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Determination of the Reasons for Degradation of a Diethanolamine Solution when Cleaning the Natural gas and Methods for Cleaning Aminic Solutions from Corrosive Active Substances

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ABSTRACT: The causes of degradation of the diethanolamine solution used in the purification of natural gas are determined. It has been established that the interaction of amine and acidic components of natural gas always produces heat-resistant salts that must be removed from the amine system. Methods for purifying amine solutions from corrosive substances using mechanical filtration and ion-exchange resins are presented. It is shown that the purification of amine solutions from foaming components by synthetic ion-exchange resins and activated carbons is quite effective and economically beneficial.

KEY WORDS: diethanolamine, degradation, natural gas, solution purification, heat-resistant salts, cations, ion-exchange resins, natural gas, mechanical filtration, activated carbon.

I. INTRODUCTION

Introduction Natural and artificial gases are the basis of the raw material and fuel base of the national economy and their is increasing on a large scale. Gases are widely used in the oil industry for the production of high-quality motor fuels, in the chemical industry for the production of polyethylene, polypropylene, plastics, detergents and other chemical compounds and preparations.

II. SIGNIFICANCE OF THE SYSTEM

The aim of the study was to choose an effective composition of sorbents, to establish aggressive components of natural gas and the causes of degradation of a diethanolamine solution during the purification of natural gas and amine solutions from foaming components. The study of literature survey is presented in section III, Proposed methodology and discussion is explained in section IV, section V covers the experimental results of the study, and section VI discusses the future study and Conclusion.

III. LITERATURE SURVEY

World practice of natural gas purification generally uses ethanolamine solutions with their various concentrations [1–4]. The absorption capacity of these solutions is not more than 0.4 mol / mol, they often foam, which causes the entraining of the active component, causing their loss. Working solutions with a multiple cycle of gas absorption and desorption



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change their physicochemical properties (specific gravity increases, concentration decreases, viscosity increases, etc.), and subsequently these spent solutions must be disposed of.

The Republic of Uzbekistan attaches great importance to the modernization of the chemical, metallurgical and oil and gas industries, the transfer of industrial enterprises to local raw materials, and the receipt on their basis of new materials suitable for export. Scientific and practical results have been achieved in the production of adsorbents based on local raw materials and their use in various industries, as well as the regeneration of spent alkanolamines. Of particular importance is the increase in the efficiency of the installation for the purification of natural gas from acidic components at gas processing plants, which will improve the economy of the republic through import substitution - the organization of the production of optimal adsorbents and reagents from local raw materials in the republic.

The effectiveness of gas purification technology is largely determined by the choice of absorbent. The higher its absorption capacity with respect to H_2S and CO_2 and other components, the less ethanolamine is required to achieve a given quality of purified gas.

Thus, the choice of absorbent requires in each case a thorough technical and economic study.

IV. PROPOSED METHODOLOGY AND DISCUSSION

Objects and methods of research: the objects of research were the absorption solution of diethanolamine (DEA), its decomposition products - hydrogen sulfide, heat-resistant salts, bound amines, amino acids, chlorides.

All studies were carried out in accordance with the relevant GOSTs. A set of modern and classical methods was used in the work, which make it possible to determine the physicochemical characteristics of a spent absorption ethanolamine solution with a content (30%) of DEA and its various condensates formed as a result of their long-term operation in the processes of absorption and desorption of hydrogen sulfide, carbon dioxide, and other sulfur-containing organic compounds.

The methods used to determine CO_2 as the total acid gas content in the alkanolamine solution and the amount of heat-resistant salts, H_2S in aqueous solutions of alkanolamines, the amine content in factory solutions by titration to $pH = 4,5$, the heat-resistant salts of aqueous solutions of alkanolamines, the foaming abilities of solutions of amines and inorganic chlorides in solutions of alkanolamines.

At the practical installation of UASO – 1,2 stages of Shurtaneftegaz JSC, a 25 % diethanolamine absorption solution (DEA) has been in operation for 2,5–3 years with continuous replenishment of fresh solution up to 0,5–1,0 % of the total volume of working solution. However, at the end of the service life or for technical reasons, this absorption solution becomes unsuitable for the effective purification of natural gas.

