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RESEARCH

Research Regarding the Anticorosiv Protection of Atmospheric and Vacuum Distillation Unit that Process Crude Oil

Due to high boiling temperature, organic acids are present in the warmer areas of metal equipment from atmospheric and vacuum distillation units and determine, increased corrosion processes in furnace tubes, transfer lines, metal equipment within the distillation columns etc. In order to protect the corrosion of metal equipment from atmospheric and vacuum distillation units, against acids, de authors researched solution which integrates corrosion inhibitors and selecting materials for equipment construction. For this purpose, we tested the inhibitor PET 1441, which has dialchilfosfat in his composition and inhibitor based on phosphate ester. In this case, to the metal surface forms a complex phosphorous that forms of high temperature and high fluid speed. In order to form the passive layer and to achieve a 90% protection, we initially insert a shock dose, and in order to ensure further protection there is used a dose of 20 ppm. The check of anticorrosion protection namely the inhibition efficiency is achieved by testing samples made from steel different.

Keywords: *corrosion, atmospheric and vacuum distillation units, anticorrosive protection, distillation colum, corrosion inhibitor.*

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1. INTRODUCTION

In order to assure the anticorrosion protection of metal equipment from VAD installations, produced by various (organic) corrosive compounds or that from crude oil processing, a there was researched solution that integrates the use of corrosion inhibitors and selection of machinery construction materials. For this purpose, there was tested the, inhibitor that has in its composition phosphate ester. In this case, on the surface of the metal, it is formed a phosphor complex that can resist at high temperature and speed of the movement of technologic fluid.

In order to achieve a high anticorrosion protection by forming passivating layer, there is initially inserted, a shock dose, and for further insurance of the fim stability of is being used a dose of 20 ppm.

Checking the anticorrosion protection and the inhibition efficiency is achieved by testing samples of corrosion of authentic steel and martensitic steel-ferrite in corrosion-sensitive areas. Corrosion speeds measured on retractable and electro immune samples of authentic steel X6CrNiMoTi17-12-2 takes very small values. By applying an effective anti-corrosion treatment with corrosion inhibitors, the cladding material of martensitic - ferrites steel columns X6CrA113 is sufficiently resistant to corrosion.

2. AIMS AND BACKROUND

Crude oil which is processed in plants VAD has a corrosive action on the metallic equipment that comes into contact, because of the presence of corrosive agents in its composition, of compounds resulting the process and of some chemicals introduced to improve its quality.

In the refinery of our country crude oil is being processed, with high content of chlorine / organic acid content and low in sulfur compounds and crude oil imports, which has low chlorine content, but high in sulfur compounds.

If crude oil is processed in the mixture, the corrosion processes are more pronounced than if a single variety of crude oil processing. The choice of

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machinery building materials is made in consideration of these issues.

Due to high boiling temperature, naphthenic acids are present in the warmer areas of metal equipment from VAD pants and determine in furnace's tubes, transfer lines, metal equipment inside the distillation columns, etc. increased corrosion processes.

In addition to the corrosive effect is noted erosion phenomena, which occurs in areas with high-speed of the fluid, in pipe elbows and heads, where fluid changes its direction.

Also, upper and lower organic acids act on metal surfaces where the temperature falls below the dew point temperature, forming aqueous acid (AD and VD tip columns, condensers, vessels, reflux, etc.)

