

OPTIMIZATION OF HEAT-AND-POWER PLANTS
WATER PURIFICATION*Yuliya Zelenko^{1,*}, Myroslav Malovanyy², Lidiya Tarasova¹*<https://doi.org/10.23939/chcht13.02.218>

Abstract. The effect of the content of natural and anthropogenic pollutants (potentially acidic organic substances, synthetic surfactants and petroleum products in water, which is exposed to desalting) on the efficiency of KU-2-8 ion exchangers has been studied. To minimize this negative influence the reagent method was used. Different natural and modified sorbents have been investigated for additional purification of water before filtration on cation-exchange filters or periodic regeneration of ion exchangers by the studied reagents.

Keywords: cation exchanger, ion exchanger, potentially acidic organic substances, synthetic surfactants.

1. Introduction

The urgency of this research is specified by the complexity of choosing the optimal technology for ionic demineralization of technical water, which is used for the railway heat-and-power plants. In particular, this is due to the need to take into account a large number of factors, the main of which are the equipment parameters (temperature, pressure), the composition of the source water, the plant capacity, the peculiar design of ion-exchange filters, the availability of ion exchanges of a particular type, the conditions for residual solutions utilization. Therefore, the choice of ionic desalting technology for technical water, ensuring the operation of heat-and-power equipment, should be based on a technological criterion, which is the degree of water purification. Several technologies meet this criterion, so further selection should be based on environmental and techno-economic criteria. The degree of ions extraction (the ratio of the number of ions extracted during the purification to the amount of salt in the source water) should be close to one. Next task is to calculate the specific costs for each of alternative

technologies and to choose the technology from the standpoint of minimum cost, as well as to find the optimal conditions for the process organization.

The processes of sodium-cationic softening of high-mineralized waters using strong and weakly acid cation exchangers for water stabilization were investigated by Gomelya *et al.* [1]. Nowadays the desalting boilers use sulfurized coal as Na-cation exchanger with a grain size of 0.5–1.2 mm and full exchange capacity of 300 g-eq/m³. The service life without replacement is 3–5 years. We propose to use a cation exchanger KU-2-8.

The purpose of this work is to study the influence of anthropogenic pollutants, namely potentially acidic organic substances (PAOS), synthetic surfactants (SS) and petroleum products, which are present in water, on the performance characteristics of ion exchanger KU-2-8 and ways of minimizing this negative impact.

2. Experimental

Ion exchangers with an initial dynamic exchange capacity (DEC) of 820 g-eq/m³, petroleum products (petrol A-80, diesel oil L and VM-6 vacuum oil) were used for the experiments. Magnesium sulfate, calcium bicarbonate, sodium chloride, hydrochloric acid and sodium hydroxide were of reagent grade. All solutions were prepared using distilled water, the content of petroleum products in which did not exceed 0.16 mg/l (which was taken into account in the calculations).

The operating conditions of the ion-exchange filter were modeled using a laboratory installation.

A column with the diameter of 50 mm was loaded with the cation exchanger KU-2-8 (load volume was 451 cm³). The water subjected to desalting was filtered through a column with the rate of 1 m/h. The samples at the column outlet were analyzed for the ions content. As a result of calculations, the total static exchange capacity and dynamic exchange capacity of cation exchangers were determined.

To investigate the influence of petroleum products on the activity of cation exchanger KU-2-8, the products (petrol A-80, diesel oil L and VM-6 vacuum oil) were

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weighed with an accuracy of 0.1 mg/l and added to the investigated solutions with the concentrations of 0.1–20 mg/dm³ under intensive stirring. Although some residual amount of oil remained on the walls of capacities, it did not affect the general character of the obtained dependencies. The columns were filled by ion exchangers, after which standard solutions of CaCl₂ or NaCl with different amounts of oil were used to determine the DEC.