It is known [5] that a solution of diethanolamine is capable of absorbing oxygen, which potentially accelerates the decomposition of amine. At a high temperature in the stripper due to the absorbed oxygen at high speed the oxidation and polymerization reactions of DEA occur. Subsequently, heavy resinous compounds form deposits over all technological equipment: in heat exchangers, refrigerators, filters, and plates of absorbers. It should be noted that the resulting resinous deposits are a catalyst for the further formation of deposits and cause intense corrosion of the equipment.

The more degradation products and heat-resistant salts in the amine solution, the less its absorption capacity. The degradation products and heat-resistant salts do not participate in the process of purification of acid gases, but are ballast in the amine composition and must be constantly removed.

The gases entering the amine purification contain oxygen and nitrogen, which are considered to cause the formation of heat-resistant salts and contribute to the chemical change of amine molecules - the formation of bicins, sarcosine and other amino acids.



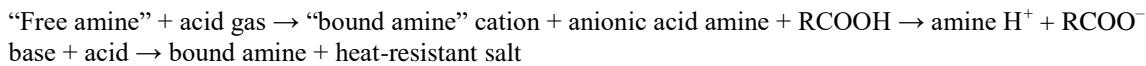
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Hydrogen sulfide (H_2S) in the regenerated amine solution is present in the form of HS^- , S^{2-} anions, and CO_2 in the form of HCO_3^- and CO_3^{2-} . These anions require the presence of cations. The amine has an alkaline base. Thus, the interaction of amine (alkali) and acidic components always forms a heat-resistant salt (HRS).

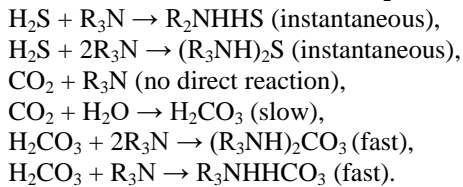
The mechanism of formation of heat-resistant salts is as follows:



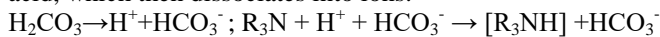
As can be seen from the presented chemical reactions, it is not possible to prevent the formation of HRS. HRS are always formed during the removal of acidic components using amines. Heat-resistant salts must be removed from the amine system. They are additional corrosion factors.

Diethanolamine DEA (tertiary alkanolamine), being an alkali, readily reacts with H_2S and CO_2 , forming water-soluble salts.

The main reactions of DEA with H_2S and CO_2 are as follows:



Tertiary alkanolamine does not have an H^+ atom in the amine group, therefore, the direct reaction of CO_2 with the formation of carbamate does not proceed, and the interaction occurs through the slow stage of formation of carbonic acid, which then dissociates into ions:



The final products are bicarbonates and carbonate.

Heat-resistant salts are usually named after the anion of the ion pair, for example, acetates, formates, thiosulfates, sulfates, thiocyanates, oxalates, butyrates, propionates, chlorides, phosphates, nitrates, etc. These salts are not heat-resistant because they do not leave the solution and do not leave the “bound” amine after passing through the regenerator solution.

The formation of heat-resistant salts is not limited to compounds resulting from reactions with contaminants that accumulate in the contactor. These are salts arising from the introduction of “antifoaming agents, corrosion inhibitors” and other special additives, as well as penetrating the amine as a result of leakage of cooling water, etc.

When the protonated amine is the salt cation, the salts are called heat-resistant amine salts (HRAS). Usually, salts in which the cationic part is not the protonated amine, but sodium or potassium, are not taken into account, which leads to an incorrect assessment of the composition of the solution. It is believed that a kind of struggle for ionic iron in the passivation layer occurs between negatively charged anions and the sulfide ion, while the anions form stable complexes of compounds.

Increased aggressiveness of production absorption solutions of ethanolamines develops during their continuous use in gas purification plants due to their contamination and impurities introduced from outside with purified gases, as well as products of oxidation and decomposition of the amines themselves, which differ in an extremely large variety depending on the totality of specific production conditions. Various studies have shown the formation and accumulation of sulfites, thiosulfates, salts and derivatives of organic acids (formic, acetic), aminoacetic acid, ethylenediamine, and many other compounds and resinous products of the so-called degradation of DEA in absorption solutions. These products have different effects on the performance of the cleaning process. Some reduce the absorption capacity of solutions, others at the same time cause them to foam in the process, others lead to the realization of high corrosion rates of equipment metal, etc.

Each mole of HRS blocks a mole of amine, preventing the purification of acid gases. All this reduces the efficiency of the system and can lead to more complicated amine circulation conditions, greater use of steam in the reboiler, low sulfur removal from the working gas, and reduced productivity.

