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CLEANING DIETHANOLAMINE SOLUTIONS FROM HARMFUL COMPOUNDS BY FILTRATION METHOD

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Abstract: The article presents the results of research on the purification of circulating DEA solutions from resinous substances on strongly basic resins A-200 and A-400 and activated carbon AG-3, with preliminary filtration of DEA solutions from mechanical impurities through quartz sand.

Keywords: natural gas, ethanolamine, ion exchange method, absorption purification, resinous substances, anionites, quartz sand, activated carbon, mechanical impurities.

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

The most widely used for the purification of natural and petroleum gases from hydrogen sulfide and carbon dioxide are amine solutions. Installations where aqueous solutions of amines are used as an absorber are commonly called amine installations. Amine plants are compact and flexible in operation with respect to changes in the composition and amount of gas to be treated.

At the practiced installation UASO - 1.2 stages of gas processing plants, a 25% absorption solution of diethanolamine (DEA) is operated for 2.5 - 3 years with continuous feeding with fresh solution up to 0.5 - 1.0% of the total volume of the working solution. However, at the end of its service life or for technical reasons, this absorption solution becomes unsuitable for effective natural gas treatment.

The gases entering the amine treatment contain oxygen and nitrogen, which cause the formation of heat-resistant salts and contribute to the chemical change of amine molecules, as well as the formation of bicines, sarcosine and other amino acids.

It is known that an amine ethanol solution is capable of scavenging oxygen, which potentially accelerates the decomposition of the amine. At a high temperature in the desorber, due to the absorbed oxygen, the reactions of oxidation and polymerization of DEA proceed at a high rate. In the future, heavy resinous compounds form deposits throughout the process equipment: in heat exchangers, refrigerators, filters, absorber trays. 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 [1]. The more degradation products and heat-resistant salts in the amine solution, the lower its absorption capacity. Degradation products and heat-resistant salts do not participate in the process of acid gas purification, but are ballast in the composition of the amine and must be constantly removed.

Hydrogen sulfide (H2S) in the regenerated amine solution is present in the form of anions HS–, S2–, and CO2 is present in the form of HCO3– and CO32–. These anions require the presence of cations. Amine is alkaline. Thus, in the interaction of an amine (alkali) and acidic components, a heat-resistant salt (TSS) is always formed.

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

"free amine" + acid gas → "bound amine" cation + anionic acid amine + RCOOH → амин H^+ + $RCOO^-$

base + acid → bound amine + heat-resistant salt

As can be seen from the presented chemical reactions, it is not possible to prevent the formation of TSS. TCC is always formed in the process of removing acidic components with the help of amines. Heat-resistant salts must be removed from the amine system. They are additional corrosive factors.

Diethanolamine DEA, being an alkali, easily reacts with H2S and CO2, forming water-soluble salts.

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

$H_2S+R_2NH \rightarrow RNHHS$ (instant),
$H_2S+2R_2NH \rightarrow (R_2NH)_2S$ (instant),
CO_2+R_2NH (no direct response),
$CO_2+H_2O \rightarrow H_2CO_3$ (slow),
$H_2CO_3+2R_2NH \rightarrow (R_2NH)_2CO_3$ (fast),
$H_2CO_3+R_2NH \rightarrow R_2NHHCO_3$ (fast).

The tertiary alkanolamine does not have an H^+ atom in the amine group, so 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:

$H_2CO_3 \rightarrow H^+ + HCO_3$; $R_2NH + H+ + HCO_3 \rightarrow [R_2NH] + HCO_3$

The end products are bicarbonates and carbonate.

Heat-stable salts are usually named after the anion of the ion pair, e.g. acetates, formates, thiosulfates, sulfates, thiocyanates, oxalates, butyrates, propionates, chlorides, phosphates, nitrates, and the like. These salts are not thermally stable because they are not removed from the solution and do not leave the "bound" amine after the solution passes through the regenerator.

The formation of heat-resistant salts is not limited to compounds resulting from reactions with contaminants that accumulate in the contactor. These are salts that appear when “antifoamers, corrosion inhibitors” and other special additives are added, and also penetrate into the amine as a result of cooling water leakage, etc.

When the salt cation is a protonated amine, the salts are referred to as heat-resistant amine salts (TCAC). 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 the negatively charged anions and the sulfide ion, while the anions form stable complexes of compounds.

DEA is relatively easily oxidized, first to α-aminoaldehyde, then to glycine, glycolic acid, oxalic acid, and finally to formic acid. These acids lead to corrosion with the formation of insoluble iron salts that can clog the equipment.

