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DEVELOPMENT OF AN AUTOMATED SYSTEM FOR THE PURIFICATION OF ALKANOLAMINE SOLUTIONS

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Abstract. The alkanolamine solutions used in natural gas purification processes are inevitably degraded over time. This occurs due to accumulation of reaction products from the reactions with carbon dioxide, hydrogen sulphide, oxygen and other impurities present in the gas streams, as well as from thermal degradation. The degradation of solutions leads to the formation of thermostable compounds that not only reduce absorption efficiency, but also increase corrosive activity. Furthermore, part of the amine turns into a bound state and becomes ballast. The necessity of purification of alkanolamine solutions is becoming more and more urgent since the cost of maintaining efficient operation of gas treatment plants grows, and environmental safety requirements increase. Purification of solutions makes it possible to prolong their service life, reduce the cost of purchasing new reagents and reduce the negative impact on the equipment. In this work the method of anion-exchange technology of purification is used. Unlike vacuum distillation

and electrodialysis, the considered technology does not require significant energy costs for generation and maintenance of vacuum, and heating of solutions, it can be easily integrated into the existing production process without any significant changes in the infrastructure. The described problem is relevant for Kazakhstan oil refineries, two of which use methyldiethanolamine, and one of which uses diethanolamine, and the existing practice of maintaining the operability of the systems is based on periodic replacement of part of the solution with pure amine. The development of automated systems for purification of such solutions makes it possible to significantly improve process control, minimise manual labour, and improve the overall economic efficiency of production.

Keywords: methyldiethanolamine, corrosion, degradation, thermostable compounds, anion exchange resin, purification, automation.

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АЛКАНОЛАМИН ЕРІТІНДІЛЕРДІ ТАЗАЛАУДЫҢ АВТОМАТТАНДЫРЫЛҒАН ЖҮЙЕСІН ӘЗІРЛЕУ

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Аннотация. Уақыт өте келе табиғи газды тазарту процестерінде қолданылатын алканоламин ерітінділері сөзсіз деградацияға ұшырайды. Бұл газ ағындарында болатын көмірқышқыл газы, күкіртті сутегі, оттегі және басқа қоспалармен реакция өнімдерінің жинақталуына, сондай-ақ термиялық деструкцияға байланысты болады. Ерітінділердің деградациясының нәтижесінде термотұрақты қосылыстар түзіледі, олар сіңіру тиімділігін төмендетіп қана қоймай, сонымен қатар коррозия белсенділігін арттырады. Бұдан бөлек, аминнің бір бөлігі байланысқан күйге өтіп, балласт ретінде әрекет етеді. Алканоламин ерітінділерін тазарту қажеттілігі газ тазарту қондырғыларының тиімді жұмысын қамтамасыз ету шығындарының өсуіне және экологиялық қауіпсіздік талаптарының артуына байланысты өзекті болып келеді. Тазалау шешімдері олардың қызмет ету мерзімін ұзартуға, жаңа реагенттерді сатып алу құнын азайтуға және жабдыққа жағымсыз әсерді азайтуға мүмкіндік береді. Бұл жұмыста анион алмасу тазарту технологиясының әдісі қолданылды. Вакуумдық дистилляция мен электродиализден айырмашылығы, қарастырылатын технология вакуумды және ерітінділерінің жылуын жасап, қолдау үшін айтарлықтай энергия шығынын қажет етпейді, және де инфрақұрылымдағы елеулі өзгерістерді қажет етпестен қолданыстағы өндіріс процесіне оңай біріктірілуі мүмкін. Сипатталған мәселе қазақстандық мұнай өңдеу зауыттары үшін өзекті болып табылады, олардың екеуі метилдиэтаноламинді, ал біреуі диэтаноламинді пайдаланады, және жүйенің функционалдығын сақтаудың қазіргі тәжірибесі ерітіндінің бір бөлігін таза аминмен мерзімді түрде ауыстыруға негізделген. Мұндай ерітіндерді тазалауға арналған автоматтандырылған жүйелерді дамыту процесті басқаруды жақсартуға, қол еңбегін азайтуға және өндірістің жалпы экономикалық тиімділігін арттыруға мүмкіндік береді.