According to the results of a large number of domestic and foreign studies, it was found that ethanolamine solutions by themselves in the initial state do not contain dissolved acid gases H₂S and CO₂ and are not corrosive. Of course, with an increase in the degree of saturation of these so-called “pure” solutions of amines with acid gases, their aggressiveness under other identical conditions increases.

V. EXPERIMENTAL RESULTS

Based on the foregoing, analyzes of the spent DEA solution that was used to purify natural gas at Shurtaneftegaz JSC were carried out. Below are the results of analyzes of the DEA spent solution (table 1) and the physicochemical parameters of the DEA spent solution (table 2).

Table 1. The results of the analysis of the spent DEA solution

The composition of the spent DEA solution	Unit of measurement	Amount in solution	Note
Concentration ДЭА 30 %			
Free DEA	%	23,07	
Associated DEA	%	6,93	
Anions of heat-resistant salts	ppm	2553	2,5 times higher than normal
Heat resistant amine salts	%	0,49	Above norm
HRS (Total Amine Content)	mol/mol	0,0125	Above norm
Strong cations	ppm	67	Above norm
Amino acids	ppm	4233	Dangerous level
Glycolate	ppm	627	1,3 times higher than normal
Acetates	ppm	439	Above norm
Bicin	ppm	1648	2,8 times higher than normal
Oxalate	ppm	498	2 times higher than normal
Gland	ppm	118	24 times higher than normal
Осажденные частицы Precipitated particles	mg/l	93	Above norm
H ₂ S	mg/m ³	15–17	Norm
CO ₂ , %	%	2,1	Norm

As can be seen from the table, the content of heat-resistant salts is –2533 ppm, at the recommended level of 1000 ppm, which means that their content is 2,5 times higher than their norm. DEA regeneration is carried out at a temperature of 125-145⁰C. These salts during the regeneration of the DEA solution do not leave the amine solution and do not leave the “bound” amine. They are more stable at high temperatures.

In addition, heat-resistant salts increase corrosion, the formation of iron sulfide, impair filtration and contribute to the entrainment of hydrocarbons. All this together has an amplifying effect on foaming, the ablation of the amine from the system increases and its productivity decreases, which leads to its frequent failures and an increased sulfur content in the gas.

In the solution, the high content of bound amine is 6,93%. The bound amine is not suitable for the absorption of acid gas and is not involved in the absorption of acidic components.

The solution contains amino acids 4233 ppm and bicin 1648 ppm. Both of them are corrosive compounds and weaken the protective layer of metal equipment and metal, and under the influence of H₂S are oxidized at an increased rate.



In addition, HRS, amino acids, bicins, and associated amines adversely affect the physico-chemical parameters of the DEA solution (Table 2).

Table 2. Physico-chemical characteristics of the spent DEA solution

Physical and chemical indicators	Unit of measurement	30% DEA aqueous solution	Spent DEA solution
pH		10,3	9,6
Viscosity (η)	sPz	2,16	4,0
Density(d_4^{20})	g/sm ³	1,104	1,057
Electrical conductivity	sm ⁻¹ ·10 ⁴ Om ⁻¹ sm ⁻¹	6,7	4,38
(δ) Surface tension (δ)	10 ³ , n/m	70,8	68,86
Foaming	sm	1,5	2,2
FoamLifetime, (τ)	sek.	Less 18–20	22–25

According to the results of three filtration cycles on ion-exchange resins, it was found that the degree of purification of ethanolamine from heat-resistant salts (HRS) was 86%, from chlorides-85%. The resin was regenerated using a solution of soda ash.

Based on the tests performed, it is recommended to design and build a centralized amine solution purification system at gas processing plants with a series connection of filters to remove foaming components (mechanical and activated carbon) and HRS (with ion-exchange resins) with a capacity of 700 m³ of ethanol amine scavenger.

With absorption desulfurization of natural and associated gases, foaming of amine solutions is a serious problem. It leads to a decrease in plant productivity, loss of working solution, and the production of substandard gas. The main cause of foaming is contamination with various impurities that enter the gas, solution or form in it as a result of equipment corrosion and amine degradation.

The short-term result is only the use of active blowing agents. Their constant treatment at first destruction, then the solution becomes sensitive to increasingly smaller numbers of foaming promoters. The most effective direction in the fight against foaming is the improvement of the technology for the preparation of raw gas and the cleaning of the absorption solution.

