

# Pollutant Sources and Foaming Control Measures of Decarbonization Solution in Natural Gas Purification Plant

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**Abstract:** Yanbei project of Schlumberger Copower Oilfield Engineering Co., Ltd. - natural gas purification plant decarbonization unit is equipped with two sets of decarbonization systems (parallel operation). The two sets of systems adopt two tower process, full lean liquid circulation regeneration process, one tower absorption (absorption pressure 5.4mpag), one tower regeneration (regeneration temperature 95°C ~ 110°C), purified natural gas carbon dioxide content  $\leq 2.5\text{vol}\%$ , single set The treatment capacity is 2300 KM<sup>3</sup> / d. This paper introduces the problems existing in the decarbonization solution of the decarbonization unit in the natural gas purification plant in recent three years, analyzes the causes of pollutants affecting the quality of the decarbonization solution, and probes into the control measures for the pollution of the decarbonization solution, so as to provide reference.

**Keywords:** Natural gas purification plant; Decarbonization solution; Foaming reason; Control measures

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## 1 Introduction

Decarbonization is the process of removing carbon dioxide from the mixed gas, which is mainly used in the treatment of raw natural gas or coal gas. The main component of decarbonization solvent is N-methyldiethanolamine (MDEA), which is usually colorless or yellowish viscous liquid. It can dissolve with water and alcohol, has low reaction heat, stable chemical properties, non-toxic and difficult

to degrade. It has strong absorption capacity for acid gases such as carbon dioxide. In the absorption process, the solubility of non-polar gases such as hydrogen, methane and higher hydrocarbons is very low, so it is difficult to purify. The loss of effective components in natural gas is small; the whole absorption process belongs to physical and chemical absorption process, and the regeneration process needs external heat source. The by-product carbon dioxide has high recovery and purity ( $\geq 99.5\%$  dry basis). After simple treatment, it can be used for carbon supplement in urea synthesis. MDEA solution decarbonization method has many advantages, such as high acid gas load, low regeneration energy consumption and low corrosion to equipment. However, foaming is easy to occur in the process of natural gas desulfurization and decarbonization<sup>[1]</sup>. After solution foaming, the treatment capacity of natural gas purification unit will be reduced, the carbon dioxide content of purified gas will exceed the standard, or the alcohol amine solution will enter the downstream unit with the natural gas flow, resulting in potential safety hazards and economic losses. Economic losses<sup>[2]</sup>. This paper introduces the changes of MDEA solution, treatment capacity and corrosion in the process of natural gas decarbonization, summarizes the actual operation experience, and puts forward some suggestions on the operation and management of MDEA solution.

## 2 The existing problems of decarbonization solution in natural gas purification plant are summarized

Since the operation of the decarbonization unit in the purification plant in 2018, only a small amount of

MDEA solution has been supplemented every year. However, with the continuous high load operation of the unit, there are gradually problems such as solution foaming in the absorption tower and regeneration tower, decarbonization efficiency decreasing, solution loss increasing, solution color changing from light yellow to dark brown, etc. when the wall thickness of the MDEA rich liquid pipeline elbow is detected,

the pipeline elbow is also detected. There are different degrees of thinning. At the beginning of 2021, the purification plant analyzed the MDEA lean solution and found that the concentration of acetate and thiosulfate ions in the solution was on the high side, while the concentration of chloride and sodium ions was on the high side. (Table 1 is the main analysis index of MDEA lean solution)

**Table 1.** Main analysis indexes of MDEA lean solution

Category	Test items	Unit	Test methods	Test results
Chemical composition	Total amine concentration <sup>a</sup>	%wt	GB/T 9722-2006	53.7
Nonmetallic anion	Acetate	mg/L	SY/T 7001-2014	675.4
	Chloride ion	mg/L	SY/T 7001-2014	85.6
	Oxalate	mg/L	SY/T 7001-2014	5.4
	Thiosulfate	mg/L	SY/T 7001-2014	96.6
Metal cation	K	mg/L	Consult HJ 700-2014	34.1
	Na	mg/L	Consult HJ 700-2014	82.6
	Fe	mg/L	Consult HJ 700-2014	5.9
	Ca	mg/L	Consult HJ 700-2014	Not detected, <5

When the concentration of acetate is high, MDEA solution is degraded after long-term use, and acetate, oxalate and other heat stable salt ions are generated<sup>[3]</sup>. Oxygen or other impurities in feed gas can react with amine to form a series of acid salts, such as chloride, formate, acetate, thiosulfate, etc. The relatively weak salt formed by H<sub>2</sub>S and CO<sub>2</sub> and amine solution will decompose during regeneration heating, while the salt formed by other acidic components in feed gas and amine solution will not decompose during heating, and can not be regenerated by heating and desorption. These salts are collectively referred to as heat stable salt (HSS). Because the anion of the thermal stable salt formed is easy to replace the combination of sulfur ion and iron ion on iron sulfide, the dense iron sulfide protective film on the inner wall of pipeline and equipment will be destroyed, and the corrosion of pipeline and equipment will be accelerated. Although the allowable concentration of thiosulfate is high, it will accelerate the formation of N, n-di (hydroxyethyl) glycine, which is the degradation product of MDEA, and N, n-di (hydroxyethyl) glycine is one of the important factors causing corrosion<sup>[4]</sup>.

