



ALGORITHMS AND SOFTWARE TOOLS FOR THE CURRENT STATUS OF THEORY AND PRACTICES OF DRYING NATURAL GASES AND TRENDS OF THEIR FURTHER IMPROVEMENT

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INTRODUCTION

Uzbekistan's economy is developing rapidly. The Republic pays great attention to the reform of production and the economy as a whole. On January 18, the Cabinet of Ministers of the Republic of Uzbekistan held a meeting dedicated to the results of socio-economic development of the Republic in 2013 and the most important priorities of the economic program for 2014.

President of the Republic of Uzbekistan Islam Karimov made a report at the meeting. In the speech of the head of state, it was noted that as a result of consistent implementation of the world's own "Uzbek model" of development and priority areas of the adopted Concept of further deepening of democratic reforms and the formation of civil society in the country, despite the ongoing crisis in the world economy, high growth rates and macro-economic balance of the country's economy have been ensured.

In his speech, Islam Karimov stressed that despite the slowdown in the global economy, Uzbekistan has secured growth dynamics and macroeconomic stability. Uzbekistan's GDP growth in 2013 was 8 percent, industrial output was 8.8 percent, agriculture was 6.8 percent, the budget was executed with a surplus, and the foreign trade balance was 1.3 billion dollars. The share of industry in GDP exceeded 24 percent. Mechanical engineering and metal processing grew by 121 percent, and the construction materials sector grew by 113 percent. In 2013, 26 thousand business entities started their activities, and their total number reached 190 thousand. Exports, despite a number of factors of instability in world markets, also increased by 10.9 percent. 18 percent of exports were sent abroad by entrepreneurs.





I. Current status of theory and practices of drying natural gases and trends of their further improvement

The presence of excess moisture in the gas causes a number of serious problems when transporting gas. When processing and transporting gas, due to a decrease in the temperature in the system, water vapor condenses and, consequently, water condensate is formed in it. The latter with natural gas components forms hydrates. Hydrates, deposited in gas pipelines, reduce their cross-section, and sometimes lead to emergency stops. In addition, the presence of water in the system increases the corrosion of equipment, especially when the raw gas contains acidic components. In connection with the above, natural and petroleum gases are subjected to drying before being fed to the main gas pipelines and in the processing cycle.

Physical and chemical properties of natural gas sulfur impurities

Currently, the production of hydrogen sulfide-containing natural gas is a significant part of the total volume of gas consumed. At the same time, the content of hydrogen sulfide H_2S in gases varies widely from a few fractions to several tens of percent. This gas is cleaned before being supplied to the consumer due to the poisonous nature of hydrogen sulfide and its corrosive activity. It is also a poison for catalysts used in various chemical gas processing processes. Due to the toxicity of hydrogen sulfide, its content in the gas supplied to the consumer in the air of populated areas is limited, and standards for its content in the air of the working area are established. Hydrogen sulfide is an acid that causes chemical and electrochemical (in the presence of water) corrosion of metals. Under certain conditions, sulfide cracking of metals occurs. However, hydrogen sulfide is the raw material for the production of so-called "gas" sulfur.

In addition to hydrogen sulfide, other sulfur components (mercaptans, carbon disulfide, carbon disulfide) may be present in the gas, which cause corrosion of equipment, poisoning of catalysts (during synthesis). When burned, they form sulfur dioxide. The content of sulfur compounds in the purified gas is normalized.

Physical and chemical properties of sulfur compounds of gas, as well as sulfur dioxide are presented in table 1.1

parametrs	H_2S	CO_2	CS_2	CH_3SH	C_2H_8	SO_2
Molecular mass	34.08	60.07	76.13	48.1	62.13	64.06
Temperature. C	-85.16	-138.9	-112	-123	-147.9	-75.5
tenderness	-60.4	-50.3	46.2	6	35	-10
boiling	100	102	279	197	226	157.8
critical	8.82	5.8	7.8	7.14	56.42	7.78
Critical pressure. KPa	98.5	140	170	145	207	122





Critic capacity, sm ³ /mol	0.284	0.26	0.293	0.268	0.247	0.268
Critic coefficient	18.66	-	62.73	24.56	26.77	24.91
Heat for steam on norm t	16.104	143.686	-	161.909	16.077	167.68
Tightness of steam	0.1768	0.530	0.159	0.233	0.249	0.230