By filtering, unwanted impurities can be removed from the system, distillation or sorption process. The technology that allows for high-quality cleaning of the solution is based on a combination of mechanical filtration and through activated carbon.

Mechanical filtration is used to remove fine particles from the system that stabilize the resulting foam. Their high content can cause erosive destruction of equipment in places where circulation speeds are high. Filters are usually installed after cleaning through activated carbon, which delays foaming components: condensate, degradation products. tests of activated carbons of grades AG-3, AG-5 were carried out in laboratory conditions. The highest activity in the extraction of foaming substances was shown by the coals AG-3 and AG-5. At the same time, the activity of AG-3 coal in foaming impurities amounted to 15–17% (mass.). Based on the conducted studies, AG-3 activated carbon is recommended for the purification of amine solutions. Foaming decreased by 20-30 times when using it for adsorptive purification of the solution from impurities. Currently, the selection of another effective and more economical sorbent is necessary.

We studied new samples of activated carbon (AG-90, AG-95, AG-3 modified, AG-3-I, AG-3-V, AG-3-O), which can trap foaming components. A comparative study of the properties of these coals and production solutions percolated through them were carried out. For this, the AG-3 used at gas processing plants served as the base component.

Table 3.Coal fractional composition

Indicator	Mass content of fractions,%				
	АГ-3	АГ-3-И	АГ-3-В	АГ-90	АГ-95
Granules over 3 mm	0,26	0,4	-	0,14	0,46
Granules from 3 mm to 2 mm	45,6	46,9	-	39,38	68,86
Granules from 2 mm to 1 mm	53,6	52,06	86,4	59,26	30,5
Granules less than 1 mm	0,26	0,4	13,2	0,41	0,2

In accordance with the requirements for adsorbents for amine purification, according to which a granule content of 2-3 mm is preferred, AG-3-B and AG-90 are excluded from further studies.

The acidity index of the aqueous extract of the selected AG-3, AG-3-I, AG-95 is 7, which indicates the absence of impurities.

In addition, comparative changes in the cleaning performance of the working solution using various adsorbents were considered (table 4).

Table 4. Comparative cleaning characteristics of working solution using various adsorbents

Working solution indicators	Saturated solution for regeneration	Regenerated 25% MDEA solution after purification on sorbents		
		Activated Coal	Sorbent Al ₂ O ₃ (D 26)	Sorbent silica gel
Solution color	gray green	light yellow	light yellow	light yellow
Density(ρ), g / cm ³	1,092	1,045	0,040	0,034
Content; H ₂ S, mg / l	863	40,0	25,0	20,0
CO ₂ , % mol	2,19	0,35	0,05	0,04
Hydrocarbons (C _n H _{2n+2}), %	28,0	30,0	30,2	30,4
pH	8,1	10,8	10,9	11,0
Solution viscosity, mm ² sec	5,1	4,5	4,3	4,2

As can be seen from the data in table 4, the given sorbents showed various positive results in terms of their absorption properties, but solid sorbents will probably surpass the activated carbon in terms of service life. The renewability of adsorbents (regeneration with hot gas) gives them an advantage in technology, with multiple cycles of use for cleaning such colloidal dispersed systems.

To study the absorption capacity of coals and adsorbents for foaming components, the fractions of the solution separated after filtration through them were analyzed for MDEA and foaming (Table 5).

Table 5. The concentration of MDEA after percolation of the solution through coals

Number of fractions	Concentration,% wt		
	AG-95	AG-3	АГ-3-И
1	30,5	32,13	32,13
2	-	-	33,13
3	32,13	33,67	33,32
4	32,84	33,55	34,15
5	-	-	34,74
6	-	-	33,2
7	33	-	-
8	33,5	-	-
9	33,91	-	-
10	-	35,34	32,72
11	-	-	32,48
12	36,89		
Stocksolution	30,22	31,29	33,08



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It is seen that the filtration of the amine solution through AG-3, AG-3-I and AG-95 provides one of the requirements for adsorbents - neutrality with respect to the absorber.

Serious complications in the operation of gas treatment plants [6] also cause the deposition of various impurities on the surfaces of pipes and equipment: pressure losses in the system increase, the efficiency of heat exchange processes decreases, heat losses increase, etc. Therefore, in all plants for the processing of acid gases, it is envisaged to clean the solutions of absorbers from impurities. For this purpose, vacuum distillation and filtration processes are used, and in some cases both processes are used.

