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Investigation of the anticorrosion properties of nano-CEC in amine environments

¹Kemelzhanova A., ¹Mukasev K., ¹Yar-Mukhamedova G., ²Lampke Th.

¹Al-Farabi Kazakh National University, Almaty, Kazakhstan

²Technische Universität Chemnitz, Germany

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Abstract: It is known that of the methods for purifying gas fraction from hydrogen sulfide is amine treatment. Various types of amines are used to remove hydrogen sulphide, carbon dioxide and carbon dioxide from petroleum gases. The choice of specific amine depends on the needs of the process. Mono-ethanolamine (MEA) (C₂H₄OH) NH₂ and diethanolamine (DEA) (C₂H₄OH) 2NH are commonly used. Both are ammonia derivatives. The develop recommendations on the choice of material from which to make equipment for amine plants, comparative studies of corrosion resistance of traditionally used low-temperature carbon steel and nano-composite coatings obtained by electrodeposition method. The research has shown, that average corrosion rate on a standard sample (without coatings) is 0.9969 mm/year. Because of this, the frequency of changing equipment for cleaning oil from acidic components (hydrogen, sulfide, carbon dioxide and carbon dioxide) on average is 1 time per two years. During the one year testing period nano-composition coatings showed protective efficacy when exposed to acidic corrosion/erosion. It should be noted that there is a likelihood of damage to the coating during mechanical action. It is established that the use of protective coatings leads to an increase in corrosion resistance 24-56 times, which indicates the expediency of their use in these operating conditions.

Keywords: nano-composite coatings, corrosion resistance, amine media, protective properties, carbon steel.

Information about author:

Aiman Kemelzhanova – PhD., Al-Farabi Kazakh National University, Kazakhstan. ORCID ID: 0000-0001-6892-2763. E-mail: aiman_90.08@mail.ru

Kanat Mukasev - Prof., Al-Farabi Kazakh National University, Kazakhstan. ORCID ID: 0000-0001-6892-2763.

Gulmira Yar- Mukhamedova - Prof., Al-Farabi Kazakh National University, Kazakhstan. ORCID ID: 0000-0001-6892-2763. E-mail: gulmira-alma-ata@mail.ru

Thomas Lampke - Prof., Dr. Thomas Lampke, Technische Universität Chemnitz, Germany. ORCID ID: 0000-0001-6892-2763. E-mail: thomas.lampke@mb.tu-chemnitz.de

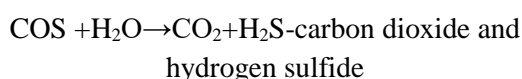
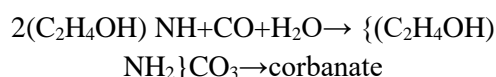
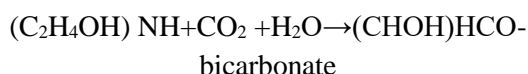
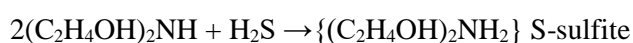
Introduction

Special interest in composites and coatings has emerged last decades in connection with sharp growth of requirements to operational properties of the materials working in the conditions of corrosive medium, friction and deterioration. In this connection working out of effective and economic methods of nano-coatings reception, studying of process of

electroplating, as well as research of electrolytic coatings microstructure influence on its properties are the actual problems of modern materials science. Generally, amine equipment is used for cleaning petroleum gases from hydrogen sulfide, carbon dioxide and carbon dioxide from petroleum gases. These substances must be removed because of their toxicity, corrosion and ability to pollute the environment. As a rule, amine plants are made of low-temperature carbon steel, while solutions of

amine dissolve copper, bronze and most alloys turn into zinc or copper [1-5]. The weakest point of the amine system is pipelines on the saturated amine line, often suffering due to intense corrosion. Iron sulfide (FeS) is formed on a metal surface under the influence of hydrogen sulfide. The stripper (amine regeneration column), which contains a lot of hydrogen sulfide and carbon dioxide, is the most corrosive [6-10]. Corrosion damage decreases at low temperatures. The average corrosion rate for conventionally used materials is 0,9873 mm/year. Therefore, it is necessary to completely change the equipment once every two years.