Түйін сөздер: метилдиэтаноламин**,** коррозия, деградация, термотұрақты қосылыстар, анион алмастырғыш шайыр, тазалау, автоматтандыру.

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РАЗРАБОТКА АВТОМАТИЗИРОВАННОЙ СИСТЕМЫ ОЧИСТКИ РАСТВОРОВ АЛКАНОЛАМИНОВ

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Аннотация. Со временем растворы алканоламинов, используемые в процессах очистки природного газа, неизбежно подвергаются деградации.

Это происходит из-за накопления продуктов реакции с углекислым газом, сероводородом, кислородом и другими примесями, присутствующими в газовых потоках, а также в результате термической деградации. В результате деградации растворов образуются термостабильные соединения, которые не только снижают эффективность абсорбции, но и увеличивают коррозионную активность. Кроме того, часть амина переходит в связанное состояние и является балластом.

Необходимость очистки растворов алканоламинов становится все более актуальной по мере роста затрат на поддержание эффективной работы газоочистных установок и увеличения требований к экологической безопасности. Очистка растворов позволяет продлить срок их службы, снизить затраты на закупку новых реагентов и уменьшить негативное воздействие на оборудование.

В данной работе использован метод анионообменной технологии очистки. В отличие от вакуумной дистилляции и электродиализа, рассмотренная технология не требует значительных энергозатрат для создания и поддержания вакуума и нагрева растворов, легко интегрируется в существующий производственный процесс без необходимости значительных изменений в инфраструктуре. Описанная проблема актуальна для казахстанских нефтеперерабатывающих заводов, на двух из которых используется метилдиэтаноламин, а на одном – диэтаноламин и существующая практика поддержания работоспособности систем основана на периодической замене части раствора чисты амином. Разработка автоматизированных систем очистки таких растворов позволяет значительно улучшить управление процессом, минимизировать ручной труд и повысить общую экономическую эффективность производства.

Ключевые слова: метилдиэтаноламин**,** коррозия, деградация, термостабильные соединения, анионообменная смола, очистка, автоматизация.

Introduction

Solutions of alkanolamines such as monoethanolamine (MEA), diethanolamine (DEA), methyldiethanolamine (MDEA) and others have found wide application in various industries. Their main purpose is purification of gases (Pal et al., 2015: 8; Dalei et al., 2020: 11), including gases, generated during waste incineration (Aouini et al., 2014: 14), from acidic components (hydrogen sulphide, carbon dioxide). Such purification provides environmental protection and protection of equipment from hazardous influence.

Alkanolamine solutions are widely used at oil refineries in Kazakhstan to purify gases from acidic components. The principle of operation is based on the ability of amines to bind acidic gases in the absorber and then to release them in the desorber (Kheirinik et al., 2018: 8). Despite the high efficiency of monoethanolamine (MEA), some plants favour diethanolamine (DEA) or methyldiethanolamine (MDEA) because of their better thermal stability (de Ávila et al., 2015: 6; Bonenfant et al., 2007: 4).

Thermal (Mahmud et al., 2018: 7; Closmann et al., 2011: 6; Davis et al., 2009: 7) and oxidative (Fredriksen et al., 2013: 8; Lee et al., 2013: 6; Chi et al., 2002: 9; Goff et al., 2004: 9; Lawal et al., 2005: 13) degradation of alkanolamines, as well as formation of thermostable compounds (TSC) lead to a decrease in the efficiency of gas purification processes. In addition, the amine decomposition products cause corrosion of equipment due to the formation of soluble complexes with iron, which represents the basis of all structural steels. Some impurities accumulated in amine solutions have surfactant properties and promote intensive foaming (Alhseinat et al., 2015: 7; Chen et al., 2011: 6). The generated foam can cause various problems in the technological process, such as amine entrainment and equipment instability. Foam suppressants are used to control foam, but their use can change the properties of the amine solution (Edalatpour et al., 2022: 8).

