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INCREASING THE EFFICIENCY OF THE GAS REFINING PROCESS THROUGH THE RECOVERY OF ALKANOLAMINES

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Abstract. In this article, the technology of gas purification from sour components by absorption method is aimed at achieving long-term use in the process of gas purification by determining the composition of used alkanolamine solutions and regenerating them. Using the ion exchange method: it is recommended to reduce the amount of active components in the solution, to compensate for this by adding new alkanolamine and piperazine; It is based on the fact that the composition additives affecting the operational properties of the used alkanolamines lead to a decrease in the amount of thermally stable salts, free elements, and heavy organic substances. With this, in turn, the physico-chemical properties of used alkanolamines, which affect the operational properties of viscosity and foaming, surface tension, were found to be in accordance with the norms, and it was recommended to reuse them.

Keywords: alkanolamine, monoethanolamine, diethanolamine, absorbent, desorption, ion exchange, filter, regeneration.

I. INTRODUCTION

Transition to low-waste and zero-waste technologies, in order to significantly reduce production waste, a number of actions are necessary, including modernization and improvement of existing technological processes in principle: use of waste in the technological system itself or in other industries; development and implementation of advanced methods of cleaning, processing and disposal of waste that cannot be used for technical or economic reasons. Only on the basis of evaluating the advantages and problems of waste disposal methods, it is possible to make a decision about the options for their future use [1]. Purification of DEA solutions by vacuum distillation has not been studied so far, therefore, studying the characteristics of working solution purification processes, developing a rational technological scheme and regimes of the process is an urgent scientific and practical problem, and the solution of this problem increases the performance of the natural gas purification process from hydrogen sulfide and carbon dioxide, as well as technical and leads to significant economic improvement [1]. Research and development of a complex technology for cleaning DEA working solutions, improving the quality of sorbents, increasing the productivity of amine gasification units, as well as providing a closed production cycle without waste as a result of the subsequent use of the generated waste [2]. Researches recommended the use of ultrasonic radiation for the regeneration of absorbent - MEA aqueous solutions and the separation of absorbed components. The desorption rate of absorbed components was studied at 25 ºC under 28 kHz ultrasonic radiation. The results showed that low concentration MEA (0.2 mol/ It is shown that the rate of desorption of absorbed components in solution l) is significantly higher under ultrasound irradiation than desorption by stirring at low temperature (25 ºC). It is also observed that the desorption rate increases with a decrease in the concentration of MEA solutions [3]. Scientists have investigated the use of amine hydrogels (AlH) to separate CO_2 from a CH_4/CO_2 gas mixture. To this end, systematic experiments were conducted to analyze the performance of AlH particles, and an amine-saturated hydrogel was prepared by mixing MEA solution with dried hydrogel particles. The authors statement shows that AlH particles absorb CO_2 with high selectivity from CH_4/CO_2 gas mixture and have higher CO_2 absorption activity compared to MEA solution; CO_2 absorption kinetics were observed with temperature, mixing intensity changes, and addn. Mixing AlH particles with the gas mixture increases the absorption rate, which means that the absorption capacity depends on the properties of AlH. Also, the addition of decane and dodecyltrimethylammonium bromide (DTAB) to the absorbing composition leads to softening of coagulation between AlH particles, increasing the rate and yield of CO2 absorption [4].

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II. METHODS AND MATERIALS

Based on the physico-chemical properties of the harmful additives contained in the 30% aqueous solution of DEA, a recommendation was made to use the immobilization method [5]. Natural river sand, activated charcoal, and Navbahor benthite were used to purify the spent ethanolamine solution. Quartz sand with a particle size of $0.34 \div 1.0$ mm was used for the filter. At a rate of 1.5-2.1 l/h, the solution was passed through a sand filter, and activated carbon was used as an adsorbent for cleaning DEA solutions from tarry substances and other impurities. In this case, a solution was passed through a 100 cm^3 layer of activated carbon at a speed of 1.5-2.1 l/h, and the resinous substances contained in it were filtered and retained [5]. The purification of bentonite from the amorphous crystalline part was carried out in the following sequence: the first step, the bentonite was washed three times in distilled water, then tindiralid and filtered; second step, washing 3 times in 0,1 normal hydrochloric acid and filtering again [5]. The diethanolamine solution, initially cleaned of mechanical impurities and tarry substances, is passed through previously prepared 100 sm^3 sorbents (A-200 or A-400 anionites) at a specified speed (1.5-2.1 l/h) and is cleaned of various salts in the solution. When the absorbent solution was purified using the above filtration method, a reduction of mechanical impurities and resinous substances up to $75.0 \div 83.0\%$ was achieved. When ethanolamine solutions were purified from salts using A-200 and A-400 anionite filters, the amount of salts in the absorbent was purified up to 85-90% [5, 6].