The compositions of petroleum gases include aliphatic hydrocarbons, hydrogen sulfide, carbon dioxide and other components. To neutralize them, amine solutions are used. Monoethanolamine (MEA) (C₂H₄OH) NH₂ and ethanolamine) DEA (C₂H₄OH)₂NH are commonly used. Each of them has its advantages and disadvantages. MEA better purify fractions from hydrogen sulphide than DEA. However, MEA can combine with other substances such as CS (carbon disulfide) and form salts that remain in the amine solution, and the presence of O enhances the process [11-21]. Over time, these salts can form deposits, which lead to loss of amine solution and causes equipment corrosion. DEA, which is chemically weaker than MEA, does not form significant amounts of salts, therefore, the solution of DEA is lost less during the formation of salts. In addition, since the chemical bond between DEA and hydrogen sulfide is weaker than that between MEA and hydrogen sulfide, less heat is required to regenerate DEA to separate absorbed hydrogen sulfide and other acidic components, therefore, to remove acidic components, gases are treated with a solution of diethanolamine (DEA):



Experiments

The composition of petroleum gases includes aliphatic hydrocarbons, hydrogen sulphide, carbon dioxide, etc. The average component

composition of high and medium pressure gas is presented in Table 1. Hydrogen sulfide must be removed because of its toxicity, corrosiveness and the ability to pollute the environment. During combustion, SO and S are formed – potentially hazardous substances. One of the ways to purify the gas fraction from hydrogen sulphide is the amine treatment. To remove hydrogen sulphide, carbon dioxide and carbon dioxide from petroleum gases, various types of amine are used.

It is known that choice of a particular amine depends on the needs of the process. Typically, mono-ethanol-amine (MEA) (C₂H₄OH)₂NH and di-ethanol-amine (DEA) (C₂H₄OH) NH₂ are used. Both are derived from ammonia.

Table 1 - Average component composition of high and medium pressure gas

Name of components	Medium pressure gas from unit 200 (% weight)	High pressure from unit 200 (% weight)
Neitrogen	0.78	1.1
Carbon dioxide	4.5	6.38
Hydrogen sulfide	22.32	19.44
Mercaptan	0.01	0.0073
Methane	24.12	28.75
Ethane	14.36	12.9
Propane	19.36	15.8
Butane	4.61	3.54
Isobutane	2.32	2.12
Pentane	2.29	0.9
Isopentane	2.34	1.51
Hexane and above	2.87	3.37
Humidity of gas (% weight)	0.36	4.22
Density at 0 ⁰ C (km/m ³)	1.175	1.144

MEA can better clean fractions of hydrogen sulphide than DEA. However, MEA can be combined with other substances such as CS (carbon disulfide) and form salts that remain in the amine solution, and the presence of O enhances the process. Over time, these salts can form a deposit, which leads to loss of amine solutions and causes corrosion of the equipment.

DEA, which is chemically weaker than MEA, does not form significant amounts of salts, so the DEA solution is lost less when forming salts. In addition, since the chemical bond between DEA and hydrogen sulphide is weaker than the bond between MEA and hydrogen sulphide, DEA regeneration requires less heat to separate absorbed hydrogen

sulphide and other acidic components; therefore, to remove acidic components, the gases are treated with a solution of diethylamine.

One of the methods of protection against corrosion damage of materials was the nanostructured composition coatings (nano-CEC) on chromium base. In order to evaluate the effectiveness of nano-CEC protective properties, it has been decided to test for corrosion/erosion resistance with corrosion obtaining samples. Samples are made of carbon steel ASTM A333 GR6:

- Carbon, % wt.=0.30 max.
- Manganese, % wt.=0.29-1.06 max.
- Phosphorus, % wt. = 0.025 max.
- Sulfur, % wt. =0.025 max.
- Silicon, % wt. = 0.10 min.

Obtaining of corrosion samples was made using electrodeposition technologies. Corrosion samples are pairwise installed on the first and third Y300 threads on the lines of the enriched amine. After the extraction of corrosion samples, a primary examination of corrosion samples was carried out, consisting of a visual and gravimetric assessment of the state of obtaining.

Results and discussions

The difference between the samples CC3112 LP installed on Y300 from the CC3212LP pervious ones consisted in the temperature of electrodeposition, and also the fact that a program was developed that provides for the installation and periodic extraction of samples for the survey. The location of the experiment is the fifth sting U300, on which there are a sufficient number of low pressure fittings, which allow installing and removing corrosion samples without affecting the technological process.

