Research of hydroabrasive wear resistance of organomineral coatings depending on operating environment conditions

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Abstract. The critical importance of corrosion protection puts it forward as a leading economic and applied problem for all countries. Costs associated with corrosion, even in developed countries, range from 1 to 3.5 per cent of gross domestic product (GDP). This article discusses issues related to the development of the composition of anti-corrosion materials from organo-mineral heterocomposites for use in structures for the storage and transportation of various aggressive liquids. Experiments were carried out in real operating conditions of equipment for storage and transportation of oil and oil products. Based on the study of the composition of associated water, taking into account the influence of mechanical impurities, the phenomena occurring on the surface of the metal were studied and the optimal composition was selected, the use of which will increase the service life.

1 Introduction

In world practice, where the oil and gas industry is one of the leading sectors of the economy in terms of GDP contribution, scientific and technical measures related to the solution of corrosion problems become extremely relevant, since hundreds of fields with several thousand reservoirs, tanks and transporting structures made of low-carbon steels are successfully operating, which urgently need protection from corrosion and wear. This actual problem creates a need for research on the development of methods and tools for protecting the equipment of the oil and gas complex, the study of the metals' corrosion decomposition mechanism in various media and the production of various materials for target purposes [1-4].

It can be noted that the selection of the necessary materials is a powerful tool for combating severe corrosion. Failures resulting from corrosion can be very costly, so preventing or reducing these effects becomes very important. Fatal failure caused by

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corrosion can be significantly reduced using anticorrosive coatings with excellent chemical and mechanical properties than the starting material. Extending the service life and performance of metal structures by applying various anticorrosion coatings is very advantageous. There are many methods of corrosion protection of metal structures against corrosion, one of which is the use of protective coatings. But in general, the protection mechanism of coatings can be divided into three, namely; creating a barrier between substrate materials and the environment, inhibiting corrosion processes and coating acting as sacrificial materials. However, now one of the newest approaches is the so-called "active-passive." It's included a coating acting as barrier layers that would not penetrate the metal surface (passively) with corrosive agents [4-6].

Nowadays, there is an extensive fleet of steel tanks and tanks that are designed to store and transport oil, petroleum products, liquids with different pH and auxiliary reagents. These structures, which have a service life of more than 10 years, are made of low-carbon steels with insufficient corrosion resistance [4, 5, 7].

The intensity of corrosion defects development on the inner surface of the process tank is influenced by the content of mechanical impurities in the pumped products, the ionic composition of the associated produced water, the flow mode and the presence of a corrosive micro flora. Failure of designs with thickness of a 5-6 mm wall comes in most cases owing to defects development in the form of separate ulcers and a flute on the lower forming internal surface of the technological tank [4, 5] that generally regarding lower part (the bottom and the lower internal wall on perimeter 1/2 ÷ 3/4 heights of the tank from the bottom).

In world practice, many researches are known on methods for protecting metal structures from damage during operation, the main part of which covers the field of research into properties, phenomena occurring on external and internal structures, the modification processes of which need to be studied to analyze the properties of the compositions being developed [8-14].

2 Methods and materials

Due to the emerging need to develop corrosion protection measures for metal structures operating in the oil and gas industry. The operational conditions of the enterprise's technological equipment were studied in order to develop and purposefully apply anticorrosion coatings for metal structures for storage and transportation of liquid raw materials and commodity products.

It is known that the use of polymeric materials and coatings based on them in anti-corrosion measures is one of the effective solutions to the problem. In this regard, for the practical implementation of the researches results, we used epoxy resin ED-20 as the main component - a polymer binder.

Applied research was carried out on production equipment and tanks for the collection and storage of oil and gas condensate of the JV "GISSARNEFTEGAZ" LLC enterprise. Epoxy binder ED-20 has been found to be the most technologically practical components of heterocomposite materials and coatings therefrom for use in process equipment.

Today, in the production facilities for oil and gas production in the fields of the process of primary oil and gas preparation for processing to protect equipment from corrosion, in the best case, if corrosion protection means are available, FL-724 coatings are used, but due to the fact that anti-corrosion coatings are imported mainly from abroad, the equipment operation in many small enterprises is carried out without the use of anticorroses. In this regard, we used St3 steel plates with the FL-724 coating and without coating as test samples.

