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THE INFLUENCE OF GAS IMPURITIES ON THE ABSORPTION OF ALKANOLAMINE SOLUTIONS

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Annotation: The article describes the causes of foaming in alkanolamines used as absorbents in the process of purifying hydrocarbon gases from acidic components, the negative consequences of foaming, and the methods of preventing foaming in the absorbent solution.

Keywords: alkanolamines, absorbent, hydrocarbon gases, acidic components, hydrogen sulfide, mercaptans, sulfides, disulfides, gas purification

INTRODUCTION

There are several methods for purifying gases from acidic components, which are divided into conventional methods—based on separating acidic components from the gas—and non-conventional methods that involve the production of elemental sulfur. Conventional methods, in turn, include absorption, adsorption, and catalytic purification techniques.

To remove H_2S, CO_2, and other impurities from natural gas, several methods are used [1]:

Chemisorption methods, based on the chemical interaction of impurities with a liquid absorbent;

- **Physical absorption**, based on the dissolution of impurities in an organic solvent;
- **Combined methods**, using both chemical and physical absorbents simultaneously;
- **Oxidation methods**, based on the irreversible conversion of impurities into elemental sulfur and other substances;
- **Adsorption methods**, based on the capture of impurities on the surface of solid materials such as activated carbon or aluminosilicates;
- **Alkaline purification methods**;
- **Non-regenerative purification methods**.

Chemical absorption processes are based on the chemical interaction between hydrogen sulfide and carbon dioxide with the active component of the absorbent.

Among chemisorbents, caustic sodium and potassium, alkali metal carbonates (sodium and potassium carbonates), and alkanolamines are widely used. The salts formed as a result of the chemical reaction between the active part of the chemisorbent and the acidic components decompose when heated. The maximum absorption capacity of aqueous chemical absorbent solutions is determined using stoichiometric calculations [2–7].

LITERATURE REVIEW AND METHODOLOGY

On an industrial scale, the most commonly used chemical absorbents include alkanolamines such as primary amines – monoethanolamine (MEA), secondary amines – diethanolamine (DEA), and tertiary amines – methyldiethanolamine, diisopropanolamine (MDEA, DIPA). Additionally, alkaline solutions and aqueous solutions of alkali metal salts (for example, potash purification using 25–30% aqueous solutions of K_2CO_3 or Na_2CO_3), as well as ferric hydroxide ($Fe(OH)_3$), are widely applied.

The main advantage of chemisorption processes – including those involving aqueous alkanolamine solutions – lies in their ability to purify gases to a high and reliable degree, independent of the partial pressure of acidic components, while ensuring minimal absorption of hydrocarbon components from the feedstock. This, in turn, contributes to the high quality of the commercial sulfur obtained from the acid gases released during absorbent regeneration [5–9].

Chemical absorption processes are characterized by their high selectivity toward acidic components, providing efficient removal of H_2S and CO_2 from gases. When amine solutions are used, sulfur-containing organic compounds are separated only in small amounts due to their dissolution in the liquid phase. In contrast, the use of alkaline solutions allows for more thorough purification from sulfur-organic compounds.

In the field of natural gas purification from acidic components, amine-based processes are considered the leading methods worldwide**.** They have been used for several decades in the purification of natural gas. Even today, amine purification units account for approximately 70% of all gas treatment facilities, maintaining their dominant position.

The most widely used ethanolamines in the processes for removing H_2S and CO_2 from gases are monoethanolamine (MEA), diethanolamine (DEA), triethanolamine (TEA), diglycolamine (DGA), diisopropanolamine (DIPA), and methyldiethanolamine (MDEA) [8–15].

Foaming of amine solutions is one of the major problems encountered in gas purification units. Foaming leads to disruption of the operating regime of the unit, deterioration in the quality of the purified gas, and, as a result, a decrease in the gas processing capacity of the equipment. When foam forms, the loss of valuable amines carried away with the gas stream increases [16].

Foaming usually occurs in absorbers; however, cases have been observed where a foaming solution also carries over into the desorber. In most cases, foaming occurs in equipment operating under high gas and liquid load conditions. The signs of foaming include an increase in foam volume on contact trays, a sudden rise in pressure differentials within the equipment, and the formation of liquid layers in the clean and acid gas separators.

The following factors may cause foaming [17]:

- an increase in the corrosion rate within the system;
- the entry of various inhibitors used during gas production into the unit;
- thermal decomposition of amines under high temperatures;
- accumulation of unwanted reaction products in amine solutions;
- ingress of heavy hydrocarbons into the absorber in the form of droplets;
- presence of mineralized water in the gas stream entering the absorber;
- introduction of mineral salts into the system together with process water during the preparation of absorbent solutions for acidic component removal.

RESULTS

Under industrial operating conditions, each of the above-mentioned factors exhibits its own specific influence. In most cases, several factors act simultaneously, making it difficult to implement effective measures to prevent foaming. Sometimes, the adopted solutions do not address the root causes of foaming but rather focus on mitigating its consequences. Foaming begins once certain substances accumulate in the solution up to a specific concentration.

Figure 1 presents the experimental results of foaming for a 25% DEA solution at 20°C in the presence of various impurities [18]. These data demonstrate that all substances contained in gas streams from the well can contribute to the foaming of amine solutions.

