Economic Aspects on the Corrosion of Condensers/Coolers Equipment at Topside of Black Oil Vaccum Distilation Column

LUCIAN GEORGESCU[1]*, GABRIELA APOSTOLESCU[2], ANA-DANIELA GEORGESCU[3], OVIDIU GEORGESCU[4], MARIA APOSTOLESCU[2]

[1] „George Bariţiu” University Braşov, Department of Researches, 3 Soseaua Vestului, Brasov, Romania
[2] Gh.Asachi” Technical University, Faculty of Chemical Engineering and Environmental Protection, 71A D. Mangeron Blvd.,700050, Iasi, Romania
[3] S.C. IPIP S.A., Ploiesti, Romania
[4] SC GEXACOR COM SRL, Ploiesti, Romania

The paper presents the corrosion aspects from the topside heat exchanger from black oil vacuum distillation column. The corrosion is generated by the technologic flow in the shell and by the cooling water inside the tubes. For measuring the corrosion rates of carbon steel OLT35K and austenitic stainless steel W1.4541 and W1.4571 the laboratory tests were conducted at 20, 50 and 70°C, for 480 hours, in condensed solutions and in cooling water. The results obtained from the chemical plant by placing probes directly in real conditions for 330 days are similar with the results from the laboratory. It was calculated the price of carbon steel tubular fascicle replacement with austenitic stainless steel.

Keywords: corrosion, aqueous medium, corrosion rate

The crude oil is processed in atmospheric distillation equipment (AD) in order to obtain liquefied petroleum gas (LPG), gasoline (petrol), diesel (fuel oil) and heavy black oil. The heavy fraction of black oil from the base of the AD column, with the temperature of 135°C is going through the convection and radiation zone of the furnace, then reaching high temperatures at 380 - 400°C enters the vaporization zone of the vacuum distillation column (VDC), in which results the vacuum distilled fraction (light, medium and heavy) and the vacuum tar.

The corrosion effects from topside of the atmospheric distillation columns for crude oils or in vacuum for black oil are generated by hydrochloric acid formed due the hydrolysis of the calcium and magnesium chlorides, of the hydrogen sulfide, of the traces of saturated monocarboxilic acids (formic, acetic) and also from naphthalene acids existing in both crude and distilled products [1 - 6]. In order to protect against corrosion, anticorrosive materials for the equipments as well as corrosion inhibitors are used [6 - 17].

Experimental part

The condenser-cooling system from topside of the vacuum distillation column (VDC) consists in a heat exchanger series (HE$_1$ and HE$_2$ from fig. 1.), whereat through tubes flows the cooling agent (water) and through inner tubular space circulates hydrocarbons with variable quantities of water, chlorines and sulfides. To prevent the decrease of the *p*H lower than 6.0 in condense resulted from the heat exchanger, the gas phase is treated with neutralizing inhibitor (NI).

Even more, in the gas pipes and inside the VDC column are introduced layered inhibitors (LI and CLI) with the role of formation through adsorption of protective anticorrosive films on the metallic surface. Vacuum distilled fractions and the tar are cooled through heat exchangers HE$_3$ - HE$_6$.

The goal of this project is focused onto the first heat exchanger into the system HE$_1$ whereat the corrosion process is enhanced much more than the other heat exchangers.

In paper [18] the thermal transfer was studied.

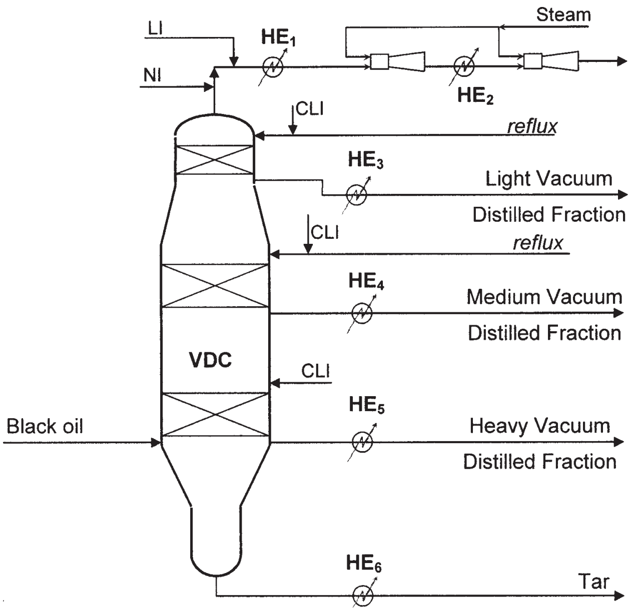

Fig. 1. Simplified display of the condenser-cooling system from topside of the vacuum distillation column.