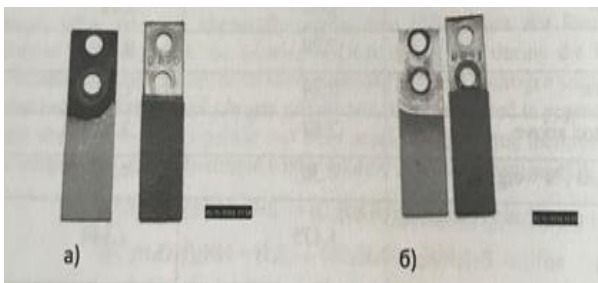


Fig. 1. a) the corrosion sample CC3112LP, installed on U300 equipment b) the corrosion sample CC3212LP, installed on U300 equipment

Corrosive samples are installed on the fifth string of U300 on the line of enriched amine and a

separation collection. As an indicator of corrosion-erosion resistance of obtaining in conjunction with the samples with the nano-CEC Cr-C, standard made of carbon steel ASTM A333 GR6 without coating are installed. Survey of the state of corrosion samples was conducted after 6 month, Fig.2:

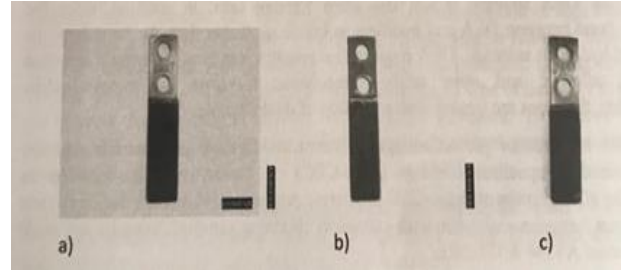


Fig.2.a) corrosive sample CC03004LP (sample D875); b) corrosive sample CC03005LP (sample D896); c) corrosive sample CC03006LP (sample D888)

According to the data obtained during the examination of corrosion samples, corrosion rates were calculated, a visual and metrological evolution of the electrodeposition obtaining state was made. On the surface of the corrosion –proof sample D875 with the electrodeposition pated by the technology of 2017 (position CC03004LP), there are no traces of mechanical and corrosion-erosive damage. The average deposition thickness, color and surface roughness have undergone changes. The corrosion rate on the standard sample D173 (without coatings) was 0.9969 mm/year, which is 32 times higher than on the D875 sample (with electrodeposition obtaining). On the figure 3 typical microstructure of corrosion defeats is shown.

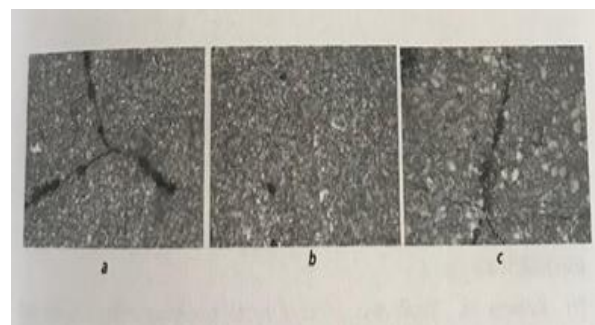


Fig.3. Typical microstructure of corrosion defeats of the nano-CEC surfaces, obtaining by electrodeposition method

On the surface of the corrosion-proof sample D896 with the electrodeposition obtaining, performed on the (fig.3), there are no traces of corrosion-erosion damage. The geometric parameters of the sample are broken (a slight bend relative to the generatrix). On the lateral surfaces, there are traces of

mechanical impact, which probably occurs when the sample is removed from the fitting. The average deposition thickness, color and surface roughness have undergone changes. Comparative analysis with the standard sample was not carried out, due to the lack of the possibility of installing the second sample at this position.

Conclusions

At the expiration of the test period, it was established that corrosion and corrosion erosion damage was not observed on the surface of corrosion samples with the electrodeposition obtaining under 303 K temperature. The average thickness of the obtaining, color and surface roughness did not undergo significant changes. In the zone of the partition between the base metal of the sample and the obtaining, the metalized coating isn't peeled off.

On the surface of the corrosion-proof sample D888 with the electrodeposition spraying technology (position CC03006LP), there are no traces of corrosion-erosion damage. On the side of the sample, the damage increased to 11 mm. An initial stage of detachment of the coating on the surface from the

side of the room is observed. The average thickness of the obtaining, color and roughness underwent changes. The corrosion rate on the standard sample D174 (without obtaining) was 0.84 mm/year, which is 24 times higher than on the D888 sample (with Electrodeposition obtaining).