Resin products - heavy resinous compounds further form deposits throughout the process equipment. 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 lower its absorption capacity. Degradation products do not participate in the process of acid gas purification, but are ballast in the amine system. This leads to a decrease in the concentration of free amine in the solution, to an increase in its corrosive activity.

According to the technology existing at the enterprise to reduce corrosion and chemical losses of DEA, a part of the solution is continuously removed for distillation. Distillation is carried out in the presence of alkali when heated. The products of side reactions decompose with the formation of diethanolamine, which again returns to the cycle.

However, as the results of studies of the CLO of Shurtanneftegaz LLC showed, the regenerated DEA solutions often contained resinous substances above the normalized values; in addition to resinous substances, DEA solutions contained impurities in the form of bound nitrogen, formic acid, nitrates, sulfates, chlorides, solid particles (iron sulfides, iron oxide, dust, sand, mill scale, oily substances) and others.

The purpose of this work was to study the possibility of cleaning the circulating DEA solution from resinous substances and other harmful impurities by the adsorption method.

To purify the DEA solution from harmful impurities, strongly basic anion exchangers A-400 manufactured by the Russian Federation and A-200 in helium form (Purolite) were used.

The preparation of resins was carried out in accordance with the requirements of GOST 20301-74; GOST 20255.1-89; GOST 20255.2-89.

Natural river sand was used to purify the spent diethanolamine solution. Large impurities and stones were separated on a 2 mm sieve, then sieved and dedusted on a 0.34 mm sieve. For the filter, quartz sand with a particle size of (0.34÷1.0) mm was used. To clean the solution from mechanical impurities, the solution is passed through a sand filter at a rate of 1.5-1.2 l/h. (Fig. 1).

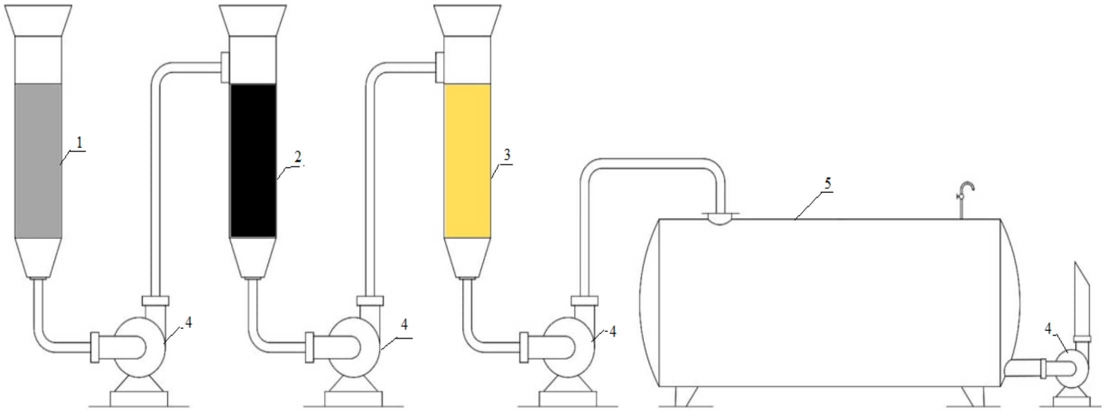

Fig.1 Purification of the spent diethanolamine solution with the filtration method.

1- Sand filter, 2- Activated carbon, 3- Anion exchanger A-200, A-400, 4- pumps, 5- tank for technical DEA

1. Characteristics of the sand filter.

The volume of sand in the column is 657 cm3.
The height of the sand layer is 55 cm.
Diameter - 3.9 cm
Sand surface area 12 cm2
The solution transfer rate is 1.5-2.1 l/hour.
Productivity - 2.11 m3/m2 s

1. Activated carbon AG-3

The volume of coal AG-3 is 100 cm3,
Weight (dry coal) - 50 g
The height of the coal seam is 46 cm.
Diameter - 1.66 cm
Cross-sectional area - 2.17 cm^2
The solution transfer rate is 1.5-2.1 l/hour.

3. Resin column AV-400

Diameter - 1.63 cm.
Volume of prepared resin 100 cm3
The height of the resin column is 48 cm.
Cross-sectional area - 2,083 cm2
The solution transfer rate is 1.5-2.1 l/hour.