VAD anticorrosive treatment facility is the introduction of corrosion inhibitors with neutralizing action in the top atmospheric distillation columns (C1), desgasolisaton(C2), stabilization (C3) and vacuum distillation (C5). Also Sulzer filling from columns C1 and C5 built from authenitic stainless steel X6CrNiMoTi 17-12-2 and X2CrNiMo 17-12-2 is protected by naphthenic corrosion inhibitors (Fig. 1 and 2)

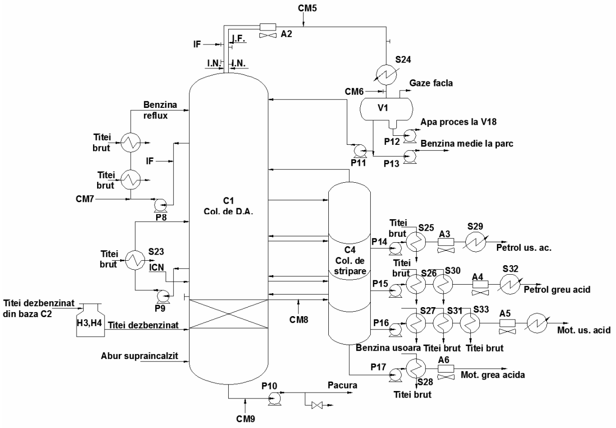

Figure 1. The technological scheme of the atmospheric distillation of crude oil plant

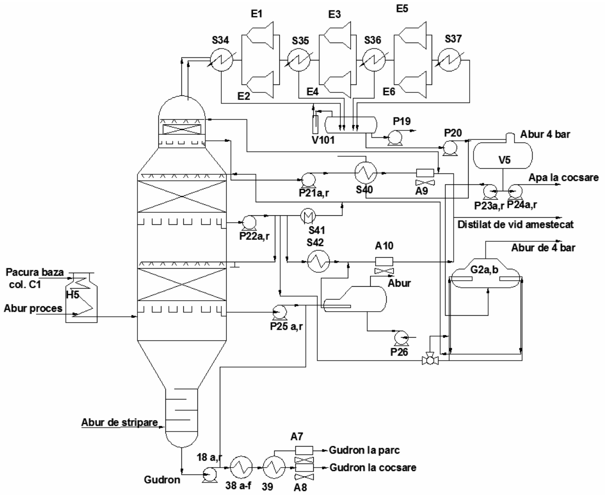

Figure 2. The principle technological scheme of of the installation of oil vacuum

In order to prevent and reduce the corrosion processes, there has been designed a monitoring program for VAD plant that processes crude oil with hing organic acidity. The program consist in the installation of samples in the plant, in ares likely to corrosion. Corrosion samples are mounted on retractable rods, wich can be extracted when needed or the momentary speed of corrosion is measured using portable devices (electroimmune). Their research leads to information on the types and intensity of corrosion.

3. EXPERIMENTAL

Experimental determinations of corrosion behavior of ferrous metalic materials, as a result of aggressive action of crude oil and distillate products from naphthenic crude oil were conducted in an industrial VAD plant. Specimens made of carbon steel S235JR (EN10027-2)-ferritic stainless martensitico steel X6CrAl13 (SR-2 EN10088-2: 1588) and austenitic stainless steels X6CrNiTi18-10, X6CrNiMoTi 17-12-2 and X2CrNiMo17-12-2 (SR EN10216 SR -2:2005) have the composition shown in Table 1.

Table 1. Chemical composition of steels investigated

No	Steel mark	The concentration of elements, %								
		C	Mn	Si	Cr	Ni	Ti	Mo	P	S
1	S235jR	0,22	0,67	-	-	-	-	-	0,049	0,035
2	X6CrAl13	0,06	0,89	0,86	13,5	-	-	-	0,032	0,014
3	X6CrNiTi 18-10	0,07	1,18	0,85	18,5	11,2	0,40	-	0,035	0,015
4	X6CrNiMoTi17-12-2	0,06	1,85	0,78	18,3	12,4	0,42	2,5	0,031	0,013
5	X2CrNiMo 18-14-3	0,03	1,72	0,83	18,1	13,7	-	3,0	0,032	0,015

For the experimental measurements there were used electrical resistances as samples and cylindrical retractable samples.

After preparation (machining followed by pickling and drying), the samples were tested under industrial conditions (immersion in the technological environment) and after original observations that were made on the condition of corrosion surfaces and quantitative determinations. Retractable samples (Fig. 3) had Φ = 10 mm diameter and length of l = 25mm.