An analysis of numerous works on the use and role of finely dispersed fillers of inorganic origin shows that most of the mineral fillers used contribute almost little to improving their physical, mechanical and operational properties [7]. They have a particle size of not more than 50-100 μm due to the absence of a grinder that allows obtaining smaller particles, i.e. smaller than 20 μm. Fillers with such granulometric composition can be used in the development and production of multifunctional composite materials used in various industrial production.

Fibrous fillers giving a reinforcing effect are the most effective for strengthening polymeric composite materials (PCM).

The reinforcement geometry has a significant effect on the properties of composite materials. Layered reinforcement increases the strength of PCM in two mutually perpendicular directions to form a layered structure with its inherent disadvantage, which leads to delamination of PCM at impact and critical loads. 3D reinforcement eliminates this disadvantage. The PCM acquires a significant impact margin due to the fact that reinforcement in the third direction prevents delamination and causes the resulting crack to choose a tortuous propagation path.

For research and further use, we selected polymer binders and structure-forming components for cold curing, as well as from kaolin products calculated at 48% of the primary processed raw materials: AKF-78 (25.7% of the output product) - intended for use in paper and paint production; AKS-30 (42.9% of the output product) - for the ceramic industry and electrical insulation materials; AKT-10 (31.4% of the output product) is not a finished raw material for glass production or a tail product. For research the effect of the nature and concentration of fillers at the processes of material wear, fillers in the presence of liquid media were used in the amount of 25 mass-part based on the processability of producing organomineral materials and polyfunctional coatings from them, in all compositions a reinforcing filler in the amount of 3 mass-part was added to increase wear resistance. Samples hardening was made at natural influence of the sun within 20 hours within ambient temperature 40-45ºC [15].

Preparation of experimental samples in the form of a metal plate with a size of 50x50 mm and cylindrical samples with a length of 50 mm, a diameter of 10 mm was made in selected forms.

The protective properties of anti-corrosion coatings were determined under static conditions at ambient temperature in various aggressive media.

The tested samples were prepared on the basis of regulatory sources GOST 9.506-87 "Unified Corrosion and Aging Protection System". The temperature of the test medium was maintained 25±1°C. The protective ability of anti-corrosion coatings was investigated in accordance with GOST 9.083-78 "Unified System for Protection against Corrosion and Aging. Paint coatings. Methods of accelerated durability tests in liquid aggressive media, "GOST 9.409-88" Unified Corrosion and Aging Protection System. Paint coatings. Methods of accelerated tests for resistance to the oil products and GOST R 54301-2011 "Rolled sheet cold-rolled electrolytically galvanized with polymer coating with continuous lines", coating adhesion was determined by the X-shaped notch method according to the standard document STO VNIIST 7.2-3152-0.0037-2011 "Paint coatings for corrosion protection of internal surface of pipes and connecting parts of oilfield pipelines. Test program and methodology". Researches of coatings for hydroabrasive wear were carried out on a disk tribometer [15].

3 Results and discussion

Experiments were carried out on the selected device, at the same time, the end frictional interaction of the cylindrical sample with the surface of the horizontally rotating disk was carried out from Steel 3. Angren kaolin AKO (tail product-waste) was selected as abrasive particles. The choice of this type of kaolin is due to the fact that it is close in nature and particle size to natural abrasives.

The test plant modes were selected constant for all types of test materials and amounted to: sliding speed v = 2 m/s, pressure P = 1.0 MPa. Researches were carried out in both dry and liquid modes, i.e. in air, water and various aggressive media. The relative wear resistance was evaluated by the formula:

$$i_{om} = \frac{I_{ca}}{I_{ga}} \quad (1)$$

where I_{ca} and I_{ra}– intensity of linear wear in dry abrasive and hydroabrasive friction modes, respectively; i_{om}– relative wear resistance.

When metal reacts with water, its dissolution or destruction occurs, since the oxygen and hydrogen atoms of water form polar molecules with two poles ("+" and "-"), which leads to the emergence of a power electric field [6.8]. For more basic research on the detection of the ions effects in solutions of the electrolyte medium, the effects of this process on the properties of heterocomposite materials were studied. Water molecules are embedded in the crystal lattice of the metal, hydration occurs on its surface, and passing into water to form an ion atom bearing a positive charge. At the same time, the electrons remaining in the metal bear a negative charge. The ion atom is surrounded by water molecules, a double electric layer is formed at the metal surface and a potential difference occurs between the metal surface and the solution layers adjacent to it.