Investigation of the water preliminary purification from emulsified petroleum products (before treating by cation exchanger KU-2-8) was carried out according to the following procedure. Glass flasks (200 ml by volume) were filled with 100 ml of water contaminated with oil, and then the calculated amounts of the sorbent were added. Natural montmorillonite clay of Yazivsky deposit (Ukraine), iron(III) chloride modified montmorillonite clay [2] and coquina of Evpatoria deposit (Ukraine) were used as sorbents for pretreatment of water before cationization. The dispersity of all samples was 0.125–0.25 mm. The flasks were sealed hermetically and the sorption process was carried out in static conditions under stirring for 60 min. The suspension was settled for 3 days until complete phase separation. Water was decanted and analyzed for the content of oil in water by infrared photometry using “MICRAN-1” device.

3. Results and Discussion

3.1. Impact of PAOS and its Minimization

PAOS is one of the most common corrosion-aggressive compounds, which is a mixture of low molecular acidic substances formed as a result of thermolysis and oxidation from natural or synthetic organic compounds under high temperature and pressure. The source of PAOS formation is water-dissolved natural humus compounds. The term “humus compounds” means

a complex of unidentified compounds, about which the following is known:

- these compounds are decomposition products of substances of animal and vegetable origin, their molecular weight is in the range of 500–25000;

- they contain both aliphatic and aromatic fragments (from formic to nonanoic acids, as well as lactic acid) with acidic functional groups (hydroxyl, carboxylic). This creates preconditions for the formation of low molecular organic substances with significant corrosion activity from such substances during thermolysis;

- humus substances are polyelectrolytes, which may be removed from water *via* treatment by coagulants with the use of anion exchange.

The only stage that provides the removal of humus compounds before water desalting, is the process of reagent treatment.

To determine the possibility of increasing the removal degree of humus compounds from water during its softening, we determined the effectiveness of anion for organic pollutants removal under the operation conditions of a sodium-cationization plant.

It is known that humus compounds are sorbed from natural water by strongly basic and weakly basic ion exchangers. The depth of such pollutants removal is usually higher using strong basic porous sorbents compared with weakly basic ion exchangers. Strongly basic anion exchangers, saturated with humus, are best regenerated with a mixture of chloride and sodium hydroxide. Their capacity to a large extent can also be restored by a solution containing only sodium chloride.

Data on the amount of humus substances which are sorbed by anion exchangers before the chloride and desorbed organic pollutants breakthrough indicate that some humus substances remain in the layer of sorbent saturated by the components to the equilibrium state (Table 1). This indicates that natural humus compounds contain a fraction which is sorbed by ion exchanges more selectively than sulfate ions [3, 4].

Table 1

Efficiency of dynamic adsorption of humus substances over anions of various types

Ion exchanger type	Adsorption degree of humus substances, %	
	before chlorides breakthrough	after saturation of ion exchanger till equilibrium
Resinex TPX-4510	63.1	1.3
Amberlite IRA67	48.3	12.0
Amberlite IRA900	51.7	16.0
Amberlite IRA478	43.4	1.1
Dauex MWA1	43.5	14.1
Levatite AP49	48.2	9.4
Levatite MP600	31.8	13.5

It was found that for the plants of water softening with its previous liming the ion exchanger Amberlite IRA900 removes about 50 % of humus substances and can be regenerated with the same solution as Na-cation filters. Since the filter cycle of the second-degree filters for water softening, as a rule, substantially exceeds the same index for the first-degree filters, the usage of the same sodium chloride solution for the sequential regeneration of cation exchangers is not accompanied by undesirable effects. Therefore, a rational decision of organizing the removal of humus substances for water softening is additional loading of sodium-cation exchange second-degree filters with the Amberlite IRA900 sorbent.

3.2. Impact of SS and its Minimization

Quite often the industrial enterprises discharge waste water containing an organic matter, in particular non-ionic surfactants. Due to infiltration into the underground horizons these substances pollute underground water. When this water enters the treatment plants, it affects the activity of ion-exchange resins. It was noted that substances of OP-7 and OP-10 type are very weakly absorbed by ion exchanges, but they affect the exchange properties of the latter with respect to inorganic ions. There is no consensus among researchers concerning the effect of SS on the performance characteristics of ion exchangers. Thus, some researches [5-8] do not observe the negative impact of SS on the exchange capacity of ion exchangers KU-2, AN-31 and others. Other authors [9-13] show the deterioration of their exchange capacity with respect to inorganic ions after the contact with SS. We have found that after 50 working cycles the dynamic exchange capacity (DEC) of cation exchanger KU-2 decreases by 11.8 %. We also studied the effect of OP-10 type SS on the exchange capacity of the weak anion exchanger AN-31, used in the closed cycle of water supply. It was found that OP-10 is absorbed by the anion exchanger according to the molecular sorption mechanism. As a result of anion exchanger regeneration with conventional reagents (NaOH, NaCl and their mixture) the exchange capacity of AN-31 is recovered by 20–50 %. Complete regeneration is observed if we use a regenerative solution of isopropyl alcohol (6.3 g per 1 g of resin).