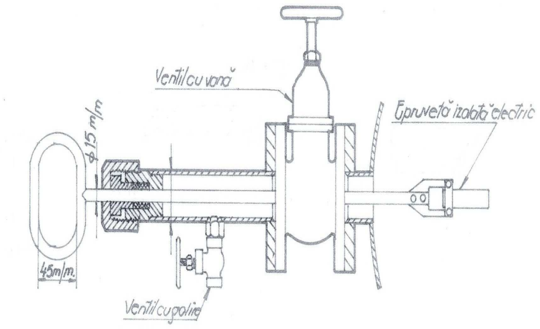

Figure 3. Device with retractable probe for corrosion measurement

The advantages presented by these samples consist in the determination of the corrosion rate at a given time, which can continue tracking the behavior of anticorrosion protection system applied.

The electrical resistance following exposure reduces its cross section and suitably modifying the electrical resistance, according to the relation:

$$R = \rho \, l/s \tag{1}$$

When:
R – electrical resistance
ρ - specific resistivity of the metal Ω mm2 / m
l – the length of the probe, m
s - probe cross section, mm2

The resistance of the tested sample is compared with the resistance of the reference sample (uncorroded).

Resistances can be measured by Wheatstone method, and the obtained values are converted into units of penetration (mm / year) or gravimetric (g/m2h).

Wiring diagram of principle of the device for measuring rate corrosion by varying the electrical resistance is shown in Figure 4.

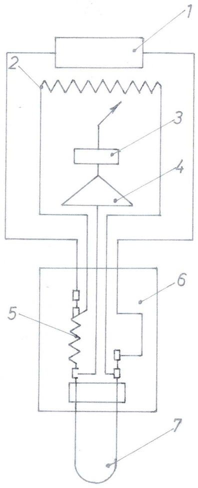

Figure 4. Wiring diagram of principle of the device for measuring the corrosion rate by determining the change in electrical resistance.

4. RESULTS AND DISCUSSION

For the protection against corrosion, inside the atmospheric distillation column C1 and vacuum distillation C5 naphthenic corrosion inhibitor is introduced through the reflux period, in column AD-C1, respectively over the three filling machines SU / ZC5, column C5, made by pump P9, shock dose of 1000 ppm for 4 hours. The result consists in forming on the metal surface of a phosphor complex that resists high temperatures and high speed of technologic fluid, insoluble in hydrocarbons.

For forming the passive layer and achieving the corrosion protection greater than 90% there is being initially inserted a shock inhibitor dose (Table 2).

Table 2. Inhibitor naphthenic shock doses

No.	Column	Area of inhibitor introduction	Inhibitor dosage		
			Quantities, ppm	Time, hours	Frequency, No. dosage/ day
1	AD–C1	Sulzer pack	1000	6	1/30
2	VD-C5	Upper Sulzer pack - VDI	800	6	1/30
		Medium Sulzer pack - VDII	800	6	1/30
		Lower Sulzer pack - VDIII	1000	6	1/30

In order to ensure continuity and compactness of the passive layer there is inserted below a maintenance dose of 20 ppm inhibitor.

Also, in order to monitor the naphthenic corrosion protection and corrosion samples there were introduced in the form of Retractable electrical resistance (ER) to the column, stainless steel and carbon steel.

Corrosion specimens electrical resistance (ER) X6CrNiMoTi 17-12-2 austenitic stainless steel mounted in the heavy gas oil from crude oil atmospheric distillation column C1 had the corrosion rate of 0.0014 mm / year after 30 days / 720 hours of testing, of 0.0009 mm / year after 60 days /1440 hours (Table 3). Instead carbon steel corrosion rate S325JR is 9 times higher. 13% Cr Steel (X6CrAl13) is the corrosion rate of 0.0059 to 0.0080 mm / year.