The mentioned negative phenomena will decrease the overall efficiency of gas purification plants due to decrease of working concentration as a result of degradation by various mechanisms, binding of amine into protonated form and carrying away together with foam. At the facilities where there are no amine solution purification units, in order to reduce the concentration of impurities, it is practiced to drain part of the contaminated solution and replace it with freshly prepared solution during repair shutdowns (Fürhacker et al., 2003: 6; Chen et al., 2020: 10). This approach does not correspond to the principles of lean production and constantly requires substantial expenses. Kazakhstan’s oil refineries are forced to purchase alkanolamines abroad due to a lack of its production.

Ion-exchange method of amine solutions purification has been successfully implemented by a number of western companies for the last 20-25 years. In the CIS countries there are no developments in this area, the reason for this may be the lack of necessary and substantial funding, the complexity of licensing and the lack of test sites. Today the most well-known companies distributing this technology are MPR Services, Inc (USA) with HSSX® technology (Ion Exchange Heat Stable Salt Removal Process) and Eco-Tec, Inc (Canada) with AmiPur™ technology.

HSSX technology uses a unique patented Versalt® resin in the process of purification of amine solutions from thermostable compounds, which has the ability to remove anions from amine solutions. The resin is heat resistant, withstanding the temperature of the working solution up to 55-60 ^{0}C. Service life of the resin is 1 year, guaranteed by the company. The resin is regenerated by alkali and retains its properties.

AmiPur™ technology utilises the highly efficient Recoflo© ion exchange process based on a strong-base monodisperse gel anionite. Monodisperse resin is used for amine purification from TSC, which, unlike ordinaryn sieve macroporous polydisperse resin, has high osmotic stability of ionite grains, higher working ion exchange capacity in a dense layer of ionite, increased surface area of interfacial contact and fast kinetics of ion exchange, higher rate and completeness of regeneration of small ionite grains with significantly lower consumption of regenerant.

In general, both described technologies are using the same principles and based on the process of ion exchange of anions present in the solution with the hydroxide ion of the resin. As a result of this exchange, the bound amine must also be regenerated by reaction of the protonated form of the amine with the hydroxide ion to form water and free amine. In total, such purification should give not only the removal of weak acid anions, but also should return the bound amine back to the system, since it acts like a ballast and does not participate in the purification of acid gases.

The aim of the present work is to develop an automated system and algorithms of its operation for purification of alkanolamine solutions, as well as to develop a system, providing continuous monitoring and quality control of solutions for further industrial integration.

Materials and methods

Laboratory tests for the selection of anion-exchange resin were carried out on a system, consisting of a peristaltic pump, an ion-exchange column and tanks with initial and purified MDEA solution. The concentration of bound amine (BA) was used as an analytical signal.

