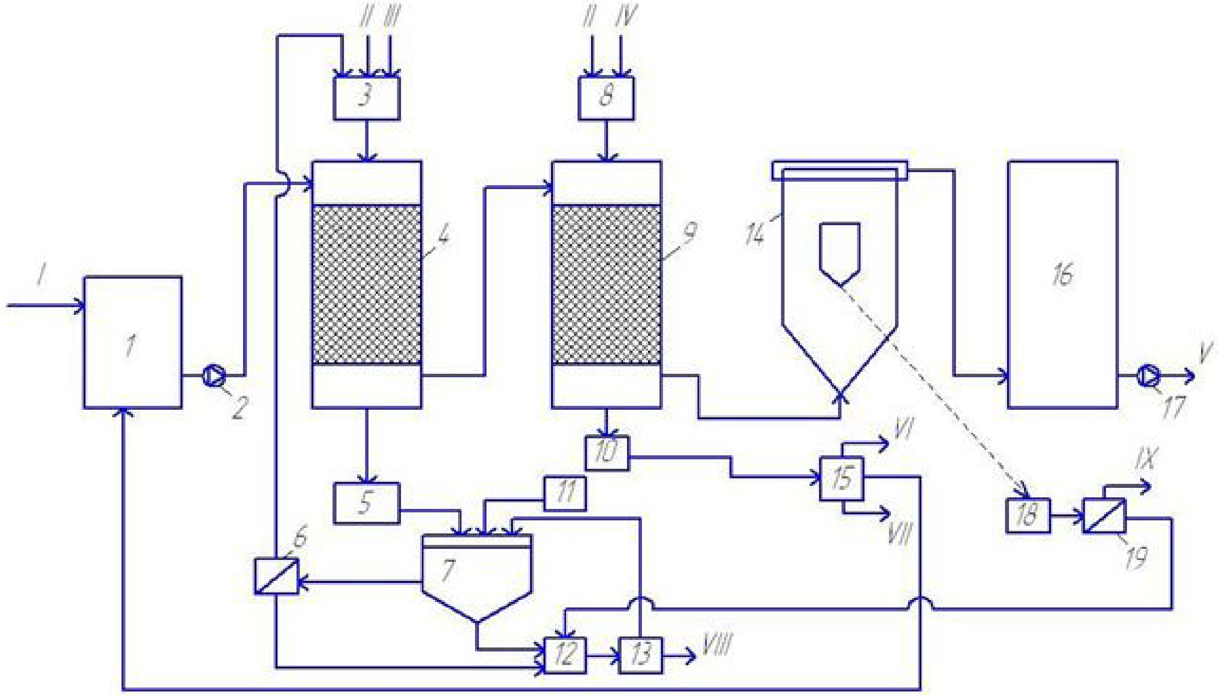
The sediment thatis formed in this process is a gypsum that can be used as a building material.

In general, the results obtained allow solving the problem of demineralization of mine waters, concentrates of baromembrane desalination of water and other wastewater. In this case, it is possible to implement the technology presented in Fig.3. In the first stage of ion-exchange purification (4), sulfates are removed from the water by an anion exchange filter in Cl^-form.Chlorides are extracted from water in the second stage of anionizing (9) on the anion exchangerAB-17-8 in the carbonate or basic form. In this case, alkalization and softening of water occurs. The precipitate of calcium carbonate and magnesium hydroxide is separated into a clarifier with a suspended sediment layer (14).

Clarified water has residual hardness from 0.5 to 2.3 mg-eq/dm^3 [10], the residual chloride content does not exceed 300 mg/dm^3, the total mineralization is less than 1000 mg/dm^3. It is advisable to use such water for feeding the water-rotation cooling systems of power plant, boiler plants, industrial enterprises. After additional treatment, it can be used as drinking water, after deep deionization, it can be used as energy water.

A 10% solution of sodium chloride is used to regenerate the ion exchanger in the sulfate form and transfer it to Cl^{-}form. After mixing the spent regeneration solution with calcium chloride, most of the sulphates are precipitated and released as gypsum. Dissolved sulfates do not affect the efficiency of desorption of sulfates from the anion exchanger AB-17-8 with the repeated use of the regenerated solution clarified on the filter (6).

Anion exchanger in the second stage of anionization is transferred to the basic or carbonate form with a solution of alkali or sodium carbonate [9]. The choice of the form of ion exchanger depends on the ratio of calcium and magnesium ions in the water supplied to the purification.With a high calcium content, deeper water softening is achieved when using ion exchanger in the carbonate formin the second stage of anionization(9). For the precipitation of magnesium hydroxide ion exchanger is better to use in the basic form.Spent regeneration solutions containing sodium chloride can be processed in an electrolytic cell to obtain solutions (up to 12%) of alkali and hydrochloric acid [4].Alkali is expediently used for the regeneration of anionite in the filter (9), the acid can be used to prepare a calcium chloride solution by interaction with calcium carbonate. Gypsum after the press filter (13) and the sediment after the press filter (19) can be used in the production of building materials.



