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RECYCLING SATURATED DIETHANOLAMINES AND REDUCING THEIR ENVIRONMENTAL IMPACT

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Abtract
The main purpose of the study is to study and analyze the causes of degradation of 25-30% solutions of ethanolamines used in natural gas purification. The negative changes in ethanolamines that affect their physicochemical properties, absorption capacity and efficiency of gas cleaning as a result of destruction were studied. It has been established that one of the main factors affecting the working properties of ethanolamines and their regeneration is their saturation with heat-resistant salts, organic acids, bicins, di-, tri-, tetraamine compounds.

Keywords: absorbent, absorption solution, alkanolamines, diethanolamine, methylmethyldiethanolamine, processing, natural gas, regeneration, saturated solution, heat-resistant salts, organic acids, bitcines, cations, medium.

INTRODUCTION

To use natural gas as a feedstock in industry, it is important to purify it from toxic compounds (H_2S, CO_2 and mercaptans), which exhibit acidic properties and cause rapid equipment degradation. The main reasons for the purification of natural gas from the above compounds are that they corrode process equipment, shorten its service life, polymerize ethanolamines as a result of regeneration of solutions at high temperatures, and reduce the efficiency of gas purification as a result of their distillation. , the formation of various metal salts in solutions leads to the failure of devices that must sit.

The process and technology of purification of natural gas from toxic compounds are selected depending on their quantity (concentration) in the gas.

The most effective method of cleaning gases from toxic compounds is the absorption method, in which in industry solutions of diethanolamines, methylmethyldiethanolamines at a concentration of 25-30% are used as an absorbent.

However, the use of these solutions as absorbents has not completely eliminated all problems in the gas cleaning process.

As a result of repeated regeneration of ethanolamine solutions at high temperatures and their reuse in gas cleaning, its physicochemical properties change dramatically. Reducing the concentration of the solution leads to an increase in specific gravity, viscosity, foam height and foam stagnation time. This increases the consumption of absorbent, which in turn increases the cost of purified gas for feedstock.

According to the results of scientific research, as a result of high temperature regeneration of ethanolamines used in the gas purification process and repeated use in the gas purification process, high temperature resistant salts (HTRS), organic acids and resinous compounds accumulate in the solution and they are kept for a long time. Consequently, a layer forms on the walls of the devices because of constant circulation, which accumulates in the filters, and it causes them to corrode and fail.

The absorbent solution becomes saturated and unsuitable for gas cleaning. As a result, a saturated solution of ethanolamine is released from the gas cleaning system into the environment through the wastewater of enterprises. The flow of up to 8-9 thousand tons of such solutions per year from gas treatment facilities leads to the following negative consequences:

1. Given that the Kashkadarya region is located in the southern part of the country, where it is hot in the sun, the toxic compounds in the ethanolamine solution accumulated on the surface in the open air evaporate under the influence of sunlight and temperature, which leads to an increase in hydrogen sulfide and carbon monoxide. This leads to the fact that the wind spreads over larger areas and pollutes the environment.

2. Ethanolamine solution, used under the influence of sun, rain and snow, is added to underground and surface water and pollutes them.

3. For many years, the accumulation of these solutions in the arable layer in the open air, their wide distribution in the environment leads to the destruction of the soil structure, the extinction of flora and fauna, the spread of various diseases among the local population. Today, Uzbekistan attaches great importance to the modernization of the chemical, metallurgical and oil and gas industries, the localization of chemical reagents and raw materials used in industrial enterprises, on the basis of which new materials suitable for export can be obtained. Scientific and practical results have been achieved in the production of absorbents based on local raw materials and their application in various fields, as well as in the disposal of spent alkanolamines. The rational use of local raw materials in the country, the organization of the production of absorbents, adsorbents and industrial chemicals on the basis of which will make it

possible to reduce the cost of products and improve the economy of the republic by reducing the import of chemicals. it is especially important to improve the efficiency of cleaning devices from components [1,2].

Improving the efficiency of gas cleaning technology is largely determined by the right choice of process. Depending on the amount of sulfur in the gas, a solution of technology and ethanolamine corresponding to this concentration is selected. The choice of absorbent in the natural gas purification process is based on the following factors.

1. The selected absorbent solution should have a pH greater than 9 (alkaline) and a low viscosity.
2. The selectivity of the selected ethanolamine should be higher for H_2S, CO_2 and toxic components, and the selectivity for hydrocarbon should be lower.
3. The absorbent must not have a negative impact on humans, the environment and must be recyclable [3-5].