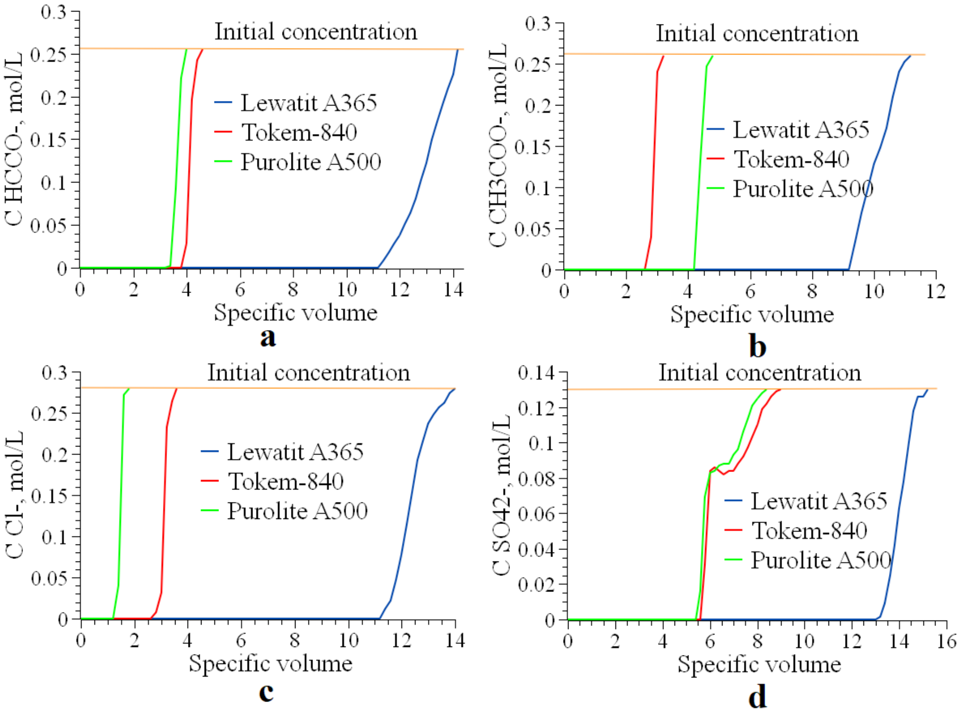
Dynamic exchange capacity (DEC) and full dynamic exchange capacity (FDEC) were used as a measure of resin performance. At this stage, these characteristics were investigated for Lewatit A365, Purolite A500 and Tokem-840 resins. All resins are strongly basic, the first two are macroporous, and Tokem-840 is gel type. In the first step, the performance of the resins was evaluated against anions of organic and mineral nature: chloride, sulphate, formate and acetate. The choice was dictated by the fact that the mentioned anions are typical components of TSC anions in alkanolamine solutions at oil plants. Chloride comes in with the water used to prepare the solutions. Sulfate is formed by oxidation of hydrogen sulfide. Acetate and formate are degradation products of amines. Solutions of the corresponding acids with hydrogen ion concentration ~0.25-0.27 mol/L were taken for the tests. The concentration of hydrogen ions after slippage, determined by acid-base titration was used as an analytical signal.

The model solution of MDEA with impurities contained 20% MDEA, 0.075 mol/L formic acid, 0.075 mol/L acetic acid, 0.0375 mol/L hydrochloric acid, and 0.01875 mol/L sulfuric acid. The concentration of bound amine was 2.58%.

Bound amine concentration and the concentration of TSC were determined by conductometric titration method. For the determination of bound amine, a 4 g sample was taken with an accuracy of 0.0001 g and titrated with 0.1N sodium hydroxide solution. Free amine and TSC concentrations were determined by titration of 0.5 g sample with 0.1N hydrochloric acid solution.

Results and discussion

The main issue of efficiency of ion exchange technology for purification of alkanolamine solutions is resin selection, since resins with similar characteristics can give very different results. Figure 1 shows the saturation curves under dynamic conditions of the resins for each anion. Based on the sorption curves, the DEC and FDEC values in the Lewatit-Purolite-Tokem resins series were calculated for chloride ion 3024, 3302 - 270, 367 - 725, 841 g×eq/m^3. For formate ion 2856, 3327 - 816, 903 - 969, 1029 g×eq/m^3. For sulphate ion 1690, 1812 - 728, 839 - 702, 806 g×eq/m^3. For acetate ion 2392, 2912 - 624, 672 - 1092, 1120 g×eq/m^3.



a - formate ion; b - acetate ion; c - chloride ion; d - sulphate ion;

Figure 1. Sorption output curves

Although in our conducted tests the best results were obtained with Lewatit A365 resin for all anions, a hydrogen ion slippage is observed on the model MDEA solution from the first batch. This resin is not suitable for use in alkaline environments. On Purolite A500 resin, slippage occurred on sample 10, while the first two samples containing no amine. The total volume of purified solution was 160 mL with an MDEA content of 16.69%. On Tokem-840 resin, slippage occurred on the 21st sample. The total volume of the purified solution was 380 ml with an MDEA content of 19.12%. Thus, the best results of the tested resins were shown by Tokem-840 resin, the efficiency of the resin was 3.8 volumes per one volume of resin. Tests with MDEA solution from the plant with 24.42% free amine, 1.21% bound amine and 1.79% TSC showed that one volume of Tokem-840 resin was able to purify 8 volumes of solution. The concentration of bound amine in sample 9 was 0.32% with a further increase to the initial value in sample 15.