Productivity - 2.36 m3/m2 s

When cleaning DEA solutions from resinous substances and other harmful impurities, activated carbon AG-3 is used as an adsorbent. In this case, the solution is passed through a layer of activated carbon with a volume of 100 cm3 at a rate of 1.5-2.1 l/h, and the resinous substances contained in it are filtered and retained [2].

A solution of diethanolamine, previously purified from mechanical impurities and resinous substances, is passed through pre-prepared 100 cm solution. After that, the saturated sorbent (ion-exchange resins) was regenerated in a 5% sodium hydroxide solution, washed with water, and sent to the next cycle of purification of the DEA solution.

When cleaning the absorbent solution by the above filtration method, mechanical impurities and resinous substances were reduced to 75.0÷83.0%. When cleaning solutions of ethanolamines from salts on anion-exchange filters A-200 and A-400, the amount of salts in the absorbent was purified to 80-85%.

During the chromatographic analysis of the results of laboratory studies (Fig. 2), comparing the composition of the initial and final ethanolamine solution for purification, we found that heavy impurities in the solution (mechanical impurities, bound amines, temperature of stable salts, etc.) are reduced compared to the initial state , the solution is purified to the required level [3].

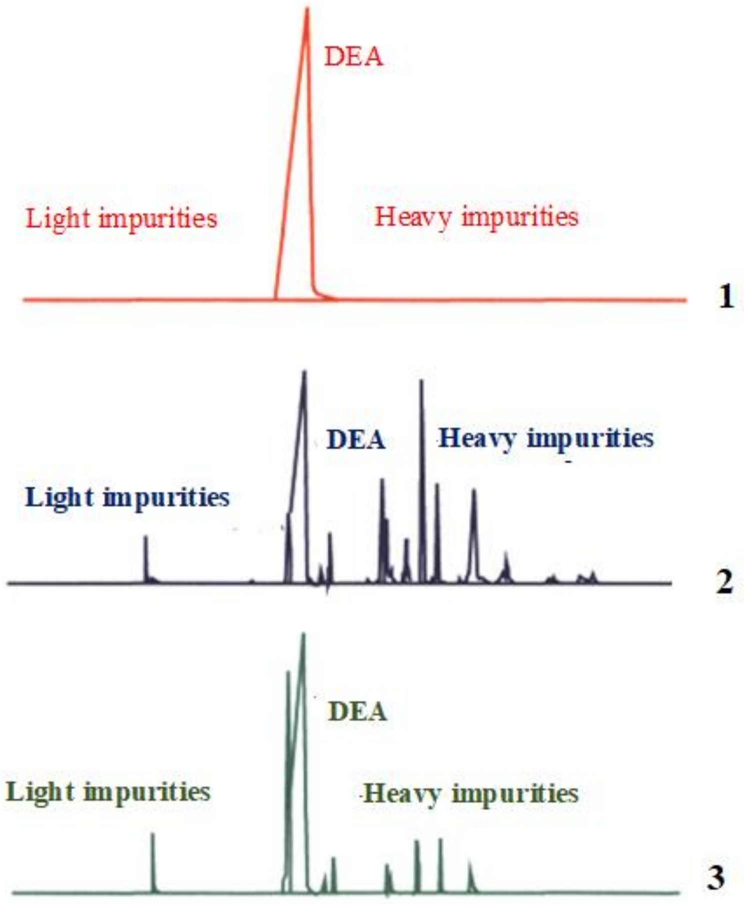

Fig.2-Chromatographic analysis of DEA 1- Chromatographic analysis of pure DEA, 2- Chromatographic analysis of waste DEA, 3- Chromatographic analysis of purified DEA.

With the help of filtration, unwanted impurities can be removed from the system, distillation or sorption process. The technology that allows high-quality purification 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, which stabilize the resulting foam. Their high content can cause erosive destruction of equipment in places where circulation rates are high. Filters are usually installed after sedation through activated carbon, which retains foaming components: condensate, degradation products. Activated carbons of grades AG-3, AG-5 were tested under laboratory conditions. The highest activity in the extraction of foaming substances was shown by coals AG-3 and AG-5. At the same time, the activity of AG-3 coal in terms of foam-forming impurities was 15–17% (wt.). Based on the studies carried out, active carbon of the AG-3 brand is recommended for the purification of amine solutions. When used for adsorption purification of the solution from impurities, foaming decreased by 20-30 times.

Currently, it is necessary to select another effective and more economical sorbent.

New samples of activated carbons (AG-90, AG-95, AG-3 modified, AG-3-I, AG-3-V, AG-3-O), which can trap foam-forming components, have been studied. A comparative study of the properties of these coals and industrial solutions percolated through them was carried out.