The purpose of the study

The main purpose of the study is to study the maximum use of chemical reagents used in the gas purification process, their synthesis based on local raw materials, the selection of an effective composition, and the identification of the reasons for the appearance of an ethanolamine solution used in the natural gas purification process. from toxic compounds. The results of the research are the choice of a method for the regeneration of the absorbent and the development of recommendations for its use as a by-product in other areas of the production of distilled ethanolamines. Objects and methods of research: The object of research is unsaturated DEA used in the purification of natural gases from hydrogen sulfide, its various concentrations, vacuum distillation, heat-resistant salts, bound amines, organic acids and amino acids.

RESEARCH OBJECTS AND METHODS

The object of research is the unsaturated DEA used in the purification of natural gases from hydrogen sulfide, its various concentrated solutions, vacuum distillation, high temperature resistant salts, bound amines, organic acids and amino acids.

All studies were conducted in accordance with state standards. In order to determine the physicochemical properties of a solution of (30%) $(HOCH_2CH_2)_2NH$ ethanolamine containing various condensates of hydrogen sulfide, carbon dioxide and other organic compounds of sulfur, resulting from prolonged work in the process of absorption and desorption, a number of modern and classical methods were used.

It is also possible to analyze the composition of aqueous solutions of ethanolamine by vibration from classical methods. The working solution is shaken a non-saturated aqueous solution of methylmethyldiethanolamine to pH = 4.5 to determine the content of CO_2, total amount of toxic compounds, high temperature resistant salts, H_2S and inorganic salts (iron sulfide, iron (III) sulfate, etc.). At the same time, the high degree of foaming of the working solution and the state of stagnation are analyzed.

Part of the experiment. 20-30% aqueous solutions of diethanolamine are used to purify natural gases from toxic compounds. As a result of repeated use of these solutions in the process of gas purification and repeated processing at high temperatures, its operational and physicochemical properties (specific gravity, viscosity, surface tension, etc.) deteriorate, amine solutions are saturated with various salts, compounds, distorted, goes to polymerization, resulting in the gas becoming unfit for purification [6,7].

When we analyzed the amines used in gas purification (Table 1), we found the following:

Table 1.Results of analysis of used DEA solution

Composition of used $(HOCH_2CH_2)_2NCH_3$solution	Unit of measurement	The amount in solution	Note
Concentration $(HOCH_2CH_2)_2NH$ 30 %			
Free $(HOCH_2CH_2)_2NH$	%	23,07	
Connected $(HOCH_2CH_2)_2NH$	%	6,93	
Anions of heat-resistant salts	ppm	2608	2.5 times higher than normal
Heat-resistant amine salts	%	0,51	above the norm
Heat-resistant salts (total content of amines)	mol / mol	0,013	above the norm
Strong cations	ppm	71	above the norm
Amino acids	ppm	4373	Dangerous level
Glycols	ppm	641	1.3 times higher than normal
Acetates	ppm	452	above the norm
Bitsinlar	ppm	1663	2.8 times higher than normal
Oxalate	ppm	507	2 times higher than normal
Salt of iron	ppm	127	24 times higher than normal
Sedimentary particles	mg / l	98	above the norm
H_2S	mg / m ^{3}	15–17	norm
CO_2, %	%	2,1	norm

As can be seen from the table, the content of high temperature resistant salts is -2533 ppm, the recommended level is 1000 ppm, which means that their amount is 2.5 times higher than the norm. $(HOCH_2CH_2)_2NH$ recovery is carried out at a temperature of 125-1450C. These salts are not removed from the amine solution during reconstitution of the DEA solution and do not leave the “bound” amine. They are more stable at high temperatures [8,9].

In addition, high-temperature-resistant salts increase corrosion, iron sulfide formation, worsen filtration, and help remove hydrocarbons. All this intensifies the foaming, leading to the removal of amine from the system and a decrease in its efficiency, which leads to its frequent failure and an increase in the amount of sulfur in the gas.

The high content of bound amine in solution is 6.93%. The bound amine is unsuitable for the absorption of sour gas and does not participate in the absorption of sour components.

The solution contains 4233 ppm amino acids and 1648 ppm bitsin. They are both corrosion-active substances, weaken metal equipment and the protective layer of the metal and oxidize rapidly under the influence of H_2S. The formation of these substances in solution can be explained as follows[10,11]:

1. The presence of oxygen, nitrogen, Na^+ , K^+ ions, along with toxic gases (H_2S, COS, CS_2, CO_2, SO_2) in the aqueous solution of natural gas and amine given in the absorption purification, leads to the formation of high temperature resistant salts and formic acid.

2. H_2S is present in the reconstituted amine solution as HS^-, S^{2-}, SO_2 as HCO_3^- and CO_3^{2-} anions. If we take into account that amines exhibit an alkaline environment (pH = 10.8), as a result of the absorption of absorbent solutions at high temperatures, the anions in the solution react directly with the amines to form high-temperature-resistant salts. These salts alter the molecule of amines, causing the formation of bitsin, sarcosine, formic acid, and other amino acids.