Austenitic stainless steels and X2CrNiNb X6CrNiMoTi 17-12-2 17-12-2 packages are built from Sulzer packing vacuum distillation column C5 of fuel oil are stable working environment in the column, with corrosion rates in the range 0, 0003 to 0.0042 mm / year (Tables 4,5,6) in the presence of corrosion inhibitor naphthenic-based phosphate ester. ER transducers are highly efficient, giving momentary value of corrosion rate, so you can act immediately, as there is a disturbance in the plant.

Table 3. Speed corrosion of the samples monnted on heany diesel pipe Sulzer packing vaccum.

No.	Monitoring specimen	Steel mark	Type of test days / hours	The corrosion rate	
				Kg, g/ m^{2}h	P, mm /year
1	CM8	S235JR	30/720	0,0120	0,0130
			60/1440	0,0082	0,0091
2	CM8	X6CrAl13	30/720	0,0053	0,0059
			60/720	0,072	0,0080
3	CM8	X6CrNiMoTi 17-12-2	30/720	0,0013	0,0014
			60/1440	0,0008	0,0009

Table 4. The corrosion rate of specimens mounted vacuum distillate I (P114) from the upper output Sulzer packing.

No.	Monitoring specimen	Steel mark	Type of test days / hours	The corrosion rate	
				Kg, g/ m^{2}h	P, mm/ an
1	CM13	X6CrNiMoTi 17-12-2	25/600	0,00027	0,0003
2	CM13	X6CrNiMoTi 17-12-2	29/696	0,00044	0,00049
3	CM13	X6CrNiMoTi 17-12-2	30/720	0,00045	0,0005
4	CM13	X6CrNiMoTi 17-12-2	35/840	0,00063	0,0007
5	CM13	X2CrNiMo 17-12-2	31/744	0,00081	0,0007
6	CM13	X2CrNiMo 17-12-2	32/768	0,00047	0,00052

Table 5. The corrosion rate of electrorezistive specimens mounted at the output of the I vacuum distillate output (P113) of the average Sulzer packing

No.	Monitoring specimen	Steel mark	Type of test days / hours	The corrosion rate	
				Kg, g/ m^{2}h	P, mm/an
1	CM14	S235JR	27/648	0,421	0,468
2	CM14	S235JR	50/1200	0,831	0,923
3	CM14	X6CrNiMoTi 17-12-2	15/360	0,00081	0,0009
4	CM14	X2CrNiMo 17-12-2	29/696	0,0012	0,0013
5	CM14	X2CrNiMo 17-12-2	57/1368	0,0014	0,0016
6	CM14	X2CrNiMo 17-12-2	70/1680	0,0016	0,0018
7	CM14	X2CrNiMo 17-12-2	96/2304	0,0020	0,0022
8	CM14	X2CrNiMo 17-12-2	124/2976	0,0029	0,0032

Table 6. The corrosion rate of specimens mounted at the output of the vacuum out distillate III (P116) of the lower envelope stuffing Sulzer

No.	Monitoring specimen	Steel mark	Type of test days / hours	The corrosion rate	
				Kg, g/ m^{2}h	P, mm/an
1	CM15	S235JR	31/744	0,158	0,176
2	CM15	S235JR	32/768	0,166	0,185
3	CM15	S235JR	34/816	0,186	0,207
4	CM15	S235JR	35/840	0,177	0,197
5	CM15	S235JR	48/1152	0,178	0,198
6	CM15	S235JR	61/1464	0,162	0,180
7	CM15	X6CrNiMoTi 17-12-2	34/816	0,0028	0,0031
8	CM15	X2CrNiMo 17-12-2	42/1008	0,0038	0,0042

From the presented data it results that the austenitic steel, leaves well in technological environment of the vacuum distillation column C5, the corrosion rates having with very low values. The samples from the top of the column have lower corrosion rate than that in the column. S235JR carbon steel is not sufficiently protected by the inhibitor introduced, having high corrosion rates, which makes manufacturing packages filled neutralized Sulzer.