In order to establish the corrosion behaviour of constitutive materials of the equipment, samples of aqueous condensed solutions were sampled from topside the column of distillation in vacuum (solution *p*H is 6.5 and it contains: diesel fuel 1 - 2%, chlorides 200 - 220 ppm, sulfide 80 - 85 ppm and water in balance) and to reproduce the accidental conditions into the industrial equipment, the condensed solutions have *p*H corrected with hydrochloric acid to *p*H = 4 (the solution composition is: diesel fuel 1 - 2%, chlorides 240 - 250 ppm, sulfide 75 - 82 ppm and water in balance).

Figure 2 presents the main components of the corrosion tester device. Each two metallic samples (3) (dimensions 50 . 20 . 2 mm), prepared for testing [9] and weighted (m^0), are totally immersed in the aggressive media from the testing vessel (2), the temperature is kept constant for the whole experiment using the thermostat (1). In order to

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* *Tel.: 0722781922; +40 232 287683 / int. 2239*

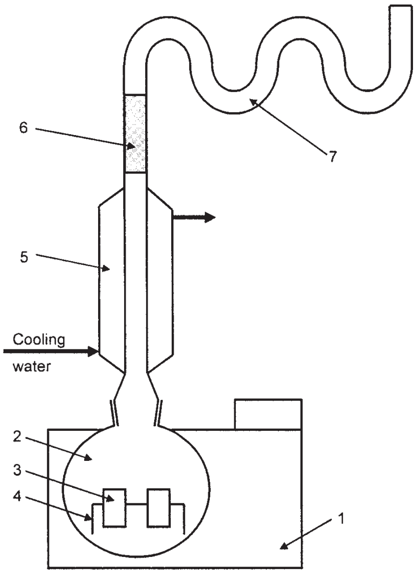

Fig. 2. Schematic display of the testing corrosion device:
1 - thermostat; 2 - testing vessel, 3 - probes, 4 - probes support, 5 - Liebig condenser, 6 - molecular sieves, 7 - hydraulic closure.

maintain the composition of the test solution and to avoid the contact with air, the ascending refrigerator (5) is equipped with molecular sieves (6) and hydraulic closure system with oil (7). The extracted samples are visual examined and then cleaned and weighted (m^f). In all the tests the solution volume - test metal surface ration was 15 mL/cm^2. The corrosion rate was calculated using the gravimetric method and it was measured as gravimetric parameter Kg [g/m^{2}h] and penetration parameter P [mm/year], using the following equation:

$$Kg = \frac{\Delta m}{t \cdot S} \quad \text{and} \quad P = 8.76 \cdot \frac{Kg}{\rho},$$

where:

$\Delta m = m^0 - m^f$ [g] is the weight variation; t [h] is testing time; S [m^2] is samples surface; ρ [g/cm^3] is samples density and 8.76 is a transformation constant.

Behaviour to corrosion was tested using these two types of condensed solutions on carbon steel OLT35K and austenitic stainless steels W1.4541 and W1.4571 (table 1.), at temperatures of 20, 50 and 70°C, for 480 h immersion.

Results and discussions

The experimental results presented in table 2 and table 3 are the average values for the two types of the tested materials.

Corrosion rate of the samples is increasing with temperature, more for the carbon steel OLT35K samples compared with austenitic stainless steel samples W1.4541 and W1.4571; in the *p*H = 4 condense the increase is more significant. During the testing, the surface of the carbon steel exhibits black deposits, more accentuated at 70°C, but the austenitic stainless steel samples remain clean.

In the VDC (the *p*H values are on a wide range, between 4.0 and 7.5) the corrosion rates of the samples placed inside the condenser, near the entrance, are 0.050 - 0.150 mm/year for the carbon steel samples and below 0.008 mm/year for the austenitic stainless steel samples. These values show that the experimental data obtained in laboratory are comparable with the results obtained in industrial facilities. The two years monitoring of the carbon steel OLT35K tubular heat exchanger - condenser HE$_1$ (with ϕ25 . 2.5 . 6000 mm pipes) reveals that the material was heavy affected by corrosion and deposits, even after this period.

On the external surface of the tubes the corrosion products have in their composition mainly iron oxides, as result of corrosive action of the agents from the technologic media over the carbon steel. Removal of the oxidized layers in scaling processes emphasizes the corrosion points and spots presented on the tubes, more evident on certain areas. Same observations can be done on the heat exchanger lid, due to the water used as cooling agent, namely the presence of tubes of iron oxides which are local forms of corrosion.