To carry out scale-up tests on purification of 1 m^3 of MDEA solution, a unit was assembled on the basis of a 40 ft container. The power supply is external, single-phase with capacity of 3 KW/hour. The reverse osmosis unit requires a tap or industrial water supply with capacity of 2 m^3/hour. To drain the concentrate after reverse osmosis process and the neutralised effluent after pilot plant operation, access to a sewer is required. The plant is suitable for purification of solutions of alkanolamines: MEA, DEA, MDEA and other alkanolamines. Table 1 shows the list of equipment of the pilot plant.

Table 1 – Construction of the pilot plant

Label	Item name	Label	Item name
CV-1	Control valve 1	pH-1	pH sensor 1
SOV-1	Shut-off valve 1	P-3	Pump 3
SV-1	Solenoid valve 1	SOV-2	Shut-off valve 2
P-1	Pump 1	DP-2	Drain pump 2
CS-1	Conductivity sensor 1	EP-1	Electrical panel 1
DP-1	Drain pump 1	ROS-1	Reverse osmosis system 1
IEC-1	Ion exchange column 1	CP-1	Control panel 1
CV-2	Control valve 2	DB-1	Distribution board 1, Автоматическое управление узлами установки на базе процессора PLC Simatic S7-1200
FM-1	Flow meter 1	E-1	Amine tank
P-2	Pump 2	E-2	Caustic tank
CV-2	Solenoid valve 2	E-3	Purified water tank
CV-3	Solenoid valve 3	E-4	Drainage tank
CV-3	Control valve 3	E-5	Technical water tank
F-1	Filter 1	SOF-1	Shut-off fittings

The plant operation consists of 5 operations, the algorithm of which is given below.

Operation 1. Preparation of purified water for washing the column, and preparation of sodium hydroxide solution. To start the reverse osmosis (RO) unit, ensure that the E-5 tank is filled with tap or industrial water. Route the drain of the concentrate to the sewer. Switch the unmarked shut-off valves in the direction from ROS-1 to vessel E-3 to the open position. Switch the automatic switches in EP-1 to the operating position. Turn on power to the P-4 pump supplying water from the E-5 tank to the RO unit. Switch on power to ROS -1. As the E-3 tank fills to the required level, switch off the water pump and ROS -1 power supply or switch the purified water flow to the E-2 tank by switching the corresponding valves in the pipeline.

Operation 2. Preparation of regenerating solution of sodium hydroxide. For convenience of operators, alkali solution with mass concentration of 3% is prepared by pouring water into the tank E-2 up to the mark 833 liters and then adding 25 kg of sodium hydroxide. Transfer of alkali should be done in portions to avoid strong heating of the solution, with using manual or automated stirring. The solution should be prepared immediately before the start of the test to prevent the solution from absorbing carbon dioxide from atmospheric air. Preparation should be carried out using personal protective equipment: goggles, gloves, respirator, protective clothing and footwear.

Operation 3. Cleaning of alkanolamine solution. Before starting the operation, switch the automats in DB-1 to the operating state. Wait for system initialization displayed on the CP-1 control panel. Check the set parameters of CV-1 valve opening and conductivity value to complete the operation. On the CP-1 panel, start operation 3 by pressing the corresponding button. After start-up, the SOV-1 valve should open and after a pause of 10 s, the amine pump P-1 should switch on. After the IEC-1 column is filled with amine solution, it will be drain back to the tank E-1. As the resin saturates, the conductivity value, recorded by the conductometric sensor CS-1 and displayed on CP-1, will increase. When the set value is reached, the amine flow into the column will be stopped. Pump P-1 will shut off and valve SOV-1 will close. After a pause, valve SV-1 will be opened and pump DP-1 will be switched on, after that amine from the column will be pumped to the tank E-1. When pumping is completed, the SV-1 valve will close and the DP-1 pump will switch off.