Dissociation of substance molecules under the action of dipole water molecules is called hydration, and the ions of substances that have passed into solution, surrounded by water molecules (Figure 1), are called hydrate ions.

When the metal is immersed in the electrolyte, the dissolution (ionization) reaction associated with the hydrating action of water molecules begins:

$$Me \rightarrow Me^{n+} \cdot mH_2O + ne \quad (2)$$

where *n* - valence of metal atoms, *e* - output electron.

At the same time, as ions go into solution, the negative charge of the metal surface will increase. The boundary layers of the solution, saturated with metal ions, will begin to acquire an increasingly positive charge. In this case, there will be a potential difference between the metal and the solution, leading to the occurrence of a metal reduction (crystallization) reaction and preventing further dissolution of the metal:

$$Me^{n+} \cdot mH_2O + ne \rightarrow Me \quad (3)$$

Finally, a point may come when the dissolution and reduction rates of the metal are equal - a state of dynamic equilibrium will occur, that is, the amount of metal ions in the solution and, accordingly, electrons in the metal will remain constant:

$$Me \leftrightarrow Me^{n+} \cdot mH_2O + ne \quad (4)$$

Thus, the metal-solution interface will be a kind of capacitor (Fig. 2), called a double electric layer.

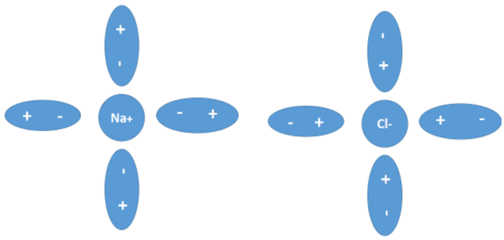

Fig. 1. Hydration of the NaCl ions dissolved in water [5]

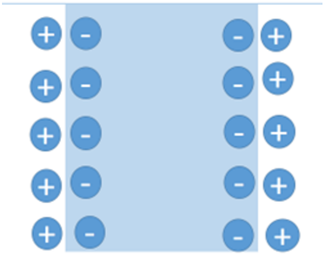

Fig. 2. Double electric layer at the metal-electrolyte boundary [5]. "+" - affirmatively charged metal ions, "-" - negatively charged electrons.

The formation of a double electric layer occurs almost instantaneously. However, the establishment of dynamic equilibrium does not mean that the metal dissolution and reduction processes have ceased. The equilibrium state is a state where the rates of ionization and crystallization reactions are equal - that is, the number of metal atoms converted to ions over a certain period of time is equal to the number of ions crystallized on the metal over the same period of time. In this case, a balance is established between the potential difference in the layer and the difference between the free energies of metal ions in the metal and in the solution. This state corresponds to the equilibrium electrode potential and depends on the properties of the ions and their concentration in the solution.

Based on the above analysis of theoretical researches, we identified the need for applied research on the analysis of the commodity water composition (Tables 1, 2) and the research of the corrosion process of oil and oil products storage equipment of the JV "GISSARNEFTEGAZ" LLC, to research the properties of coatings based on organomineral hetero composite materials in various media.

The results analysis of the corrosion destruction research of the tanks surface, which are operated at the production facility of the JV "GISSARNEFTEGAZ" LLC, showed that not only that part of the equipment that contacts oil and oil products is exposed to the corrosion process (Figure 3 (b)) and commercial water (Figure 3 (c)), but also upper (Figure 3 a), which is due to the fact that CO_2, CO_2 and mineralized product water vapors are collected on the surface of the tank, which leads to corrosion of structural steel from which tanks and tanks for the storage and collection of oil and oil products are made. At the same time, during electrochemical corrosion, uneven corrosion prevails with ulcerative corrosion destruction (Fig. 3 (d)), which leads to a decrease in the wall thickness of the equipment and production losses.

a *b* *c* *d*

Fig. 3. Tanks surfaces photos for collection and storage of oil and oil-gas products of the JV "GISSARNEFTEGAZ" LLC: a) top part (5-6 belt), b) middle part (3-4 belt), c) bottom part (1-2 belt), d) tank bottom, e) uneven corrosion of tank surface, f) destruction of tank surface during corrosion

For researches the composition of the commodity water, samples were taken to analyze the field of two different fields of the JV "GISSARNEFTEGAZ" LLC: Shakarbulak, operated in aggressive water-oil media with mechanical inclusions, and the Northern Guzar field, operated to collect gas condensate.