For this, the AG-3 used in gas processing plants served as the basic component.

Table 1

Fractional composition of coals

Index	Mass content of fractions, %				
	AG - 3	AG -3-И	AG -3-В	AG - 90	AG - 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 smaller 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 the content of 2-3 mm granules is preferable, AG-3-V and AG-90 were 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 indicators of purification of the working solution using various adsorbents were considered (table 2).

As can be seen from the data in Table 2, the given sorbents showed various positive results in terms of their absorption properties, but solid sorbents will apparently outperform activated carbon in terms of service life. The renewability of adsorbents (hot gas regeneration) gives them an advantage in technology, with repeated use for the purification of such colloidal disperse systems.

Table 2

Comparative characteristics of purification of the working solution using various adsorbents

Working solution indicators	Saturated solution for regeneration	Regenerated 25% MDEA solution after purification on sorbents		
		Activated-coal	sorbent Al_2O_3 (Д 26)	Sorbent silica gel
Mortar color	gray green	light yellow	light yellow	light yellow
Density (ρ), г/см^3	1,092	1,045	0,040	0,034
Content; H_2S, mg/l	863	40,0	25,0	20,0
CO_2, % mole	2,19	0,35	0,05	0,04
hydrocarbons (C_nH_{2n+2}), %	28,0	30,0	30,2	30,4
pH	8,1	10,8	10,9	11,0
Solution viscosity, mm2s	5,1	4,5	4,3	4,2

Thus, as a result of preliminary evaluation tests of the sorption capacity of coal samples, it was found that AG-3 > AG-95 > AG-3-I are suitable for use in desulfurization technology [4].

Results of analyzes of two filter cycles of sorbents A-200 and A-400;

- both anion exchangers purify the amine solution from TSS and chlorides;
- in terms of TSS sorption, the A-400 filter has better performance than the A-200: the degree of purification of the solution with anion exchangers was 65 and 44%, respectively;
- according to the sorption of chlorides, the indicators for A-400 are better: the degree of purification by A-200-39%, A-400-56%.

Based on the tests carried out, it is recommended at gas processing plants to design and build a centralized system for cleaning amine solutions with a series connection of filters to remove foaming components (mechanical and with activated carbon) and TSS (with ion-exchange resins) with a capacity of 700 m3 of diethanolamine absorber.

Filtration of the DEA solution from resinous substances, thermally stable salts and mechanical impurities and its reuse in the gas cleaning process did not completely solve the problem. One of the important issues is to increase the efficiency of gas cleaning by improving the physicochemical and working properties of technical DEA, purified in the filtration process. To do this, when conducting a physicochemical analysis of a purified technical solution of DEA, the following was established.

Physiochemical properties	Indicators of a 30% aqueous solution of technical DEA obtained by the ion-exchange method
pH раствора	9,8
Viscosity, сПз	2,8
Surface tension, dyne/cm	71,35
Absorption volume, mol/mol	0,40-0,44
Selectivity for H_2S, CO_2, %	95,0
Foaming cm/min	2,3
Foam stability, sec	13
Amount of amine	21,3

Studies were also carried out to restore the physicochemical and working properties of a purified diethanolamine solution. In order to improve the physicochemical and performance indicators of technical monoethanolamine, nitrogen-sparing additives-activators were added to it [5]. As a result, the pH of the solution increased from 9.8 to 10.4, the absorption volume increased from 0.40-0.44 mol/mol to 0.45-0.50 mol/mol, the foaming height increased from 2.3 centimeters to 2 .1 centimeter, managed to reduce the stagnation time from 13 seconds to 10 seconds. It can be seen that the viscosity of the solution (from 2.6 cps to -2.8 cps) and surface tension (from 76.66 dynes/cm to 76.35 dynes/cm) did not change. As a result, it was possible to increase the efficiency of gas cleaning and extend the service life of the absorbent solution.

Based on the foregoing, the following conclusion can be drawn: the correct choice of the method and technology for the regeneration of the diethanolamine solution, the prevention of corrosion and failure of instruments and equipment due to the accumulation of various salts and organic acids in the absorbent solution, which adversely affect the gas cleaning process, an increase in the absorption volume of the absorbent solution , the reuse of the technology used in the gas cleaning process, the reduction in the amount of imported diethanolamine as a result of the increase in the activity of diethanolamine based on local raw materials has established itself as one of the practical solutions to the current problem.

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