II. Comparative characteristics of dehumidifiers

Currently, deg solution is mainly used for drying natural gases in the fields. The use of the Tag is isolated, although it is known that the TAG has found wider application abroad, due to its low losses at gas drying plants and other technological advantages. Currently, it is possible to produce triethylene glycol for the needs of the gas industry. Therefore, the restriction in the use of the Tag is removed due to its scarcity. The main indicators that characterize glycols as a desiccant are the depression of the gas dew point by moisture, losses with the desiccated gas, the regenerability of the saturated solution, etc. The following is a comparative assessment of the DEG and TEG parameters required when selecting a desiccant for gas drying plants.

Comparing data from the table. 2.1 in the context of the required gas drying depth for Northern gas pipelines, it can be indicated that at reduced contact temperatures, both glycols can be used with almost the same technological efficiency. As for high contact temperatures and high concentrations of solutions, the advantage of the Tag is obvious. This advantage is especially important in the summer months, when it is not possible to cool the gas below the temperature of 25-30 °C. In table. 2.1 provides theoretical data. In the conditions of the gas condensate recovery system, equilibrium gas drying is almost never achieved. Therefore, you will need a solution of a higher concentration, which is more difficult to obtain.

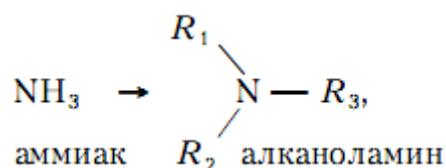
In cases where it is not possible to cool the gas below the temperature of 25-30 °C, it is very difficult to achieve drying of the gas to the dew point of -10 °C and below using deg solutions. For example, at a pressure of 4.0 MPa and a contact temperature of 30 °C to dry the gas to the dew point of -16 °C (equivalent to the dew point of -10 °C at a pressure of 7.35 MPa, required by OST 51.40-83), a solution of deg concentration of 99.2% wt is required. (taking into account the actual conditions of the process, at least 99.5% by weight). Due to a number of reasons (equipment wear, lack of an effective system for cleaning the glycol solution from the ingredients, insufficient degree of vacuuming, etc.), such a degree of solution regeneration is practically difficult to achieve in production conditions. At the same time, it is sufficient to dry the gas to this depth a Tag solution of 98.4% concentration (taking into account the actual



process conditions of at least 98.6% by weight), which is easily achievable. The required level of residual pressure in the system will not be less than 400 mm Hg.

Physical and chemical properties of ethanolamines and their aqueous solutions

Alkanolamines (amino alcohols, oxy-amines) can be considered as derivatives of ammonia, in which one or more hydrogen atoms are replaced by an alcohol radical or an alcohol and a hydrocarbon:



where R1 is an alcohol radical, such as C₂H₄OH; R₂, R₃ is either an alcohol or hydrocarbon radical, or H⁺. According to the degree of substitution of the central nitrogen atom by alkyl radicals, amines are divided into primary, secondary and tertiary.

Amines contain at least one hydroxyl group (-OH) and one amino group >N-. The presence of a hydroxyl group reduces the pressure of saturated vapors and increases the solubility of amine in water, and the amino group gives aqueous solutions the alkalinity necessary for interaction with H₂S and CO₂, which in the aqueous medium dissociate with the formation of weak acids. Ethanolamines are colorless, viscous, hygroscopic liquids that mix with water and lower alcohols in all respects, they are almost insoluble in non-polar solvents.

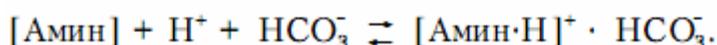
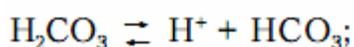
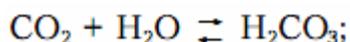
Chemosorbents are usually used in the form of aqueous solutions. The concentration of amine in the solution can vary widely, it is chosen based on experience and for reasons of corrosion control (see below). The mass concentration of alkanolamines in water is 10-60 %. Pure amines are viscous liquids with a high freezing point (with the exception of DHA and MDEA). However, aqueous solutions of ethanolamines are less viscous and freeze at low temperatures (below minus 10 °C), which makes it possible to use them in industry.