3.3. Impact of Emulsified Petroleum Products and its Minimization

Petroleum products are impurities, which are common in both surface and underground sources, that enter them as a result of ducts, transport accidents, untreated water discharge, etc. This situation is especially typical of the sources located in the area of railway and

road transport enterprises, as well as enterprises related to oil extraction and processing. Figs. 1-3 show the dependencies of DEC on the content of oil and petroleum products in the solution with respect to two model tests: filtration with assigned flow rate of regulating solution (DEC_r) and filtration to the establishment of the controlled ions (Ca²⁺, Mg²⁺) equilibrium (DEC_{eq}). The increase in oil content leads to a systematic reduction of DEC values of ion exchangers. Especially significant changes are observed within the range of oil and petroleum products concentration of 70–90 mg/l (by 60–62 %). In other words, a particularly strong loss of ion exchangers' activity occurs at some threshold value of oil concentration.

The analysis of the results presented in Figs. 1-3 allows us to conclude that in all cases, with an increase in the concentration of investigated petroleum products, there is a general tendency towards reduction of ion exchanger capacities. Particularly significant reductions in ion exchanges DEC are observed in the range of petroleum products content of 10–20 mg/l. There is an express systematic reduction of the dynamic exchange capacity of ion exchangers in a series: petrol → diesel fuel → motor oil. It should be noted for motor oil (Fig. 3) that after the exhaustion of ion exchangers capacity their ability to restore properties during regeneration sharply decreases. As for petrol, this process is less expressed and the DEC values slightly deviate from the results obtained using a standard saline solution without petroleum products.

The mechanism of petroleum products influence can be related to the purely mechanical blockage of the surface of ion exchanger grains or may be conditioned by the sorption of hydrocarbon molecules and even their partial introduction into the structure of the hydrocarbon skeleton of the net polymer [14]. To determine the mechanism of hydrocarbons interaction with the surface of ion exchangers, we conducted experiments on the treatment of investigated ion exchanger KU-2-8, contaminated with petroleum products, by the high-purity hexane. For this purpose, the sample of ion exchangers was filled with hexane of P.A. grade and after a certain time, the content of petroleum products in the liquid phase was determined using an automatic analyzer of petroleum products in water ("Mikran" device). A series of individual experiments showed that the content of petroleum products differs from the same determination using "Mikran" by no more than 6 %. We observed the significant duration of the petroleum products extraction from the ion exchanger by hexane, which confirms rather strong connections between the molecules of petroleum products and the surface of ion exchangers. The possibility of partial introduction of chemisorbed molecules of petroleum products into a divinyl-styrenic matrix of an ion exchange resin is not excluded. It should

be noted that a hexane treatment of investigated ion exchange resins, contaminated with petroleum products, increases their content in hexane only to a small extent.

From the technological standpoints it would be advisable to pre-clean water from petroleum products to

prevent the mudding of the cation-exchange surface. Based on our research [15-17], the use of natural sorbents is promising. We studied the sorption properties of natural and modified sorbents for petroleum products. Results are presented in Fig. 4.