The sampled probe of water from the Shakarbulok field is transparent, colorless without sediment with the smell of oil products. Results of chemical analysis of water are presented in Table 1.

Analyzed water is a weak brine of chloride-calcium type with density - 1.081 g/cm^3, with total mineralization - 113.8 g/l, metamorphization (rNa/rCl) - 0.91, sulphate coefficient (rSO_4/rCl) - 0.007 and chlorine bromine coefficient (Cl/Br) - 353.

The ion-salt composition of water is dominated by chlorine ions - (68.7 g/l) and alkali metals (Na) - (40.6 g/l), calcium ions - (2.96 g/l) 5.3 times more than magnesium ions (5.35 g/l), sulfate - and hydrogen carbonate - ions are 0.67 g/l and 0.89 g/l, respectively.

The selected water sample of the Northern Guzar deposit (Table 2) is transparent, colorless with the smell of hydrogen sulfide and brown colloidal sediment.

Table 1. Chemical composition of gas condensate product water

Ions	Contents, in			Microcomponents contents, mg/L			
	mg/l	mg-ekv/l	%-ekv				
Na^+	40607.9	1765.5	45.1	J	4.8	NH_4	405.0
Ca^{2+}	2965.92	148.0	3.78	Br	194.67	H_2S	18.16
Mg^{2+}	535.04	44.0	1.12	B_2O_3	111.64	Ba^{2+}	0.03
Cl^-	68732.1	1938.3	49.5	CO_2	46.2	HK	1.55
SO_4^{2-}	674.86	14.06	0.36	CO_2	0.0	Φ	0.20
HCO_3	317.2	5.2	0.14	Fe^{2+}	66.64		
CO_3^{2-}	0	0	0	Fe^{2+}	0.0		
Total	113833	3915.1	100				

Continuation of table № 1

Ions	Sulphate ratio	
Na^+	rNa/rCl	0.91
Ca^{2+}	(rCl-rNa)/rMg	3.9
Mg^{2+}	$(rNa-rCl)/rSO_4$	-
Cl^-	rCa/rMg	3.4
SO_4^{2-}	rSO_4/rCl	0.007
HCO_3	Cl/Br	353
CO_3^{2-}		
Total		

Table 2. Chemical composition of commercial oil water

Ions	Contents, in			Microcomponents contents, mg/L			
	mg/l	mg-ekv/l	%-ekv				
Na^{+}	12651.38	550.06	45.2	J	4.8	NH_4	220.0
Ca^{2+}	921.84	46.0	3.8	Br	102.68	H_2S	40.06
Mg^{2+}	145.92	12.0	1.0	B_2O_3	62.78	Ba^{2+}	0.018
Cl^{-}	20795.87	586.46	48.2	CO_2	0.0	HK	0.90
SO_4^{2-}	316.85	6.6	0.54	CO_2	0.0	Φ	0.085
HCO_3	890.6	14.6	1.2	Fe^{2+}	48.62		
CO_3^{2-}	24.0	0.4	0.06	Fe^{2+}	0.0		
Total	36740.46	1216.1	100				

Continuation of table № 2

Ions	Sulphate ratio	
Na^{+}	rNa/rCl	0.93
Ca^{2+}	(rCl-rNa)/rMg	3.02
Mg^{2+}	$(rNa-rCl)/rSO_4$	-
Cl^{-}	rCa/rMg	3.8
SO_4^{2-}	rSO_4/rCl	0.01
HCO_3	Cl/Br	202
CO_3^{2-}		
Total		

The analyzed water is a very weak brine with a density of 1.023 g/cm^3, with total mineralization of 35.7 g/l, metamorphization (rNa/rCl) - 0.93, sulphate coefficient (rSO4/rCl) - 0.01 and chlorine bromine coefficient (Cl/Br) - 202.