Mechanism of absorption of H₂S, CO₂ and other sulfur components

The mechanism of absorption of H₂S and CO₂ by aqueous solutions of amines is discussed further. Alkanolamines, being alkalis, easily react with acidic gases H₂S (CO₂), forming water-soluble salts. The following reactions occur:



Tertiary alkanolamine does not have a mobile H^+ atom in the amine group, so it becomes impossible to proceed a direct and rapid reaction with CO_2 on the carbamate type, and the interaction is carried out through a preliminary and slow stage of formation and dissociation of carbonic acid:



The final products of the reaction are bicarbonate and carbonate. Thus, the difference in the reaction rates of tertiary amines with H_2S (instantaneous reaction) and CO_2 (slow reaction) is much greater than for primary and secondary amines. This makes it possible to use in practice tertiary amines for selective extraction of H_2S from mixtures of it with CO_2 .

In accordance with the above chemical reactions of H_2S and CO_2 with amines, the concentration of active (free) amine in solution can be calculated by the equation

$$C_{\text{ж}} = C_{\text{ж}_0} (1 - \alpha_A - n\alpha_B),$$

where $C_{\text{ж}}$ is the concentration of free amine, mol/l; $C_{\text{ж}_0}$ is the initial concentration of amine, mol/l; α_A and α_B are the saturation of amine, respectively, H_2S (A) and CO_2 (B), mol/mol; n - stoichiometric coefficient (for primary and secondary amines $n = 2$, for tertiary amines $n = 1$).

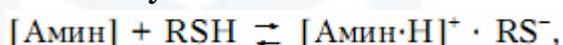
The literature data on the temperature dependence of the rate constant of CO_2 interaction with ethanolamines are summarized as the following equations:

For MDA $\lg r_B = 11,070 - 2140/T;$

For DEA $\lg r_B = 10,046 - 2050/T;$

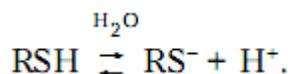
For MDEA $\lg r_B = 8,932 - 2426/T,$

where GW is measured in $1/(\text{mol}\cdot\text{s})$. The reactivity of alkanolamines varies in the series: primary > secondary > tertiary and correlates with their alkalinity. Carbon dioxide forms various by-products with alkanolamines. The mechanism of their formation is not fully understood. Some of them are destroyed at the stage of regeneration of the absorbent and again secrete alkanolamine, the other part is not regenerated, causing loss of amine. The largest number of non-regenerated compounds is typical for primary alkanolamines. Mercaptans, being acids, react reversibly with alkanolamines to form water-soluble mercaptides:



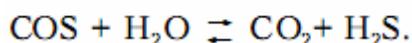


This reaction is preceded by the dissolution of mercaptans in the absorbent and



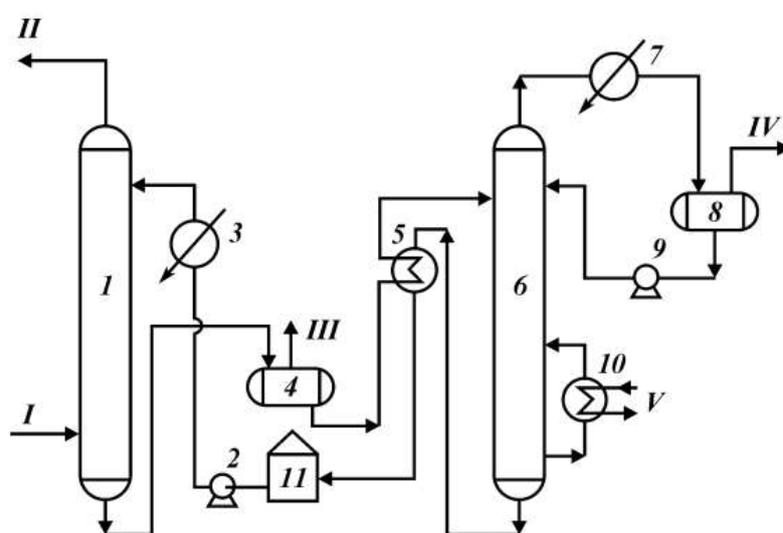
dissociation into ions:

The acidity of mercaptans is much lower than that of H₂S and CO₂, so that the latter displace mercaptans from I x compounds with amines. Mercaptides are unstable compounds that easily break down when heated. Carbon monoxide in aqueous solutions of amines is hydrolyzed:



The heat required for regeneration of the saturated solution is transmitted to the solution in reboilers heated by low-pressure steam. The acid gas from the desorber is cooled to condense most of the water vapor contained in it. This phlegm condensate is continuously returned back to the system to prevent an increase in the concentration of the amine solution. Usually this phlegm is fed to the top of the desorber, slightly above the entrance of the saturated solution to condense amine vapors from the acid gas stream.

The scheme provides an expander (eraser), where by reducing the pressure of the saturated solution, physically dissolved hydrocarbons and partially hydrogen sulfide and carbon dioxide are released in the absorbent. After cleaning, the expansion gas is used for its own needs as a fuel gas or compressed and fed to the source gas stream. In some cases, the expander is mounted with a column for cleaning the released gas.



Picture 1: scheme of one-pointed cleaned gas mixture ethanolamine. 1- gas to cleaning II-cleaned gas III- expander gas IV- steaming. 1-absorber. 2,9- pumps. 3,7- refrigerators 4-expander 5- heatchanger, 6- desorber 8- separation



A scheme with separated flows of regenerated solution of the same degree of regeneration is widely used in industry (Fig. 2.2). The main amount of regenerated solution (70-80 %) with an increased temperature is fed to the middle part of the absorber - this improves the absorption kinetics of acidic components and promotes the hydrolysis of COS to H₂S and CO₂. In order to obtain a fine gas purification, the remaining amount of solution (20-30%) is further cooled in an air or water cooler and fed to the top of the absorber. This scheme reduces operating costs, since only part of the solution is subjected to deep cooling.

This scheme, with a certain increase in the multiplicity of the circulation of the absorbent, allows compared with the usual scheme of this type to reduce the steam consumption for the regeneration of the solution by up to 10-15%, with minor capital additional costs for binding the second flow of the regenerated solution.

When cleaning a gas with a high content of acidic components, when a large amount of absorbent is needed, it is advisable to double the expansion (weathering) of the saturated amine at different pressures. At the I stage of the process and at a pressure of 1.5-2.0 MPa, the main amount of dissolved hydrocarbons is released from the solution, which provides a further low content of them in acid gas (<2% vol.) - this guarantees the high quality of the resulting sulfur. This stream of expansion gas is either used for its own needs in the form of fuel gas, or after rough cleaning from hydrogen sulfide (or without it) is compressed and mixed with the main stream of raw gas entering the treatment. At stage II, at a pressure close to atmospheric pressure, without thermal regeneration, a stream of acid gas is released from the solution, which, after water is extracted from it and cooling, can be directly directed to the sulfur production plant. This reduces the steam consumption for regeneration of saturated amine solutions to 10%.

In the scheme, a pump is additionally installed to supply the saturated solution from the second eraser to the desorber, which operates under extremely unfavorable conditions (a high degree of amine saturation with acid gases and a relatively high temperature of the solution) - this is a disadvantage of the scheme.

When cleaning a gas containing along with H₂S and CO₂, carbon disulfide in the absorber can be provided with a zone of absorption and hydrolysis of COS, consisting of 5-8 plates, where a regenerated amine solution with an increased temperature of 60-80 °C is fed. In this case, the solution flows from the upper zone of the absorber to the lower part of the hydrolysis zone for effective management of the process.





CONCLUSION

During the performance of this article work identified and studied:

- Comparative characteristics of dehumidifiers are analyzed;
- Physical and chemical properties of ethanolamines and their aqueous solutions have been studied;
- The mechanism of absorption of H_2S and CO_2 and sulfur components has been studied;
- Technological schemes of gas purification process with water solutions of amines have been studied;
- Proposed adsorption treatment of natural gas from sulfur compounds with zeolites;
- Intensification of the process of natural gas purification from H_2S and CO_2 and organosulfuric compounds;
- Application of water-non-water absorbents based on diethanolamine and methyldiethanolamine.

New technologies for processing natural and associated gas are considered.

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