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Current Problems of Amine Treatment of Natural Gases and Ways to Solve Them

Yuldashev Tashmurza

Karshi of Engineering and Economics Institute. Uzbekistan, Karshi. Department of Oil and Gas Processing Technology

ABSTRACT: The process of amine purification of natural gases from acidic impurities has been analyzed, the problems accompanying it and the ways of their solution have been considered. Such problems as optimization of amine solution compositions and acid gases emitted, problems of pollution of amine solutions by different impurities, destruction of amines, high energy consumption for their regeneration are analyzed. The issues of foaming in the absorber and ways to reduce it, the main directions of utilization of spent amines are considered.

KEYWORDS: amine purification, acid gases, alkanolamines, regeneration, foaming, defoamers, destruction, filtration, utilization.

I. INTRODUCTION

The most important stage of preparation of natural gases for processing is purification from acid impurities, first of all, from hydrogen sulfide and carbon dioxide as a result of which commodity gas and acid gases - raw materials for production of gas sulfur are formed [1].

Alkanolamines are widely used for purification of gases from acid impurities, as they possess low viscosity, effectively purify gas in a wide range of partial pressures of H_2S and CO_2 , almost do not absorb hydrocarbons (HC) [1].

However, the technology of absorption with alkanolamines has serious drawbacks: high energy costs for regeneration of amines, destruction of amines, their contamination by various impurities, foaming during absorption, etc. When using amine purification there are tasks that require serious research and finding ways to solve them, for example: the choice of absorption parameters to ensure that commercial gases meet the necessary requirements, which are constantly tightening; ensuring (in the purification of high-sulfur gases) the optimal composition of sour gases sent for the production of gas sulfur. Important tasks are also: utilization of spent amine solutions, development of an amine regeneration process that does not require high energy costs and prevents the destruction of amines, the use of effective defoamers and antifoaming agents to solve the problems of foaming in the absorption of alkanolamines and many others [2].

The subject of this article is the problems in the operation of amine gas purification units and ways to solve them.

II. OPTIMIZATION OF ACID GASES COMPOSITION

At use of sour gases as a raw material for sulfur production an important factor is concentration of hydrogen sulfide in them. At increase in the content of carbon dioxide combustion of sour gases in furnaces of a thermal stage worsens, decrease in concentration of reacting components reduces their conversion [1]. In order to increase hydrogen sulfide concentration in sour gases, it is necessary to select at purification of natural gases the corresponding absorbent selective to H_2S . However, today the Mubarek Gas Processing Plant (MGPZ) - the main producer of sulfur in Uzbekistan - uses diethanolamine (DEA) as an absorbent which is not selective for H_2S . It is possible to replace the absorbent with a tertiary amine such as methyldiethanolamine (MDEA), which is selective to hydrogen sulfide and practically does not extract CO_2 , but in this case in the product gas may remain more CO_2 than it is required. To increase selectivity to H_2S , it is possible to use a mixture of DEA with MDEA, which is selective to hydrogen sulfide, but not to exceed the allowable content of carbon dioxide in the product gas, it is necessary to select the optimum content of MDEA in this mixture.

The expected improvements in the unit operation when replacing the amine are as follows: increase of sulfur yield; improvement of economic indicators of sulfur production amine purification processes; increase of equipment service life; reduction of absorbent recirculation and water steam supply for regeneration; reduction of COS and CS_2 formation during sulfur production [2].

Table 1. Composition of acid gas at different ratios of amines [3]

Absorbent	MDEA 70% : DEA 30% (35% solution)		DEA (40% solution)	
	compositions I		compositions II	
Sour Gas	kg/h	wt%	kg/h	wt%
Hydrogen sulfide	81743.94	69.15	61293.18	51.85
Carbon dioxide	32035.59	27.10	52486.35	44.4
Water	3877.37	3.28	3877.37	3.28
Methane	520.14	0.44	520.14	0.44
Methylmercaptan	35.46	0.03	35.46	0.03
TOTAL	118212.50	100	118212.50	100.00

We performed simulation of amine purification using DEA-MDEA mixture at different amine ratios using the universal simulation system AspenHYSIS [3]. The feasibility of the proposed technical solutions is illustrated by the results of the calculations (Table 1).