The ion-salt composition of water is dominated by chlorine ions - (20.8 g/l) and alkali metals (Na) - (12.6 g/l), calcium ions - (0.92 g/l), magnesium ions (0.14 g/l), sulfate - and hydrogen carbonate - ions are 0.31 g/l and 0.89 g/l, respectively. Iodine - 4.8 mg/l, bromine - 102.68 mg/l, boron oxide - 62.78 mg/l were installed in the microcomponent composition of water.

Based on the analysis of the corrosive medium composition, the quantitative and qualitative composition of the corrosive medium was selected for further researches of the coatings properties. In this regard, we selected three mediums: aqueous (H_2O), salt (NaCl) and acid (H_2S) for experimental researches.

The obtained results showed that the relative hydroabrasive wear resistance of epoxy compositions filled with kaolin grade AKF-78, AKS-30, AKT-10 in hydroabrasive media is always higher compared to abrasive wear resistance in dry friction. The highest hydroabrasive wear resistance in both dry and liquid friction is observed in samples with filler AKT-10, and the lowest with filler AKF-78 (Fig. 4).

Based on the fact that the surfaces of the process tanks are exposed to thermal and radiation effects of the environment, it is advisable to use coatings containing electrically conductive fillers, such as graphite, carbon black, etc., in a small amount. This is due to the fact that the outer surfaces of the containers are subjected to thermal and radiation exposure to the environment. Fillers - graphite, carbon black and other ingredients containing flaky carbon - increase the light stability, radiation resistance, as well as the electrical conductivity of the coatings [8, 16-19].

 https://doi.org/10.1051/e3sconf/202340105072

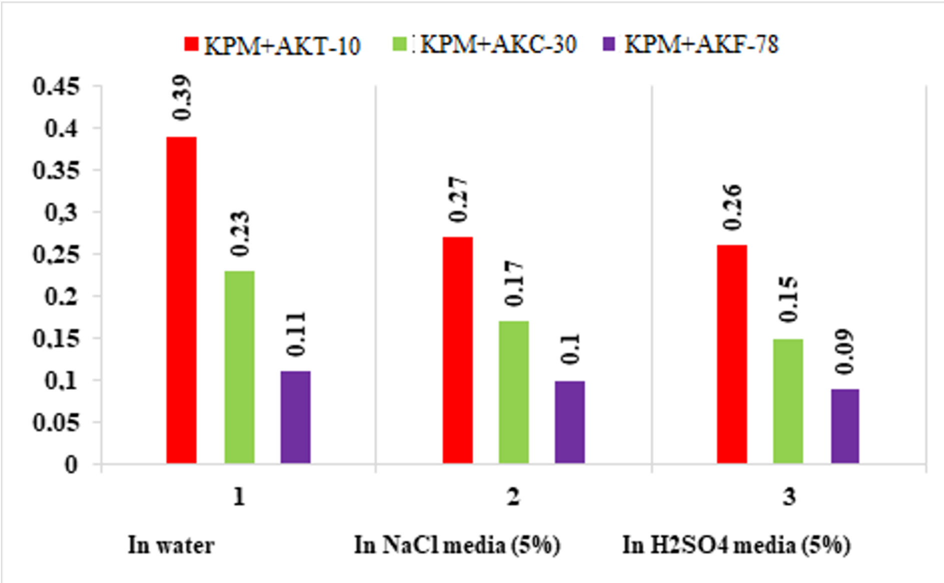

Fig. 4. The dependence of the coating wear resistance on the filler type in various media

The results of researches conducted at the JV "GISSARNEFTEGAZ" LLC in the period 2017-2021 on vertical tanks with a volume of 500 m^3, consisting of 6 belts, showed an increase of the equipment service life and tanks for the collection, storage and transportation of oil and oil products, taking into account the application of the desired type of coating, specifically taking into account their functional properties.

Tests to determine corrosion resistance were carried out on the internal surfaces of gas condensate collection tanks in the North Guzar and Shakarbulak fields.

Corrosion resistance was studied by gravimetric analysis in different media close to the chemical activity of 250 days (Table 3).