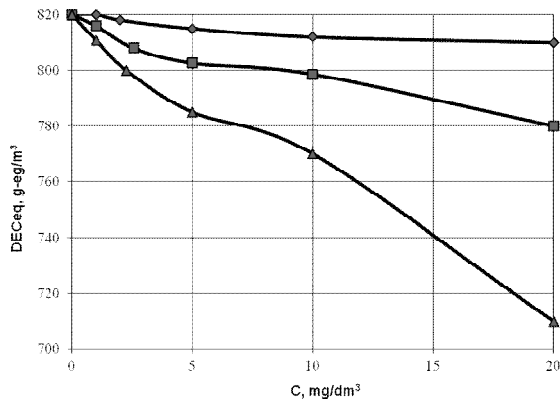


Fig. 1. DEC_{eq} vs. petroleum products concentration for petrol A-80 (◇); diesel oil L (□) and VM-6 oil (Δ)

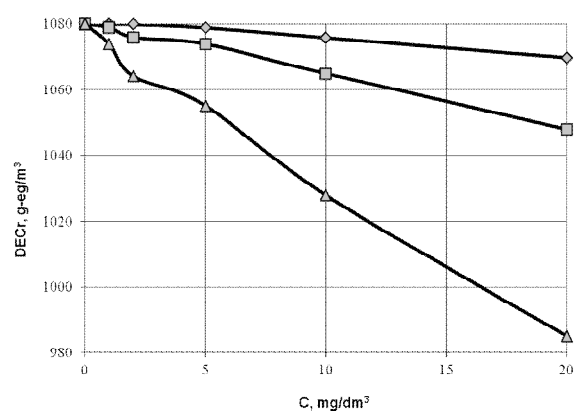


Fig. 2. DEC_τ vs. petroleum products concentration for petrol A-80 (◇); diesel oil L (□) and VM-6 oil (Δ)

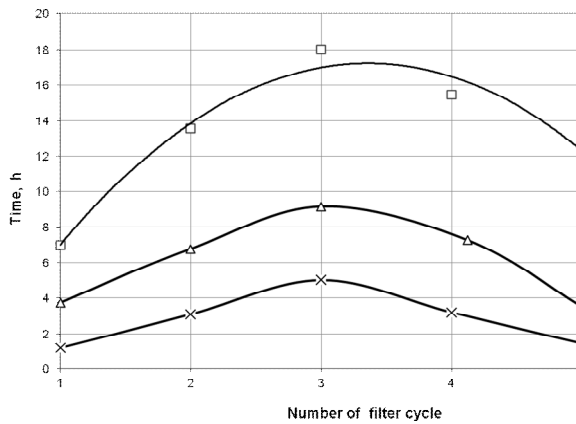
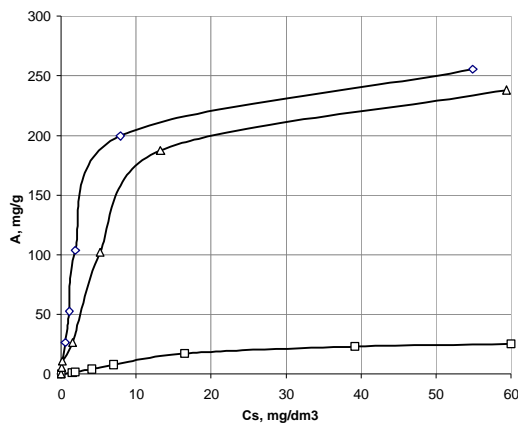
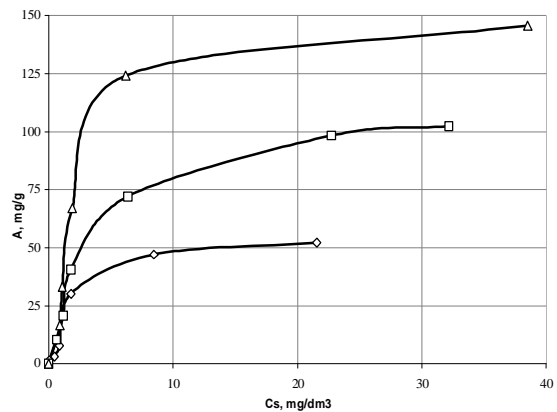


Fig. 3. Effect of petroleum products type on duration of filter cycle: A-80 (□); diesel oil L (Δ) and VM-6 oil (×)



a)



b)

Fig. 4. Sorption isotherms of diesel oil (a) and crude oil (b): iron-containing clay (◇); coquina (□) and natural clay (Δ)

