A Method for Reducing Corrosion During Gas Purification from Sulfur Components

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Abstract: At the Gazli Gas Processing Plant, the process of purification of gases from acidic components with metildietanolamin solution leads to the occurrence of corrosion in technological systems. It was therefore tested by gravimetric methods with an anticorrosion inhibitor at a temperature of 120 0 C and several different concentrations, and inhibition technology was proposed.

Keywords: hydrogen sulfide, carbon dioxide, corrosion, gas condensate, hydrocarbon, inhibitor, metildietanolamin, gravimetrik, sulfur, desorber, TFO (thiosemicarbase-based inhibitor) desorber, division.

Introduction. Corrosion damage to metal products, equipment, structures and devices worldwide account for 25-30 % of annually produced metals.

Therefore, it is possible to study the causes of corrosion in each production plant and achieve high efficiency in protection with anti-corrosion coatings and effective inhibitors suitable for this environment.

In particular, the main goal of the study was to reduce the corrosion rate at the Gazli GPP.

An aqueous solution of methyldiethanolamine 35-40 % is used to purify natural gases from acidic components at the Gazli GPP.

When cleaning a solution of saturated methyldiethanolamine, H₂S and CO₂ included in its composition have an aggressive effect on the metal, leading to chemical corrosion of the metal and forming the following mechanisms of corrosion reactions.

$$CO_{2(\Gamma)} \leftrightarrow CO_{2(c)}$$

 $CO_{2(c)} + H_2O_{(c)} \leftrightarrow H_2CO_{3(c)}$
 $H_2CO_{3(c)} \leftrightarrow HCO^{-1}_{(c)} + H^+_{(c)}$
 $HCO^{-1}_{(c)} \leftrightarrow CO^{2-}_{(c)} + H^+_{(c)}$
 $2H^+_{(c)} + 2e^- \leftrightarrow H_{2(c)}$
 $H_2S_{(\Gamma)} \leftrightarrow H_2S_{(c)}$
 $H_2S_{(c)} \leftrightarrow HS^-_{(c)} + H^+_{(c)}$
 $HS^-_{(c)} \leftrightarrow S^{2-} + H^+_{(c)}$
 $2H^+_{(c)} + 2e^- \leftrightarrow H_{2(\Gamma)}$

The composition of the methyldiethanolamine solution in the desorber of the Gazli Gas Processing Plant is shown in Table 1 below.

When cleaning gases from acid components, corrosive products in instruments and equipment are exposed to hydrogen sulfide, along with moisture, carbon dioxide, and therefore it is necessary to take measures to protect process equipment from corrosion.

Table 1.

The composition of the methyldiethanolamine solution for gas treatment of the Gazli GPP

	me/m²	Purified solution (methyldiethanolamine)			Saturated solution (methyldiethanolamine)				
		ation	Mole/	H ₂ S Mole/ mole	Conce ntratio n C%	CO ₂ Mole/ mole	H ₂ S Mole/ mole	Мех/ пре. мг	pН
1	4	9,5	0,05	0,02	9,3	0,27	0,03	0,007	8,2
2	5	33,8	0,04	0,06	33,4	0,27	0,12	0,007	8,3
3	4	7,1	0,03	0,02	6,9	0,51	0,02	0,003	7,9
4	7	33,8	0,01	0,06	33,4	0,27	0,12	0,004	8,0
5	7	33,1	0,01	0,05	32,7	0,28	0,09	0,007	8,4
6	10	40,0	0.02	00,1	39,5	0,17	0,11	0,004	7,8

Desorbers at the Gazli GPP are made of steel $09\Gamma2C$ and 12X18H10T, and the corrosion rate is high, mainly due to the absence of alloying elements in steel $09\Gamma2C$. It is for this reason that the studies considered measures to reduce the corrosion rate of steel grade $09\Gamma2C$ [1].

It is noteworthy that the corrosion properties of $09\Gamma2C$ steels under the action of CO_2 and H_2S gases were not considered. Alloys containing $09\Gamma2C$ steel in the presence of dissolved hydrogen sulfide and carbon dioxide in various media have a significant effect on the formation kinetics and composition of corrosion products. The question of the joint influence of these two factors on the development of corrosion processes is still open.

Based on this, studies of the corrosion process were carried out in time, temperature, pH and various concentrations of the medium. [2,3,4].

Research method. On the basis of the given data, studies of laboratory work on the gravimetric method of corrosion rate according to GOST 9.905-82 were carried out. Then 0.5 l of a saturated solution of methyldiethanolamine (pH of the medium <6.8) is transferred into the flask. After thorough cleaning and drying, a plate made of $09\Gamma 2C$ steel with an area of 22 sm^2 is weighed on an analytical balance and placed in a solution. At a temperature of $120 \, ^{0}C$ and $360 \, h$ without inhibitors and inhibitor solutions, tests were carried out. A corrosion inhibitor of the TFO brand (thiosemicarbazidebased inhibitor) was used as an inhibitor (Fig. 2).