The research results showed (Table 3) that the composition with filler provided the greatest protection against corrosion in various media, AKF-78 the compositions with AKT-10 and AKS-30 turned out to be relatively weak compared to AKF-78 in terms of protection. These results are explained by their chemical composition. As a part of AKF-78 filler the content of aluminum oxide is 35-47% [20]. In conditions of hydroabrasive wear, compositions with filler AKT-10 are preferred, and for corrosion protection AKF-78. Analysis of the research results show the feasibility of using the two fillers together, using their protective properties as much as possible.

In all cases, the protective ability of the coatings is not inferior to the control sample of a three-layer coating based on enamel FL-724 (TU 6-10-778-76).

Considering the wear resistance and corrosion resistance, the criterion for choosing the optimal composition was the adhesion strength of the coatings, which is the main indicator characterizing the service life of the coatings. Further researches were aimed at developing the optimal composition of heterocomposite materials, the results of the researches are given in (Table 4).

Table 3. Results of gravimetric method for determination of the anticorrosion coating protection degree (Z %) depending on filler type

Fillers in ED-20-based coatings	Holding time, (in days)				
	50	100	150	200	250
	In water				
AKT–10	99.3	98.7	97.5	97.3	97.4
AKC–30	99.4	98.9	97.7	97.5	97.5
AKF–78	99.9	99.6	99.4	99.4	99.4
	In NaCl (5%) media				
AKT–10	82.8	81.4	81.0	81.1	81.0
AKC–30	84.7	82.6	82.4	81.5	81.4
AKF–78	89.5	88.4	88.3	88.3	88.3
	In Na_2CO_3 (5%) media				
AKT–10	85.8	84.4	82.4	82.4	81.4
AKC–30	87.8	86.4	85.4	84.4	84.4
AKF–78	95.2	94.0	94.0	93.9	92.9
	In H_2SO_4 (5%) media				
AKT–10	81.4	80.3	80.4	80.3	80.3
AKC–30	82.6	82.0	81.6	81.5	81.5
AKF–78	85.4	84.3	84.4	83.3	83.3
Note: in all compositions: ED-20 = 100 mass parts, PEPA = 12 mass parts, graphite = 2 mass parts					

Table 4. Adhesion strength of anticorrosion organomineral polyfunctional coatings depending on the filler type

Components of compositions and their adhesion properties	Compositions (weight parts) and adhesion properties (on a 5-point scale)						
	1	2	3	4	5	6	7
ED–20	00	00	00	00	00	00	00
DBF	0	0	0	0	0	0	0
PEPA	10	10	10	10	10	10	10
AKF–78	–	5	10	15	20	25	30
AKT–10	30	25	20	15	10	5	-
Adhesion on the 5-point scale on the St3 surface	5	5	4	3	2	2	2
Note: All compositions contain: graphite-2 mass parts; reinforcing filler in the amount of 3 mass parts							

Table 4 shows that the best adhesion strength of samples Nos. 1, 2 and 3, with the best corrosion-protective properties of sample No. 7, the most resistant to both hydraulic wear and corrosion is coating composition No. 2.

4 Conclusions

As mentioned above, in the process of oil production, reservoir water is extracted from its deposits along with oil, which contains various salts, as well as mechanical inclusions, which expose the lower part of the technological tanks to abrasive wear and thus accelerate the corrosion process. In the course of studying this phenomenon on tanks it was established that the lower belt of the tank generally is exposed to hydroabrasive wear and intensive corrosion, the top belt can be subject generally to corrosion from influence, oil raw materials and vapors of oil and oil products. In this regard, the entire inner part of the tank during pilot tests and studies was covered with anticorrosion composition No. 2.

For achieving the goal of the research, one of the tasks set was to increase the service life and protect the internal surface of the process tank from hydroabrasive wear and corrosion. In this regard, we selected process equipment operated in Shakarbulak field of the JV "GISSARNEFTEGAZ" LLC with a working volume of 428 m^3 (standard tank of 500 m^3), height h = 7.5 m, R = 4.263 m as an object for implementation and performance of pilot tests. As a result of the research, an optimal composition was developed for protecting metal structures from hydroabrasive wear using a heterocomposite coating consisting of a thermosetting binder, a plasticizer, a hardener, an inorganic filler of Angren kaolin AKT-10 in an amount of 25 mass parts, and AKF-78 in an amount of 5 mass parts, and various reinforcing fillers, including those of natural origin, which are waste products.

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