The filtration process is the most common for cleaning acid absorbers from various impurities. This process includes, as a rule, two steps: the first is a rough cleaning of the solution from solid impurities on various filters, and the second is its fine cleaning of dissolved impurities. The latter process is carried out using various adsorbents or ion exchange filters. The adsorption method is most often used. In this case, only part of the solution after rough cleaning is subjected to additional filtration in order to extract smaller particles and dissolved substances from it.

At present, in gas processing plants, carbon (activated AG-3) and belting filters are used to filter amine solutions, which remove mechanical impurities, heavy hydrocarbons, and others that promote foaming. However, according to the data, activated carbons do not adsorb corrosive heat-resistant salts (HRS) and chlorides.

"Pyrolight" company has proposed synthetic ion-exchange resins for the purification of industrial amine solutions from foaming components. Laboratory tests, conducted by the Department of Oil and Gas Processing UzLITIneftgaz, showed their high efficiency in the removal of chlorides, thermostable salts by anion exchangers A-400 (D-4053) and A-600 (D-4054). Resin sample with high basic functionality Neutral Macronet D-4006 proved particularly defoaming. Macronet inert D-4006 has an advantage over coal AG-3 adsorption of foaming impurities and purification from chlorides. A-400 and A-600 gel anion exchangers effectively remove heat-resistant salts and chlorides with a low content of them [7].

A great advantage of ion exchangers is their high strength properties, the absence of dusty fractions, which make it possible to exclude high transparency filtrates. The maximum ambient temperature at which D-4006, A-400 and A-600 can be operated is -120 °C and 60 °C, respectively. Anion exchangers are thermally stable both in salt and in the form of a free base, but quaternary amino groups are unstable, therefore, a temperature above 60 °C is not recommended.

The decisive factor in assessing the prospects for the use of selected ion exchangers is the possibility of a sufficiently effective and cost-effective multi-cyclical regeneration of them.

A pilot industrial assessment of the properties of the proposed sorbents was carried out under production conditions in the following order:

- purification of the MDEA solution from foaming substances on the sorption material "macronet";
- purification of the MDEA solution from thermostable salts and chlorides using anion exchangers.

According to the "Pyrolight" company, the pilot plant was mounted in such a way that it was possible to check the cleaning on a smaller volume of the solution (2,5 m³) circulating in a closed circuit [7].

Before the start-up of the installation, anion exchangers were regenerated with 5% caustic; before this, the filters were loosened. Filtrate samples were analyzed every hour at the inlet and outlet according to the following indicators: amine concentration in solution, content of heat-resistant salts and chlorides. When filtering, discoloration of the solution was observed; at the end of the test, it became light both at the inlet and at the outlet.



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VI.CONCLUSION AND FUTURE WORK

The causes of degradation of the diethanolamine solution of natural gas purification are determined. It was found that the interaction of amine and acidic components of natural gas always forms heat-resistant salts, which must be removed from the amine system.

Increased aggressiveness of industrial absorption solutions of ethanolamines develops in the process of their continued use in gas purification plants due to their contamination and impurities introduced from outside with the cleaned gases, as well as the products of oxidation and decomposition of the amines themselves, which differ in an extremely large variety, depending on the totality of specific production conditions.

Thus, as a result of preliminary assessment tests of the sorption ability of coal samples, it was found that AG-3> AG-95> AG-3-I are suitable for use in desulfurization technology.

The results of the analysis of two filter cycles of sorbents A-21 and A-23;
- both anion exchangers clear the amine solution from HRS and chlorides;
-absorption of HRS filter A-23 has better performance than A-21: the degree of purification of the solution with anion exchangers was 60 and 44%, respectively;
-absorption of chlorides is better for A-21: the degree of purification at A-21-23%, A-23-56%.

The third cycle was carried out on an A-400 filter to obtain more complete information about the sorption capacity of anion exchangers: the content of HRS decreased to 0,05%, the amount of chlorides to 4 mg / l.

According to the results of three filtration cycles on A-21, it was found that the degree of ethanolamine purification from HRS was 86%, from chlorides-85%. Resin regeneration was carried out using a solution of soda ash.

Based on the tests performed, it is recommended to design and build a centralized system for purification of amine solutions at gas processing plants with serial connection of filters to remove foaming components (mechanical and activated carbon) and HRS (with ion-exchange resins) with a capacity of 700 m³ of ethanolamine absorber.

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