1 - reservoir of mine waters (concentrates, sewage water); 2, 17 - pumps; 3, 8, 11 - supply tanks; 4, 9 - anion-exchange filters (AB-17-8); 5, 10 - receiving reservoirs of spent regeneration solutions; 6 – belt filter;7 - sump tank; 12, 18 - slurry storage facility; 13, 19 - auger filter press; 14 - clarifier with a suspended sediment layer; 15 - electrolyte tank; 16 - clarified water tank;

I - supply of mine (sewage) water (concentrate); II - water supply;III – $CaCl_2$; IV - supply of sodium carbonate (alkali); V - water supply to the consumer; VI - solution of hydrochloric acid; VII - alkali solution; VIII - gypsum for recycling; IX - sediment for recycling

Figure 3. Schematic diagram of demineralization of mine (sewage) water (concentrates)

Thus, the ion-exchange separation of chlorides and sulfates allows creating a low-waste technology for the demineralization of mine and other wastewater.

Conclusion

When using anion exchanger AB-17-8 inCl^{-}form,it is possible to purify wastewater from sulfates in the presence of chlorides at a sulfate concentration up to 2000 mg/dm^3. The efficiency of separation increases with a decrease in the concentration of anions in water. It is shown that desorption occurs quite efficiently with repeated use of deoxidized regeneration solutions.

A principal technological scheme for the demineralization of mine and waste water is proposed based on the ion-exchange separation of chlorides and sulfates, basifying the water on the anionite in the basic form, which allows obtaining water with mineralization < 1000 mg/dm^3, hardness< 2.3 mg-eq/dm^{3}when the wastes are completely recycled.

References

1. Chetverik M. S. (2017) Problemy obespecheniia naseleniia prodovolstviem, presnoi vodoi, elektrojenergie i ih vzaimosvjaz s dobychei poleznyh iskopaemyh [Problems of supplying the population with food, fresh water, electricity and their interrelationship with the extraction of minerals], *Metallurgicheskaya i gornorudaya promyshlennost* [Metallurgical and mining industry]. No 1 (304), p.p. 97-106.
2. Gusev N. N. (2007) Himicheskii sostav shahtnyh (karernyh) vod [Chemical composition of mine (open cut) waters]. *Shahtnye i karernye vody predpriiatii ugolnoj promyshlennosti. Spravochnyj obzor* [Mine and open cut waters of coal industry enterprises. Reference review]. Moscow, Tsentralnyi izdatelskii dom [Central Publishing House], p.p. 70-116.
3. Gavrishin A. I., Borisova V. E., Toropova E.S. (2016) O formirovanii himicheskogo sostava gruntovyh vod v shahtinsokom uglenosnom rajone vostochnogo Donbassa [On the formation of the chemical composition of groundwater in the coal mined area of the eastern Donbas]. *Zhurnal "Uspehi sovremennogo estestvoznanija"* [Journal "Success in Modern Natural Science"]. No 5, p.p. 111-115.
4. Masloboev V. A. (2017) Metody snizhenia koncentracii sulfatov v stochnyh vodah gornorudnyh predpriatii [Methods of reducing the concentration of sulfates in sewage waters of mining enterprises]. *Vestnik Kolskogo nauchnogo centra RAN* [Bulletin of the Kola Science Center of the Russian Academy of Sciences]. No. 1 (9), p.p. 99-115.
5. Selitsky G.A. (2009) Ochistka prirodnyh i stochnyh vod ot sulfatov [Purification of natural and waste water from sulphates]. *Vodoochistka* [Water purification]. No 8, p.p. 29-32.
6. Voytovich S. P. (2015) Geohimicheskie osobennosti shahtnyh vod ugol'nyh bassejnov Ukrainy i Rossii [Geochemical features of mine waters of coal basins of Ukraine and Russia]. *Molodoi uchenyi* [Young Scientist]. No 23, p.p. 395-397.
7. Voytovych S. P. (2015) Heokhimichni osoblyvosti pidzemnykh i shakhtnykh vod vuhilnykh baseyniv Ukrayiny (na prykladi Chervonohrads'koho hirnychopromyslovoho rayonu ta Tsentral'noho Donbasu [Geochemical features of underground mine water and coal basins of Ukraine (on the example of Chervonograd mining region and Central Donbass]. *Naukovyy visnyk Natsional'noho hirnychoho universytetu* [Scientific Bulletin of National Mining University]. No 2, p.p. 23-30.
8. Trus I. M., Hrabitchenko V. M., Gomelia M. D. (2013) Otrymannya sirchanoyi kysloty pry elektrokhimichniy pererobtsi elyuativ, shcho mistyat sulfaty [Sulfuric acid in electrochemical processing of eluate containing sulfates]. *Skhidno-Yevropeyskyy zhurnal peredovykh tekhnolohiy* [Eastern European Journal of advanced technologies]. No 4/6 (64), p.p. 10-13.
9. Gomelya N. D., Trus I. N., Nosacheva Yu.V. (2014) Ochistka vody ot sulfatov izvestkovaniem pri dobavlenii reagentov soderzhashhih aliuminii [Purification of water from sulfates by liming with the addition of reagents containing aluminum]. *Himiia i Tehnologiia Vody* [Chemistry and Technology of Water]. No 2, p.p. 129-137.
10. Lebedev V. N., Lokshin E. P., Barmin I. S. (2007) Desulfataciia stokov himicheskoi ochistki baddeleitovogo koncentrata Kovdorovskogo GOKA [Desulfation of drains of chemical purification of baddeleyite concentrate of Kovdorovsky MPP]. *Obogashhenie rud* [Concentration of ores]. No 3, p.p. 42-44.

«The publication contains the results of studies conducted by President's of Ukraine grant for competitive projects Ф-70 of the State Fund for Fundamental Research»