A. Results and discussions

Despite the variety of gas purification methods, the absorber must meet stable general requirements: the absorber must have a high absorption capacity of acidic components, despite their content in the gas being in a large interval; the partial pressure of the absorber should be low, because its loss in the process is reduced; for good contact with gas, the viscosity of the absorbent should be low; should be insoluble in hydrocarbons; should be neutral to hydrocarbons and inhibitors; low corrosion activity; resistant to oxidation and thermal decomposition; do not react with various compounds; stable to the formation of foam; the boiling point of the absorber should be lower than that of all components [7]. It should be noted that the presence of polyethylene polyamines in the composition of the used alkanolamines increases the viscosity and foaming properties of the solutions along with extinguishing the operational activity of absorbents. For this reason, it is necessary to separate the thermal degradation products of amine from the maximum solution composition [8]. During the research, the composition of the working solution used in the purification of natural gas was analyzed (Table 1) [9]. The data in the table shows that the amount of alkanolamines in the working solution is reduced to 70-75%, along with amino acids, glycolates, acetates, the amount of heat-resistant salts is 2,5 times higher, bicines (N, N-Bis(2-hydroxyethyl) glycine; diethylolglycine ; diethanol glycine; dihydroxyethyl glycine) amount increases by 2,8 times, oxalates by 2 times, besides, the amount of iron increases by 24 times [9, 10].

Component	**Unit of Measure**	**Amount in Solution (%)**	**Reminder**
Unreacted DEA	%	22.37	
Associated DEA	%	7.6	
Anions of heat-resistant salts	ppm	2553	2.5 times higher than the norm
Heat-stable amino salts	%	0.49	above the norm
Heat-resistant salts	Mol/mol	0.0125	above the norm
Strong cations	ppm	67	above the norm
Amino acids	ppm	4233	dangerous level
Glycolates	ppm	627	1.3 times higher than the norm
Acetates	ppm	439	above the norm
Let them go	ppm	1648	2.8 times higher than the norm
Oxalate	ppm	498	2 times higher than the norm
Iron	ppm	118	24 times higher than the norm
Precipitated particles	mg/l	93	above the norm
H2S	mg/m3	15-17	norm
CO2	%	2.1	norm

TABLE I. Composition of components of ethanolamines used in natural gas purification

Based on the physico-chemical properties of the harmful additives contained in the 30% aqueous solution of DEA, studies were conducted on the method of immobilization [11]. Navbahor bentonite purified from amorphous part, activated carbon and A-200 or A-400 anionites were used to purify the used ethanolamine solution. It should be said that during research, a special method of cleaning the amorphous crystal part included in bentonite was recommended, and it was found that bentonite together with activated carbon can be one of the important components in absorbing tarry substances [12]. Quartz sand with particle sizes of $0,34 \div 1,0$ mm was used for the filter. At a speed of 1,5-2,1 l/h, the solution was passed through a sand filter, and activated carbon was used as an adsorbent for cleaning DEA solutions from tarry substances and other impurities. For this, the working

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solution was passed through a 100 sm^3 layer of activated carbon, and the resinous substances contained in it were filtered and retained [13]. Diethanolamine solution purified from mechanical impurities and tarry substances is passed through pre-prepared 100 sm^3 sorbents (A-200 or A-400 anionites) at a specified speed of 1,5-2,1 l/h, and is cleaned of various salts in the solution. When the absorbent solution was purified using the above filtration method, a reduction of mechanical impurities and resinous substances up to $75.0 \div 83.0\%$ was achieved. Analysis shows that when ethanolamine solutions are purified from salts using A-200 and A-400 anionite filters, 85-90% of salts in the absorbent are lost. Tables 2 - 4 show the results of purification of DEA working solution according to the proposed system [13, 14].

Component	**Unit of Measure**	**DEA Working Solution**	**Purified Solution in Activated Charcoal**
Unreacted DEA	%	23.06	23.1
Associated DEA	%	6.96	6.415
Anions of heat-resistant salts	%	5.14	4.84
Heat-stable amino salts	ppm	4229	3985
Heat-resistant salts	ppm	629	586
Strong cations	ppm	441	409
Amino acids	ppm	1649	1027
Glycolates	ppm	496	414
Acetates	mg/l	118	110
Let them go	mg/l	93	90
Oxalate	%	2.4-2.8	0.7-0.9
Iron	%	2.5-3.5	1.5-1.7
Precipitated particles	%	3.5-4.0	3.4-3.87
H2S	mg/m3	15-19	15-19
CO2	%	2.2	2.2
Sodium (Na+) salts	mg/l	62.1	59.1
Potassium (K+) salts	mg/l	12.7	11.7
Ant acid	mg/l	666.3	659.1

TABLE II. 3-step purification of the DEA working solution using the ionization method Stage 1 pointers The amount of the transferred working solution is 12 l, the degree of purification is 2 - 36%

As can be seen from Table 3, working DEA solution passed through activated carbon reduces the amount of sulfur-containing organic compounds, as well as reduces the amount of heavy oxygen substances and tar compounds, such as bitcins [14].