Operation 4. Resin regeneration. The operation is started automatically, the valve CV-2 must be opened to the set value. Valve SV-2 is opened and pump P-2 starts taking the alkali supply from tank E-2. The alkali is drained into the tank E-4, the operation continues until the set volume of alkali is passed through the column, the volume is recorded by the flowmeter FM-1. After that the pump P-2 is automatically switched off and the valve SV-2 is closed. The next stage is alkali draining from the column, for this purpose SV-3 valve is opened and DP-1 pump is started, the alkali is drained into the tank E-4. After the specified time the SV-3 valve is closed and the DP-1 pump is switched off. As the E-4 tank is filled it is necessary to neutralise the solution with acid to neutral reaction after which the salt solution can be flushed to the sewer by starting the DP-2 pump.

Operation 5. Washing the resin from alkali. To start the operation, valve SOV-2 is opened; valve CV-3 must be opened to the set value. Pump P-3 is started, water supply goes from tank E-3, the end of washing is controlled by pH-meter, when the set value is reached, valve CV-3 is closed, pump P-3 is switched off. Water is drained the same way as alkali was drained from the column. Upon completion of the operation, the automatics will start a new cycle from Operation 1. Figure 2 shows the scheme of the plant.

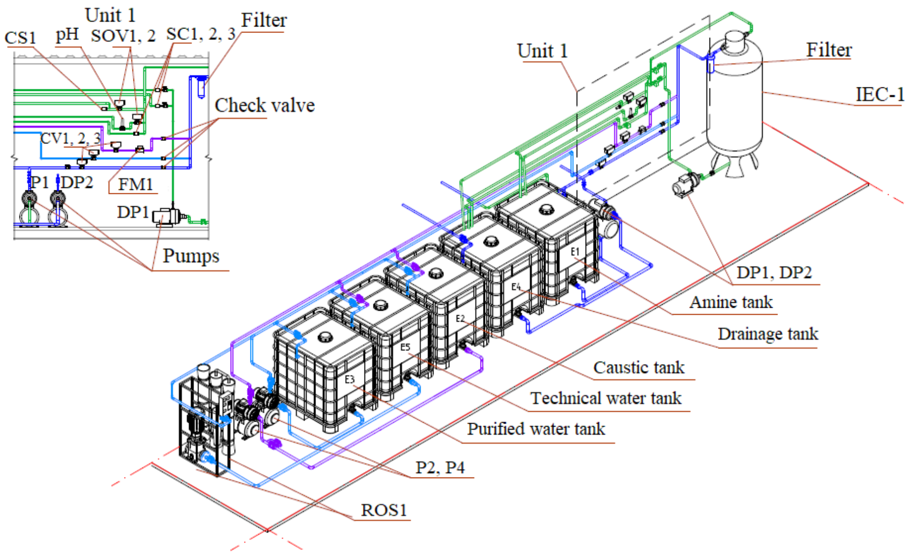


Figure 2. Pilot plant

The purification of 1 m^3 of solution was performed online to simulate plant conditions when the purified amine returns to the original tank. This approach is more time consuming, but allows purification without stopping the process (on the plant) since there is no reduction in the volume of amine in the system. The resin volume is 200 litres, the solution feed rate is 200 litres per hour, and a sample of the solution was taken every hour to determine the degree of purification. Table 2 shows the dependence of the bound amine concentration on the sample number.

Table 2 – Solution composition depending on purifying time

№	0	1	2	3	4	5	6	7	8	9	10	11
C BA, %	1,21	1,2	1,15	1,04	0,63	0,58	0,46	0,38	0,24	0,18	0,15	0,12

Since the process conditions at the production site are practically constant, the composition of the generated harmful substances also remains unchanged. For operative control of contamination it is optimal to use conductivity measurement method. The Figure 3 shows a graph of direct relationship between the electrical conductivity of MDEA solution and the degree of its contamination at different temperatures. Thus, knowing the current parameters of the solution, it is possible to determine in real time the need for purification or replacement of the amine, allowing to optimize the technological process. Equations for these dependencies were derived from the experimental data. Since the amine contamination may be more significant than the investigated sample, extrapolation, based on the equations, will provide data on specific conductivity at values outside the investigated range.