DEA solution contains bitsin, sarcosine, formic acid and other amino acids above normal. All this is a strong corrosive, and its abundance in solution leads to rapid corrosion and failure of technological equipment[12,13].

When we analyze the composition of the unsuitable DEA solution used in the gas treatment plant, we can see that the amount of degraded amines along with salts and formic acid also exceeds the norm. Its content in the solution is 9.92%. This in turn adversely affects the working properties of the absorbent, lowers the pH, increases the surface toughness, increases the foaming process and stability. All of this reduces the

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absorption capacity of the amine solution, causing the amines to escape from the system with the purified gas, causing it to shrink.

The presence of high temperature resistant salts in the methylmethyldiethanolamine solution leads to saturation of the filters used in the cleaning of absorbents. The long-term storage of these salts in the solution and their constant circulation with the absorbent solution leads to corrosion of technological devices. Most importantly, these salts prevent H_2S from being absorbed into the solution. As a result, gas cleaning efficiency decreases [14,15].

The analysis of the physicochemical properties of the working absorption solution with a saturated-unsaturated methylmethyldiethanolamine solution is given in the table below(Table 2).

Table 2. Physicochemical properties of the used methylmethyldiethanolamine solution

Physicochemical parameters	Unit of measurement	30% aqueous solution of DEA	Used DEA solution
pH		10,8	9,6
Viscosity (η)	сПз	2,16	4,0
Density (d_4^{20})	g/cm3	1,104	1,36
Electrical conductivity	$sm^{-1}\cdot10^4Om^{-1}cm^{-1}$	6,7	8,38
Surface tension (δ)	10^3, n/m	70,8	66,86
Foam	cm	1,5	2,4
The stagnation time of the foam, (τ)	sec.	Less 10–15	22–25

In addition, high temperature-resistant salts, amino acids, bitsins, and their associated amines adversely affect the physicochemical properties of the DEA solution.

The changes in the physicochemical parameters of methylmethyldiethanolamine solutions depending on the composition of the products of distillation are shown in Table 3.

Table 3.Changes in the properties of methylmethyldiethanolamine solution in the presence of methylmethyldiethanolamine degradation products

№ experience	The composition of the products of the destruction of methylmethyldiethanolamine in amine solution; %	Surface tension, 10^3, n/m	Absorption rate of sour components, g/sm³ x min.	dynamic viscosity in 25°C, mPa x c
1	0,0	70,8	0,30	2,16
2	1,5	68,32	0,24	2,41
3	5,8	72,12	0,23	3,07
4	7,5	72,65	0,17	3,65
5	15,0	73,12	0,11	3,92

Thus, 60-65% of the DEA solution, which is disposed of as a technological waste, was technically verified, which could be reused in the gas purification process, and the remaining 35-40% cubic meters could be used as demulsifiers in oil and gas extraction and dewatering.

DISCUSSION OF THE RESULTS

A 30% absorption solution of methylmethyldiethanolamine is continuously added to the working solution in the absorption purification devices from toxic compounds in gas processing plants for 2,0–2,5 years in the amount of lost absorbent volume. However, due to the long continuous operation of this absorbent solution at high temperatures, the alkaline environment in the solution and the acidic environment of the components absorbed into it, as well as several other technical reasons, this absorbent solution becomes unsuitable for effective purification of natural gas.

From the above analysis, it can be seen that DEA solution reacts with oxygen under the influence of high temperature to form compounds, which potentially accelerates amine degradation. Due to the oxygen absorbed at high temperatures in the desorber DEA, the oxidation and polymerization reactions of occur at high speeds. Later, these heavy resin compounds form layers, plugs, as a result of which the technological devices remain in the pipes, heat exchangers, refrigerators, filters, absorber plates. It should be noted that the resin layers formed make it difficult for gas and liquid to move freely through the devices. The accumulation of resinous layers on the inner surface of the structures, on the surface of the plates, leads to the accumulation of slag under the influence of temperature, followed by corrosion of the equipment.

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Accumulation of degraded amines and temperature-resistant salts in a methylmethyldiethanolamine solution increases its viscosity and reduces surface tension, along with reducing its absorption capacity. Degradation products and high temperature resistant salts do not participate in the purification process of sour gases. The presence of elements such as oxygen and nitrogen in the gases supplied to the absorption purifier leads to the formation of high temperature resistant salts and leads to the chemical transformation of amine molecules to promote the formation of bitsin, sarcosine and other amino acids.

When the methylmethyldiethanolamine solution is reconstituted, hydrogen sulfide (H_2S) is present as HS^-, S^{2-}, and carbon dioxide (CO_2) as HCO_3^- and CO_3^{2-} anions. This requires that the anions be cations. Amin has an alkaline basis. Thus, the interaction of amine (alkaline) and acidic components always results in temperature-resistant salt.