The highest foaming tendencies are observed in the presence of surface-active materials (SAMs), certain corrosion inhibitors, and hydrocarbons with boiling points **above 100°C (such as condensates and oil).**

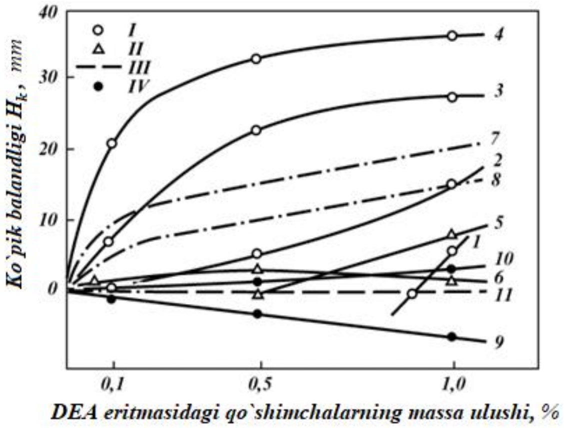

Figure 1. Graph showing the dependence of the foaming properties of a 25% DEA solution on various additives.

I – paraffin; II – naphthene; III – condensate fraction; IV – alcohol;
1 – pentane; 2 – octane; 3 – nonane; 4 – undecane; 5 – cyclohexane; 6 – cyclopentane; 7 – condensate fraction (150°C); 8 – condensate; 9 – methanol (technical grade); 10 – residue from methanol distillation (10%); 11 – pure DEA solution.

It has been proven that foaming typically occurs in equipment operating under high gas and liquid load conditions [19]. An increase in the pressure differential within the column is considered an external indicator of foam formation; therefore, monitoring this parameter is essential for timely detection of foaming.
The intensity of foaming also depends on the surface tension of the absorbent — the lower the surface tension of the solution, the easier the foaming process occurs. Thus, the presence of surface-active substances in the absorber reduces surface tension and promotes foaming. The effect of a mixture of salts such as $MgCO_3$, $CaCO_3$, KCl, and K_2SO_4 on foaming has been demonstrated [20]. It was found that calcium and magnesium carbonates cause the most intensive foaming.

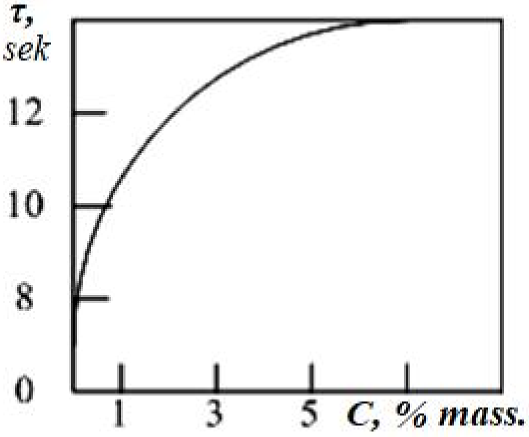

Figure 2. Dependence of foam lifetime τ (sec) on salt concentration C (%) in an MEA solution.

To prevent foaming, the following main measures should be implemented:

1. Reduce the concentration of impurities in the inlet gas that cause or promote foaming to the minimum permissible level. This can be achieved by efficient use of an inlet separator or by washing the gas with an absorbent such as water or a stable hydrocarbon fraction before entering the unit.
2. Prevent hydrocarbon condensation by feeding the regenerated amine into the absorber at a temperature 2–5°C higher than the outlet gas temperature.
3. Perform periodic washing and cleaning of equipment from sludge and solid deposits.
4. Continuously filter the amine solution to remove mechanical impurities – this is the most effective preventive measure. A portion of the circulating solution (5–20%) is directed for filtration, typically using regenerated amine. The solution first passes through a filter paper coated with a pre-applied filter mixture to remove mechanical particles. In domestic sulfur purification units, filtering mixtures such as *Perlite powder*, *activated bleaching carbon*, and *fiber filters* are commonly used.

After mechanical filtration, the amine solution is directed to an activated carbon adsorber to remove hydrocarbons, amine degradation products, and other impurities. After passing through the carbon filter, the solution is sent through a cartridge filter to capture fine carbon particles carried over from the adsorber. It is recommended to direct about 5–20% of the solution flow through the carbon filter and up to 100% through the mechanical filter.

During filtration, even though the flow rate can reach 20–60 L/(min·m²) in some cases, it is recommended to maintain a rate of 10 L/(min·m²) for optimal operation. The height of the adsorbent layer in a single adsorber is typically 3–4 meters. According to operational data, for stable process performance, the concentration of impurities in the amine solution should not exceed 2 g/L.

5. Use antifoaming agents as an effective means of foam suppression. These defoamers are introduced into the system in small amounts when foaming occurs, usually as a 2–5% solution in amine or water. However, excessive addition of defoamers can have the opposite effect – stabilizing the foam.

DISCUSSION

Among siloxane compounds, D.C. Antifoam, A Splastic, Compound (USA), Antifron (Germany), and Rodolsil–426 R (France) are used.

In Russia, the antifoaming agents VIPIGAZ-1, KE-10-12, KE-10-21, and I-1-A emulsions are produced. These agents are non-toxic, explosion-safe, and non-flammable, with active components that boil at temperatures above 300 °C.

Polysiloxanes $(Re_2SiO_3)_n$ are colorless, oil-like liquids with varying molecular weights and viscosities. Siloxane liquids possess high thermal stability. Their foam-suppressing properties appear in acidic, alkaline, and neutral environments even at very low concentrations (0.0001–0.001%).

Antifoaming agents reduce the strength of the film separating gas bubbles and the liquid phase. Their antifoaming properties are most effective once their concentration exceeds the critical limit. In desulfurization units, special tanks and dosing pumps are installed for feeding antifoaming agents. When necessary, the antifoaming agent is introduced into the regenerated amine stream before entering the absorber using dosing pumps. The supply of the antifoaming agent into the pipeline ensures its uniform distribution within the absorbent.

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