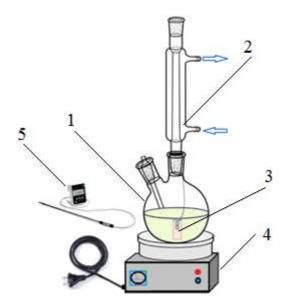


Figure 2. Laboratory instrument for the gravimetric study of corrosion inhibitors.

1-flask; 2-refrigerator; 3-metal plate; 4-heater; 5-thermometer.

The metal plate is then cleaned with grinding paper and weighed on an analytical balance. The results are recorded and calculated using the following formula.

1).
$$K_{grav} = \frac{(m_1 - m_2)}{S \cdot \tau}$$
;

2).
$$\gamma = \frac{W_0}{W_{\text{MHT}}}$$
;

The following formula.

2).
$$\gamma = \frac{W_0}{W_{\text{uhr}}}$$
;

3). $Z = \frac{W_0 - W_{\text{uhr}}}{W_0} \cdot 100\%$.

According to these formulas, the rate of corrosion (K_{grav}) , the coefficient of braking (γ) and the degree of protection from corrosion (Z) [5,7,8].

where: m_1 - is the mass of the metal plate at the beginning of the study, g: m_2 - is the mass of the metal plate after exposure, g: W_0 - is the decrease in the mass of the metal in an inert solution, W_{ing} - is the decrease in the mass of the metal in the solution under consideration, S - is the surface of the metal plate, sm²: t_1 exposure time, hour.

Table 2 Results obtained by the gravimetric method on plates made of steel 09\(Gamma\)2C in solution with and without inhibitors

Inhibitor concentration, mg/l	Mass of the metal plate m_I , g	Weight of metal plate m_2 , g	$\Delta \mathbf{m} = m_1 - m_2, \Gamma$	Corrosion rate, g/m ² *s. (υ=Δm/S·τ)	γ	Z, %
0	16,0163	15,9283	0,0880	0,1111	-	-
25	16,0531	16,0223	0,0308	0,0388	2,85	65,0
50	16,0816	16,0607	0,0209	0,0263	4,21	72,2
75	16,0621	16,0530	0,0091	0,0114	9,67	89,6
100	16,0389	16,0343	0,0046	0,0058	19,13	94,7

As a result of the research, the image of metal plates in inhibitory and non-inhibitory media with an AD106-C microscope approaching 80 times is shown in Figure 3.





Figure 3. Microscopic view of 09Γ2C metal samples in a) inhibitor and b) inhibitor solutions.

According to the results of gravimetric analysis, it was found that with inhibitor a) there is no corrosion of the inhibitor complex in the steel sheet, and without inhibitor b) the solution has uneven corrosion, wounds and pits on the metal sheet[9,10].

Based on the results of the study, a technological scheme was developed for the use of a new type of corrosion inhibitor TFO in technological devices in order to sharply slow down corrosion in gaseous media. (Figure 4).

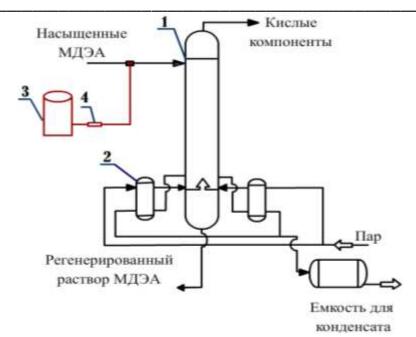


Figure 4. Technology of application of anticorrosive corrosion inhibitor TFO, which occurs during amine gas purification from acidic components.

1-desorber; 2 - evaporator; 3 - container for corrosion inhibitor; 4 - pump.

In Scheme 4, since desorber 1 is the main corrosion site, corrosion inhibitor TFO 3 with a saturated solution of methyldiethanolamine, which must be regenerated in reboiler 2, is fed into the desorber by diaphragm pump 4. [6,11]

Results and its discussion. Changing the concentration of the TFO inhibitor had a high impact on the anticorrosion efficiency and corrosion rate, which was reflected in the results obtained. For example, at a temperature of $120~^{0}$ C, the corrosion rate in a metal plate without inhibitors was $0.1111~\text{g/(sm}^{2} \cdot \text{h)}$, and the corrosion rate decreased to $0.0058~\text{mg/(sm}^{2} \cdot \text{h)}$ when the inhibitor concentration reached 100~mg/h. l.

Correspondingly, the anti-corrosion efficiency of the inhibitor was 94.7 %, the braking coefficient was 19.13%.

This is due to the fact that at high temperatures the adsorption capacity of the inhibitor is lower than the desorption capacity, and an increase in temperature breaks the electrostatic bonds between the inhibitor and iron atoms on the surface of the steel sample. The results of this study showed that the TFO inhibitor is a good effective inhibitor in amine gas cleaning, and the use of 0.1% corrosion inhibitor against corrosion in gas cleaning from sulfur compounds showed high efficiency.

Conclusion. It can be concluded from the article that the concentration of the corrosion inhibitor TFO of 0.1% turned out to be quite effective when cleaning gases with methyldiethanolamine solutions to reduce the corrosion rate in devices and technological systems under the influence of acidic components.

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