During the 6 month testing period nano-coating showed a protective efficiency when exposed to acid corrosion/erosion. It should be noted that there is a possibility of damage to the coating during mechanical impact.

It is established that the use of protective coatings leads to an increase in corrosion resistance 24-56 times, which indicates the expediency of their use in these operating conditions.

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Аминдік ортадағы нано қаптаманың қорғаныстық қасиеттерін зерттеу

¹Кемелжанова А.Е., ¹Мукашев К., ¹Яр-Мухамедова Г.Ш., ²Лампке Т.

¹Әл-Фараби атындағы Қазақ Ұлттық Университеті, Алматы, Қазақстан
²Хемниц Технологиялық Университеті, Алмания

Түйіндеме: Газ фракциясын күкіртсутектен тазарту әдістерінің бірі аминді өңдеу болып табылады. Мұнай газдарын күкіртті сутектен, көмірқышқыл газынан тазарту үшін аминдердің әр түрлі түрлері қолданылады. Белгілі бір аминді таңдау процестің қажеттілігіне байланысты. Жиі қолданылатын моноэтанолламин (MEA) (C₂H₄OH) NH₂ және диэтанолламин (DEA) (C₂H₄OH) 2(NH). Екеуі де аммиактың туындысы. Амин зауыттарына арналған жабдықты таңдау бойынша ұсыныстар әзірленді, дәстүрлі пайдаланылатын төмен температуралы көміртекті болаттар мен электроқоздыру нәтижесінде алынған нанокөміркіттік қаптамалардың коррозияға төзімділігіне салыстырмалы зерттеу жүргізілді. Зерттеулер көрсеткендей, стандартты үлгідегі коррозияның орташа жылдамдығы (жабылмаған) жылына 0,9969 мм-ді құрайды. Осыған байланысты майды қышқылдық компоненттерден (сутегіден, сульфидтен, көмірқышқыл газынан) тазартуға арналған жабдықты ауыстыру жиілігі орта есеппен екі жылда бір рет болады. Бір жылдық сынақ кезінде нанокөміркіттік қаптамалар қышқыл коррозиясына / эрозияға ұшыраған кезде қорғаныс тиімділігін көрсетті. Бұл жерде механикалық әсердің салдарынан қаптаманың бүліну мүмкіндігі бар екенін атап өткен жөн. Қорғаныс қаптамаларды қолдану коррозияға төзімділіктің 24-56 есе жоғарылауына әкелетіні анықталды, бұл олардың осы пайдалану жағдайларында қолданудың орынды екендігін көрсетеді.

Түйінді сөздер: нано-композитті қаптама, коррозияға төзімділік, аминдік орта, қорғаныстық қасиеттері, көміртекті болат.

Исследование защитных свойств нано-КЭП в аминных средах

¹Кемелжанова А.Е., ¹Мукашев К., ¹Яр-Мухамедова Г.Ш., ²Лампке Т.

¹Казахский Национальный Университет имени Аль-Фараби, Алматы, Казахстан

²Хемницкий Технологический Университет, Германия

Аннотация: Известно, что один из способов очистки газовой фракции от сероводорода является аминная обработка. Различные типы аминов используются для удаления сероводорода, диоксида углерода из нефтяных газов. Выбор конкретного амина зависит от потребностей процесса. Обычно используются моноэтаноламин (MEA) (C_2H_4OH) NH_2 и диэтаноламин (DEA) (C_2H_4OH) $2(NH)$. Оба являются производными аммиака. Разработаны рекомендации по выбору материала, из которого изготавливают оборудование для аминных заводов, проведены сравнительные исследования коррозионной стойкости традиционно используемых низкотемпературных углеродистых сталей и нанокompозитных покрытий, полученных методом электроосаждения. Исследования показали, что средняя скорость коррозии на стандартном образце (без покрытий) составляет 0,9969 мм / год. Из-за этого частота смены оборудования для очистки масла от кислотных компонентов (водорода, сульфида, диоксида углерода) в среднем составляет 1 раз в два года. В течение одного года испытаний нанокompозиционные покрытия показали защитную эффективность при воздействии кислотной коррозии / эрозии. Следует отметить, что существует вероятность повреждения покрытия при механическом воздействии. Установлено, что использование защитных покрытий приводит к увеличению коррозионной стойкости в 24-56 раз, что свидетельствует о целесообразности их использования в этих условиях эксплуатации.

Ключевые слова: нано-КЭП, коррозионная стойкость, аминная среда, защитные свойства, углеродная сталь.

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