5. CONCLUSION

The crude oil processed in the atmospheric distillation of crude oil fuel and vacuum (VAD) is aggressive action on the metal equipment by the presence of corrosive agents in the actual composition of the compounds resulting in processing of petroleum and chemicals introduced results to improve product quality.

The paper deals with a combined method of corrosion inhibitors, corrosion protection and selection of materials for the construction of metallurgical equipment for processing crude oil with high content of naphthenic acids.

Corrosion protection monitoring program of the VAD plant that processes crude oil with high organic acid content is achieved through: a) analysis and high quality crude oil and aqueous condensate wave of reflux, b) installation of the corrosion samples in areas susceptible to corrosion; c) valves and pipe wall thickness measurement using ultrasound; d) penetrant nondestructive method e) determination of metals (Fe, Ni, V) of heavy crude oil, vacuum distillate I, II and III, f) inspection equipment during servicing. Industrial tests were performed with samples and electroreizstente retractable corrosion of carbon steel and austenitic stainless steels.

For corrosion protection package filler made of steel Sulzer X6CrNiMoTi X2CrNiMo 17-12-2 and 17-12-2, within the atmospheric crude distillation column DA and DV vacuum distillation of fuel oil was used on a corrosion inhibitor ester on the metal surface a protective layer of phosphor.

The polarization curves of steel in condensate X6CrNiMoTi 17-12-2 at the top of by the atmospheric distillation column C1 there is found that the presence of 1% naphthenic acid corrosion is 0.004 mA/cm2 current and corrosion potential 120 mV, which correspondie to a corrosion rate of 0.0047 mm / year (Figure 5).

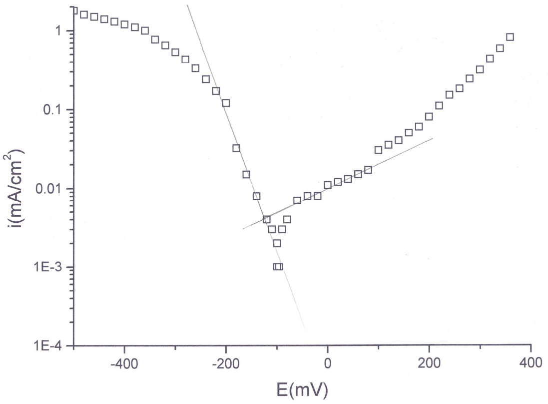

Figure 5. Polarization curves of steel in the austenitic X6CrNiMoTi 17-12-2 condensate from the top 1% DV column naphthenic acids

At the addition of the naphthenic acids there is found that at a temperature of 250 C, there is caned the inhibition of corrosion processes by forming a protective film of iron naphthenate and corrosion inhibitor.

The condensate from the tip of the vacuum distillation column C5, ionization occurs first and then distilling the metal protective film formation.

The corrosion current is 0.00037 mA/cm^2, and the corrosion rate is of 0.0042 mm / year (Figure 6).

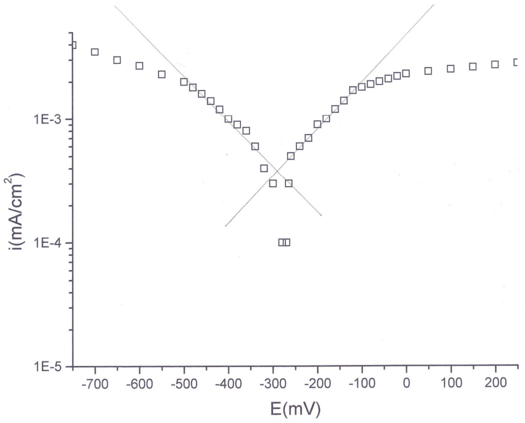

Figure 6. Polarization curves of austenitic steel X6CrNiMoTi 17-12-2 in condensation on top of the column with 1% DV naphthenic acids

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