### 3 Analysis of pollution sources affecting decarbonization solution of natural gas purification facilities

#### 3.1 The operation fluctuates greatly

The results show that the system has fast loading and

unloading, large fluctuation of working pressure, too much external heat supply of reboiler in regeneration tower, too fast gas-liquid contact speed, and excessive stirring of amine solution. Defoamer can effectively reduce the surface tension and completely diffuse in the gas-liquid interface, thus reducing the surface elasticity and viscosity. Defoamer molecules are easy to disperse and absorb, resulting in a low strength surface film. In the diffusion process, defoamer molecules can effectively reduce the thickness of liquid film of bubbles, destroy the stability of bubbles and make bubbles explode. The diffusion coefficient of defoamer must be greater than 0 in order to be a thermodynamic spontaneous process. If the foaming agent of the defoamer is determined by many experiments, it means that the defoamer will not be spontaneously and evenly dispersed on the surface of the defoamer, so it can continue to play the defoaming role. There are two kinds of Defoamers in common use, one is the foaming agent which can reduce the surface tension of two layers of liquid film to form the breaking point, the other is the foaming agent which can inhibit the formation of bubbles.

#### 3.2 Surfactants

Surfactant is easy to cause solution foaming. Common surfactants include corrosion inhibitors and lubricants. The mechanism of surfactant affecting the foaming of MDEA solution is that the surfactant molecules are arranged on the surface of the liquid

membrane in an orderly manner, and the hydrophilic groups of the molecules continuously attract the liquid part of the liquid membrane. Lipophilic groups can effectively prevent liquid evaporation, and at the same time, these two functions make bubbles relatively stable and not easy to break.

### 3.3 The influence of solid particles

The solid particles in the solution mainly contain corrosion products, such as steel slag in pipes, FES, Fe in carbon steel equipment, etc., and activated carbon which plays a role of filtration is gradually crushed and becomes finer in the process of use. These solid particles gather in the liquid film of the bubble, increase the surface viscosity and flow resistance of the liquid film, slow down the flow of the liquid film, and increase the stability of the bubble. Iron sulfide particles have the greatest influence on the foaming performance. Moreover, the suspended iron sulfide Solid Particles in the solution, when flowing at high speed in the heat exchanger pipeline, will accelerate the iron sulfide film falling off, thus accelerating the corrosion of pipeline and equipment.

### 3.4 Natural gas contains H<sub>2</sub>S

If natural gas contains H<sub>2</sub>S, H<sub>2</sub>S will react with MDEA solution to reduce the active components in MDEA solution, which is also a kind of pollution. At the same time, Fe reacts with H<sub>2</sub>S in process gas to form FES (Fe + h<sub>2</sub>s-fes + H<sub>2</sub>), which can promote the fusion of MDEA solution with a small amount of hydrocarbons. In natural gas of absorption tower, hydrocarbons can become strong foam stabilizers and cause severe froth.

## 4 Research on the control measures of decarburization liquid foaming in natural gas purification plant

### 4.1 Amine purification unit

The device mainly removes the thermally stable salt from the system to reduce the corrosion of the equipment, reduce the increase of bound amine and reduce the foaming frequency, so as to improve the efficiency of decarbonization solution. In order to keep the solution clean, a bypass filter system is used to effectively remove mechanical impurities, iron sulfide and decomposition products. Filter about 10%

MDEA solution (6 ~ 7m<sup>3</sup> / h) before the inlet of lean solution pump. In the first step, a mechanical filter with a filtration accuracy of 10 μ m is used to remove large solid particles from the solution. In the second step, the activated carbon filter is used to remove the small particles while desorbing the decomposition products of the solution. In the third step, the mechanical filter with a filtration accuracy of 5 μ M can filter the activated carbon powder and other small particles carried upstream<sup>[5]</sup>. By adopting the above measures, the mechanical impurities, iron sulfide and decomposition products in MDEA solution are greatly reduced, and the solution system is gradually stable.

### 4.2 Purification of feed gas

Feed gas contains many components, such as oily wastewater and various surfactants, which can cause bubbles in the solution. Therefore, before the introduction of feed gas, a coalescence filter is set up, and a filter element with a filtering accuracy of 10 μ m is used to remove most of the solid impurities and oil impurities in the gas phase. The pollution and loss of MDEA solution caused by solid-liquid impurities carried by gas phase are reduced as much as possible.

### 4.3 Strengthen the blowdown and make up the desalted water in the system. If necessary, the solution can be filtered by external circulation online

The foaming of MDEA solution is mainly affected by the impurities entering the solution, the solution itself and the thermal stability of decomposition products. The impurities and sediments can be discharged from the system through low point blowdown, and the frequency and duration of blowdown can be increased appropriately, and then the desalted water can be added to maintain the liquid phase equilibrium of the system. When the solubility of MDEA is lower than 40%, fresh solution should be added to keep the overall concentration of the solution at about 45%. When the impurity content of the solution is large, the external filtering and degreasing device can be used to filter the MDEA solution online to remove most of the system It can be divided into solid impurities, sediment and oil impurities<sup>[6]</sup>. In addition, underground tanks and storage tanks storing MDEA solution are protected with nitrogen to prevent oxygen in the atmosphere from polluting the solution.

## 5 Summary

Through the study of decarbonization solution, it is found that: it is widely used in coal acid gas purification and acid gas removal of gas, oil field gas, refinery gas and city gas, and has good selective adsorption effect on H<sub>2</sub>S and CO<sub>2</sub>. It is commonly used in the purification of synthetic ammonia, methanol production gas and natural gas purification process. According to the characteristics of decarbonization solution, this paper analyzes the existing problems of decarbonization solution in natural gas purification plant and the causes of pollution sources of decarbonization solution, and puts forward the strategy of decarbonization solution in natural gas purification plant.

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