The same metallic materials there were tested in the lab for the corrosion effect of the cooling water after 600 h at 20°C temperature. The results shows that the cooling water has a high aggression on the carbon steel, with

Table 1
CHEMICAL COMPOSITION OF THE STAINLESS STEEL FROM WHICH SAMPLES WERE MANUFACTURED

No.	Stainless Steel	Composition, %									ρ, g/cm^3
		C	Mn	Si	Cr	Ni	Ti	Mo	P	S	
1.	OLT35K	0.18	0.52	0.26	0.04	-	-	-	0.016	0.020	7.850
2.	W1.4541	0.07	0.80	0.46	18.9	10.25	0.47	-	0.019	0.016	7.900
3.	W1.4571	0.05	0.65	0.53	19.1	12.50	0.58	2.58	0.018	0.015	7.950

Table 2
CORROSION RATE DETERMINATION FOR OLT 35K CARBON STEEL SAMPLES
TESTED FOR 480 h IN COLLECTED CONDENSE

condense pH	Temperature, °C	samples		Kg, g/m^{2}h	P, mm/year
		m^0, g*	Δm, g*		
4	20	15.7662	0.1806	0.164	0.183
	50	15.5767	0.2823	0.258	0.288
	70	15.2940	0.4673	0.427	0.476
6.5	20	15.7585	0.0456	0.0417	0.0465
	50	15.7125	0.0724	0.0674	0.0752
	70	15.6400	0.1324	0.1232	0.1375

*average values from 12 samples tested in the same conditions

Table 3
CORROSION RATE DETERMINATION FOR AUSTENITIC STAINLESS STEEL SAMPLES TESTED FOR 480 h IN COLLECTED CONDENSE

condense pH	Temperature, °C	samples		Kg, g/m²h	P, mm/year
		m^0, g*	Δm, g*		
W1 4541 austenitic stainless steel					
4	20	15.8030	0.0050	0.0046	0.0051
	50	15.7982	0.0056	0.0051	0.0056
	70	15.7922	0.0067	0.0061	0.0068
6.5	20	15.8370	0.0025	0.0023	0.0026
	50	15.8345	0.0041	0.0037	0.0041
	70	15.8304	0.0045	0.0041	0.0046
W1 4571 austenitic stainless steel					
4	20	15.9630	0.0039	0.0036	0.0040
	50	15.9590	0.0044	0.0040	0.0044
	70	15.9544	0.0050	0.0046	0.0051
6.5	20	15.8488	0.0025	0.0023	0.0025
	50	15.8462	0.0038	0.0035	0.0038
	70	15.8422	0.0040	0.0037	0.0041

*average values from 12 samples tested in the same conditions

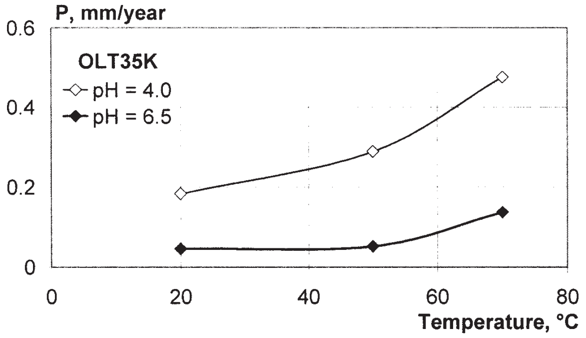

Fig. 3. Corrosion rate of the carbon steel OLT35K samples

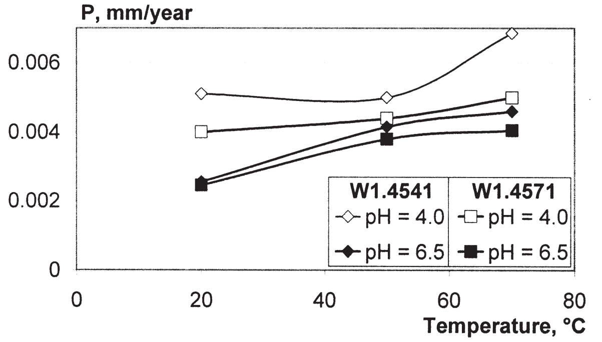

Fig. 4. Corrosion rates of the austenitic stainless steel samples

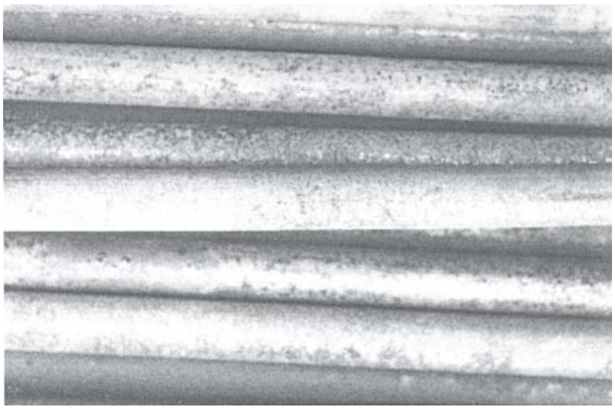

Fig. 5. Local corrosion presented as points and spots and iron oxides deposit on carbon steel tubes of the heat exchanger (external surface) - macroscopic picture

corrosion rates of 0.237 - 0.292 mm/year; for austenitic stainless steel the corrosion rate is with 1 - 2 order of magnitude smaller (0.0035 - 0.0041 mm/year).