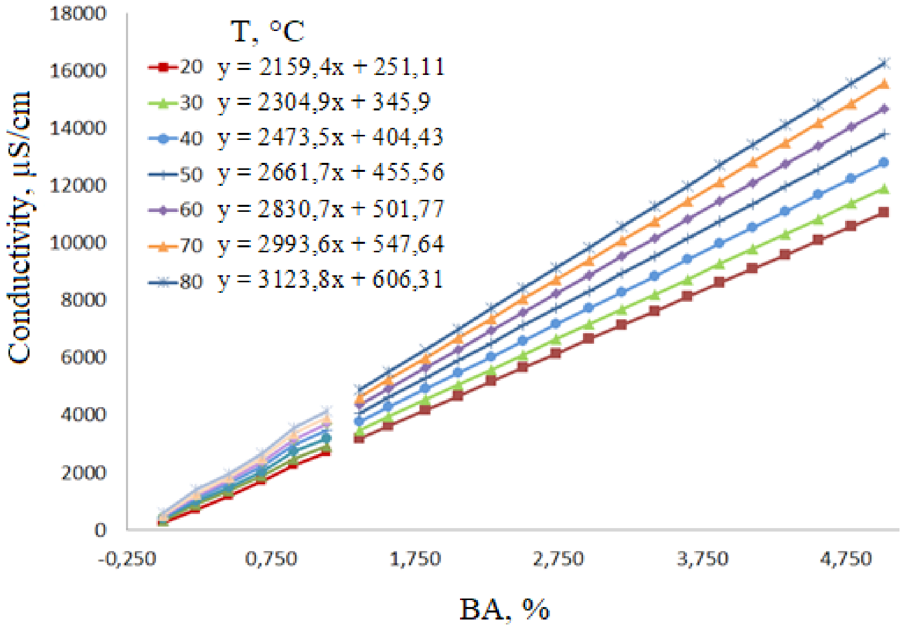


Figure 3. Dependence of electrical conductivity on the content of bound amine at different temperatures

Conclusions

The research presented in this paper demonstrates the potential and efficiency of anion exchange technology for the purification of alkanolamine solutions. By effectively removing thermostable salts and other impurities, this process significantly extends the service life of amine solutions, minimises corrosion processes and improves the overall efficiency of gas treatment plants.

Selection and testing of various anion exchange resins showed that Tokem-840 resin demonstrates the best performance in terms of dynamic exchange capacity and selectivity for the target anions in MDEA solutions. The developed automated solution purification system allows a continuous operation, can be easily integrated into the existing technological process, and minimises manual labour.

It is possible to estimate the potential economic benefit from the introduction of the proposed technology on the example of one of the Kazakhstan's oil plants with the volume of the system is 860 m^3. The existing practice is based on replacement of 30% solution with fresh solution, i.e. 258 m^3 of solution needs to be replaced. At a concentration of 24%, 62 tonnes of pure MDEA will be required (density of MDEA is 1.04 g/cm^3, for simplicity of calculations density of 1 g/cm^3 is taken), which at its cost of 1,003,800 tenge per 1 tonne will amount to 62,235,600 tenge. The only purchased reagent required for purification of such volume of solution is sodium hydroxide, approximately 10 tonnes of which is required; at a cost of 210,320 tenge per 1 tonne, the total cost will be 2,103,200 tenge. One-time costs of resin purchase will be 2,337,302 tenge at the price for 1 m^3 and 35,059,530 tenge for 15 m^3. Costs for resin are significant, but it will work in the once-a-year-operation-mode for many years. At the same time, replacement of 30% of the solution only lowers the concentration of impurities, but does not remove them completely.

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