The mechanism of formation of heat-resistant salts is as follows:

The mechanism of formation of high temperature resistant salts is as follows:

"Free amine" + sour gas → cation "bound amine" + anionic acid amine + RCOOH → amine H^++ $RCOO^-$

amine + acid → bound amine + High temperature resistant salts.

From the chemical reactions given, it is clear that the formation of high temperature resistant salts cannot be prevented. High temperature resistant salts are always formed during the separation of acidic components using amines. Therefore, high temperature resistant salts must be separated from the solution during the absorption process.

DEA (tertiary alkanolamine) is an alkali that reacts easily with H_2S and CO_2 and forms water-soluble salts.

H_2S and CO_2 main reactions with DEA are as follows:

$H_2S+R_3NH \rightarrow R_2NHHS$ (sek), $H_2S+2R_3NH \rightarrow (R_3NH)_2S$, (sek),

CO_2+R_3NH (no direct reaction), $CO_2+H_2O \rightarrow H_2CO_3$ (slow),

$H_2CO_3+2R_3NH \rightarrow (R_3NH)_2CO_3$ (fast), $H_2CO_3+R_3NH \rightarrow R_3NHHCO_3$ (fast).

The tertiary alkanolamine amine group does not have an N^+ atom, so the direct reaction of CO_2 to form carbamate does not continue, and the interaction occurs through a slow phase of carbonic acid formation, which is then broken down into ions:

$H_2CO_3 \rightarrow H^+ + HCO_3^-$;

$R_3N + H^+ + HCO_3^- \rightarrow [R_3NH]^+ \ HCO_3^-$

The final products are bicarbonate and carbonates.

The formation of high temperature resistant salts is not limited to compounds formed as a result of reactions with contaminants accumulated in the contactor. These include the addition of absorbent solution anti-foaming agents, their anti-corrosion inhibitors and other various additives, and the addition of water contaminated with various compounds from the cooling devices to the ethanolamine solution to form various salts and compounds.

The cation of the salts binds to the protonated amine to form ethanolamine salts resistant to high temperatures. Normally, the cation fraction, non-protonated amines, sodium and potassium salts are not taken into account when analyzing the purity of solutions after their recovery in production, which leads to incorrect analysis of the solution composition and this has a negative effect on the gas purification process. With the anions in the solution, the sulfide ions try to interact with the iron ions under favorable conditions (temperature, pressure, and solution medium). In doing so, the anions form stable complex compounds.

As a result of long-term operation of absorption solutions in gas purifiers, the high aggressive properties of ethanolamine solutions increase. Oxidation and decomposition occur between amines entering the gas purification process by regeneration with acidic components in the purified gases, sulfites, thiosulfates, salts and derivatives of organic acids (ants, vinegar), amino acetic acid, ethylenediamine and many other compounds and DEA degradation resinous substances are formed. These products have different effects on the technological parameters of the cleaning process. Some reduce the absorption capacity of solutions, while others simultaneously lead to their foaming in the technological process, the realization of high corrosion of metal equipment, and so on.

High temperature resistant salts block ethanolamines and prevent the absorption of sour components in natural gas. All this reduces the efficiency of gas cleaning and increases the viscosity of ethanolamine. As a result, steam consumption in rebels increases when the absorbent is reabsorbed. The increase in vapor consumption, in turn, leads to an increase in the temperature in the devices and an increase in the state of degradation of amines in solution.

CONCLUSION

Numerous domestic and foreign studies have shown that ethanolamine solutions do not contain H_2S and CO_2 and do not have corrosive properties when dissolved in the initial recovery state during gas purification. However, after application of ethanolamine in the purification process, the solution is saturated with sour gases and the saturated ethanolamine solution is recovered at high temperatures, the presence of nitrogen, oxygen and other similar oxidizing substances in the solution in various ways can lead to the destruction of amines and the formation of di-, tri-, tetra-compounds by the combination of several molecules.

The causes of degradation of saturated-unsaturated DEA solution used in natural gas purification have been identified. The interaction of the acid components of amine and natural gas always results in the formation of high-temperature-resistant salts, which, while reducing the efficiency of gas purification, form salt layers that remain in the passages in the devices. Degraded amines corrode devices because they contain a variety of organic acids.

The following positive results are obtained by secondary processing of the saturated ethanolamine solution.

1. As a result of secondary processing of saturated ethanolamine solution, it is possible to return 50-60% DEA to the gas purification process.
2. Recommendations for the use of ethanolamines in other areas of production (in the process of drilling wells, extraction of surfactants, etc.) will be developed.
3. Contamination of groundwater and surface water is prevented.
4. During the warmer months of the year, exposure to sunlight reduces the evaporation of toxic gases from the solution and prevents environmental pollution.
5. Soil damage is reduced, the structure is preserved. Negative impacts on flora and fauna are reduced.

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