Component	**Unit of Measure**	**DEA Working Solution**	**Refined Solution in Bentonite**
Unreacted DEA	%	23.09	21.5
Associated DEA	%	6.94	0.48-0.69
Anions of heat-resistant salts	%	5.32	0.019-0.028
Heat-stable amino salts	ppm	4235	92.2-97.6
Heat-resistant salts	ppm	629	81-86
Strong cations	ppm	436	73.1-79.2
Amino acids	ppm	1644	997.6
Glycolates	ppm	497	111.5-115.8
Acetates	mg/l	117	7.0-9.0
Let them go	mg/l	91	6.5
Oxalate	%	2.42-2.83	2.2-2.5
Iron	%	2.55-3.65	2.55-3.65
Precipitated particles	%	3.53-4.10	3.53-4.10
H2S	mg/m3	14-17	14-17
CO2	%	2.13	2.134
Sodium (Na+) salts	mg/l	62.1	58.2
Potassium (K+) salts	mg/l	12.7	11.2
Ant acid	mg/l	664.3	660.1

TABLE III. 3-step purification of the DEA working solution using the ionization method Stage 2 pointers [14]. The amount of spent working solution is 12 l, the degree of purification is 56-63%

It is planned to clean the metal salts of the DEA working solution in anionites, and from the results of Table 4, it can be seen that the theoretical estimates have been proven in experiments, including the amount of sodium from 63,3 to 0,94 mg/l, manganese from 90,8 to 0,023-0,032 mg/l, we can see a decrease in the amount of potassium from -13,74 to 0,043 mg/l, Ca from 83,2 to 26,2 mg/l, Fe from 119 to 7,2-9,1 mg/l [15]. In the course of the research, a comparison was made in the main physico-chemical

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Component	Unit of Measure	DEA Working Solution	Purified Solution in Anionites
Unreacted DEA	%	23.072	23.02
Associated DEA	%	6.96	0.54-0.72
Anions of heat-resistant salts	%	5.24	0.02-0.03
Amino acids	ppm	4236	92.2-97.4
Glycolates	ppm	628	81.1-86.3
Acetates	ppm	436	73.4-79.2
Let them go	ppm	1644	102.1-108.4
Oxalate	ppm	496	112.3-115.5
Ant acid	mg/l	666.3	36.2-41.3
Precipitated particles	mg/l	92	6.9
Mechanical compounds	mg/m3	778-1098	179.4-190
Sulfur preservatives	%	2.4-2.8	2.4-2.8
Resin compounds	%	2.5-3.5	2.5-3.5
Hydrates	%	3.5-4.0	3.5-4.0
H2S	mg/m3	15-17	15-17
CO2	%	2.1	2.1
Metals:	mg/l		
Sodium		63.3	0.94
Manganese		90.8	0.023-0.032
Potassium		13.74	0.034-0.043
Calcium		83.2	26.2
Iron		119	7.2-9.1

TABLE IV. 3-step purification of DEA working solution by ionization method Stage 3 pointers [14]. The amount of the transferred working solution is 125 l, the degree of purification is 50-56%

parameters of alkanolamines used in the purification of natural gas. The results of the comparison are presented in Table 5 [15].

Property	DEA 30% (Pure) Aqueous Solution	DEA Working Solution
pH	10.2	9.1
Viscosity (η) sPz	2.06	3.89
Density, g/cm^3	1.02	1.38
Surface Tension (δ) 103, N/m	71.8	66.9
Thickness of Foam, cm	1.45	2.52
Foam Residence Time, sek.	less than 12-16	21-26

TABLE V. Basic properties and physico-mechanical indicators of DEA working solution

Studies of the physical and mechanical parameters of alkanolamines used in clean and natural gas purification show that the viscosity of the solution has almost doubled, and the density has increased from 1,023 to 1,39 g/sm3, which means that with the increase in gas absorption resistance, the gas purification activity has decreased and natural gas components have become absorbent. with the increase in the period of being in the environment, it also causes the realization of additional chemical reactions [16]. Thus, the processes of formation of many products (complex ethers, carboxylic acids, anhydrides and chlorates of carboxylic acids) through chemical changes in the conditions of the amine system were proved, the realization of hydrolysis, hydrotation, heterocyclization reactions was substantiated, and the factors of change in element composition were proved [16].

III. CONCLUSIONS

The composition of working ethanolamine solutions used in the purification of natural gases from sour components using alkanolamines was determined. Using the ion exchange method, the content additives affecting the operational properties of the used alkanolamines are based on the reduction of the amount of thermally stable salts, free elements, heavy organic substances, the physico-chemical properties affecting the operational properties of the purified alkanolamines, viscosity and foaming, surface tension are determined and reused.

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