Bentonite clay, modified with iron(III) chloride and coquina were found to be the best sorbents (Fig. 4). Thus, the sorption capacity of the material based on a modified clay relative to the petroleum products is 271 and 145.8 mg/g for diesel oil and crude oil, respectively. Similar values for coquina are 238 and 102.4 mg/g, respectively. The sorption ability of iron-containing clay is much higher compared with that of natural clay, which is due to the clay matrix modification. Sorption ability of iron-containing clay and coquina is higher in the case of absorption of diesel fuel compared with absorption of crude oil, which can be explained by the physical and chemical properties of sorption materials, as well as the chemical composition of contaminating petroleum products. In the case of iron-containing clay, sorption takes place due to the active centers located on the sorbent surface and mesopores, *i.e.* sorption in the micropores is actually absent. The porosity of coquina is provided by meso- and macropores, therefore the long-chain hydrocarbons can fill the pores and the surface of the sorbent.

The purified mixture can be used for the production of a road surface in the form of a plasticizing additive [16, 17]. The spent sorbents are also useful as an effective addition to the charge for the production of claydite and bricks. Taking into account the increased plasticity of discharge clay that absorbed resins and asphaltenes, it is expedient to use it as a raw material for the production of claydite. Such additive will provide the production of a product with greater mechanical strength. Moreover, the crystallization of the crude mass in the baking process increases. The content of petroleum products in the clay increases the material porosity and reduces the energy costs for raw material burning off; hence, the costs of production as a whole are reduced. Another application area of the sorbents saturated with petroleum products is their use as a part of a complex charge for the implementation of environmentally friendly processes for the restoration of domestic phosphorus by the natural gas in the presence of sodium sulfate [18]. Utilization of this waste can be carried out in the process of thermo-oxidation decomposition [19], the final product of which is a valuable raw material for the production of a number of building materials.

4. Conclusions

The results obtained confirm the necessity of introducing measures to minimize the negative impacts of impurities present in the water supplied for ion-exchange demineralization and subsequently used in heat-and-power plants. To reduce the negative influence of the PAOS on the activity of cation exchanger KU-2-8, it is

expedient to organize the process of humus substances removal for water softening *via* loading the second-degree Na-cation exchangers with the sorbent Amberlite IRA478. In the conditions of plants operating with its previous liming the ion exchanger Amberlite IRA478 removes about 50 % of humus substances and can be regenerated with the same solution as Na-cation filters. Since the filter cycle of the second-degree filters for water softening, as a rule, substantially exceeds the same index for the first-degree filters, the usage of the same sodium chloride solution for the sequential regeneration of cation exchangers is not accompanied by undesirable effects.

To minimize the negative impact of SS on the activity of cation exchangers KU-2-8 it is advisable to periodically regenerate cation exchanger with the isopropyl alcohol, which allows to completely restore the exchange capacity of ion exchangers. The spent isopropyl alcohol may be used as a part of detergents (liquid soaps). SS content in these products would improve the quality of liquid soaps.

To minimize the negative impact of emulsified petroleum products on the activity of cation exchangers KU-2-8, it is expedient to predict the stage of water preliminary purification from petroleum products using natural sorbents: iron-containing bentonite clays or coquina.

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ОПТИМІЗАЦІЯ ПРОЦЕСУ ОЧИЩЕННЯ ВОДИ ТЕПЛОЕНЕРГЕТИЧНИХ УСТАНОВОК

Анотація. Досліджено вплив вмісту природних та антропогенних забруднювачів – потенційно кислих органічних речовин, синтетичних поверхнево активних речовин та нафтопродуктів у воді, яка піддається знесоленню, на працездатність йонітів КУ-2-8 та шляхи мінімізації цього негативного впливу. Показано, що мінімізація впливу цих речовин на активність катіоніту КУ-2-8 можлива реагентним методом – внаслідок додаткового очищення води перед подачею на катіонітні фільтри або періодичною регенерацією йоніту реагентом, який екстрагує кольматовані забруднювачі на поверхні. Досліджена ефективність застосування для очищення води від емульсованих нафтопродуктів природних та модифікованих сорбентів.

Ключові слова: катіоніт, йонний обмін, потенційно кислі органічні речовини, синтетичні поверхнево-активні речовини.