Figure 1 shows the dependence of the rate constant of amine degradation under the action of CO₂ on temperature. The graph shows that MDEA is more stable than DEA, and with increasing temperature this difference becomes even more significant.

As mentioned above, the degradation of amines is maximal at high temperatures (80-110°C) and high concentrations of carbon dioxide. But desorption processes are also carried out at higher temperatures (up to 120-130°C), under such conditions during regeneration decomposition of even chemically stable alkanolamines is inevitable, especially under the influence of oxygen, which, in turn, comes from the water present in the gas and in the solution of amine.

Defoamers are divided into groups according to how they are introduced into the solution. Some antifoamers are injected in advance to prevent foaming (antifoaming agents), while others are injected when foam has already formed (antifoaming agents proper). In this case, antifoaming agents should not be introduced before the formation of foam, and antifoaming agents are not effective when foam is already formed. However, for simplicity, in the future we will refer to all of these substances as antifoamers.

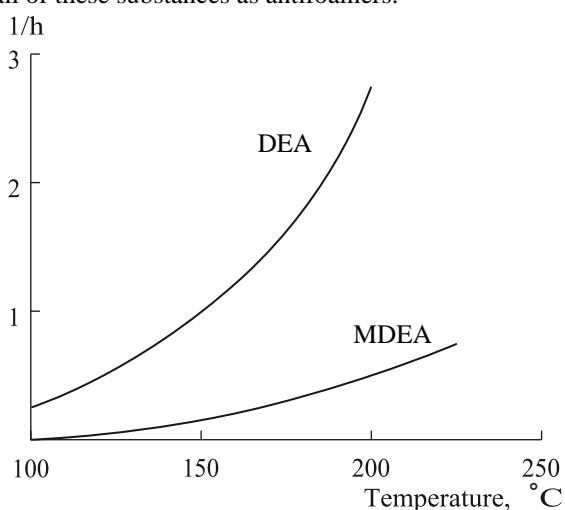


Fig. 1. Dependence of the rate constant of the thermochemical degradation of alkanolamines on temperature at CO₂ pressure > 0.1 MPa [3].

III.CLEANING OF THE ABSORBENT SOLUTION BY FILTRATION.

To reduce foaming it is also necessary to act on its causes: during foaming, non-wetted substances (impurities, corrosion products) adhere to the gas bubbles, thereby increasing the rate of foaming; together with them, passing into foam, high-boiling paraffin HCs are predisposed to increase the rate of foaming.

IV.DISPOSAL OF SPENT AMINE SOLUTION.

There are several known ways to dispose of spent amine solution. One way is disposal in thermal decontamination furnaces or disposal as liquid waste [7].

There is also the following method of disposal: water is distilled from the spent amine solution at atmospheric pressure and temperature in a cube up to 160°C. The aqueous distillation with up to 1% amine content is neutralized with sulfoantartic acid esters or alkylbenzene sulfonic acid, resulting in a surfactant solution. The cube residue is distilled under vacuum (10-20 mm Hg) to yield three fractions. The first (10-15% monoethanolamine solution) is returned to the first distillation stage, the second (98-99.6% monoethanolamine) is a commercial product. The third fraction (cube residue in the amount of 1.5-5% of the weight of monoethanolamine solution) is neutralized with acid, and the resulting solution is used as a reducing agent in the production of leather and fur. Thus, a complete recycling of the spent amine solution takes place [7].

Thus, this work analyzes the problems of amine purification and proposes possible ways of their solution: selection of optimal composition of alkanolamine mixture, maintenance of technological conditions, prevention of ingress of undesirable substances into the absorbent solution, as well as the use of special defoamer reagents to reduce foaming in the absorbent solution.

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