The monitored heat exchanger from the topside of the black oil vacuum distillation column, presented after 5 years of work 587 cancelled pipes from the total number of 2820 carbon steel pipes OLT35K, almost 20.8%, being affected of corrosion phenomena of much inside as well as outside. The repairs and the deposition cleaning were done during the standard revisions and also during the accidental breaks induced by the fascicle pipes leakage.

In table 4 is presented the price calculations for the carbon steel tubular fascicle versus austenitic stainless steel condenser HE_1, from topside of the vacuum distillation column.

The costs involved into manufacturing austenitic stainless steel tubular condenser W1.4571 ϕ25 . 2.5 . 6000 are 280,000 EUR, while the carbon steel tubular fascicle OLT35K are 80,000 EUR, meaning de 3.5 times lower (a difference of 200,000 EUR). These supplemental costs are

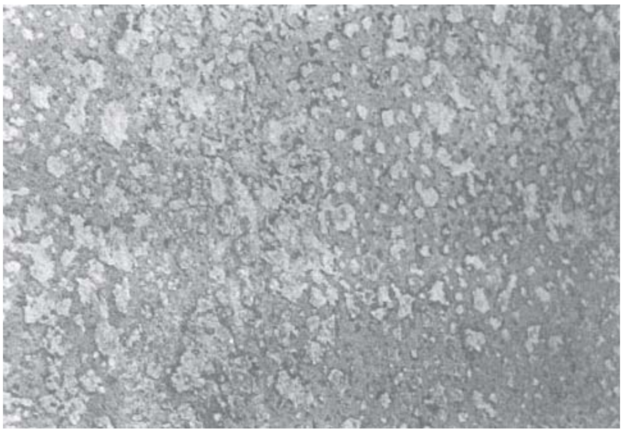

Fig. 6. Ferric oxides and forms of local corrosion on the carbon steel lid of the heat exchanger (water recycled as cooling agent) - macroscopic picture

Table 4
PRICE CALCULATIONS FOR THE CONDENSER HE$_1$, FROM TOPSIDE OF THE VACUUM DISTILLATION COLUMN OF BLACK OIL

No.	Outlay elements	Value, EUR	
		Carbon steel	Austenitic stainless steel
1.	Materials	37,600	195,100
2.	Supply costs (10% from 1)	3,760	19,510
3.	Labor costs	13,930	19,000
4.	Overhead cost (135% from 3)	18,810	25,650
5.	Price (1 + 2 + 3 + 4)	74,100	259,260
6.	Profit (8% from 5)	5,900	20,740
7.	Final price (5 + 6)	80,000	280,000

easy redeemed from the extended running period of the tubular condenser as well as the increased safety, a better heat transfer due to lower deposits into the system and the maintenance in work decrease.

At each accidental break of the system will be required: technical study and repairing solution, the disjoint of lids, mechanic or chemical cleaning, occlusion of broken pipes with corks, pressure tests; these costs added to the production losses give a total of 56,400 EUR. The restarting of the line costs 11,000 EUR. If only three accidental breaks occurs in 5 years because of broken pipes on the condenser, the over costs are going up to 202,200 EUR.

After a medium lifetime of 5 years the replacing of the tubular condenser (consisting in the following operation: normal shutdown of the equipment, disjoint the vessel, replace and assembling of other new one with carbon steel fascicle, test and prove of tight fitting under pressure and starting the equipment) costs 83,000 EUR.

Thus, the total costs rise to 285,200 EUR, meaning that the recovery of the construction and mounting costs of the tubular fascicle from austenitic stainless steel is realized after 5- 6 years of functioning, without considering the increased safety and maintenance in work and accidental losses through imperfect fitting of the pipes. Considering that the tubular fascicle from austenitic stainless steel presents reliable performances for 20 - 25 years or even more without any stop due to the of lack of corrosion.

Conclusions

Laboratory tests on the corrosion of OLT35K carbon steel and W1.4541 and W1.4571 austenitic stainless steel in condensed solution from topside of the vacuum distillation column and in cooling water shows that both liquids have a high corrosion aggression on carbon steel. The corrosion rates values for the austenitic stainless steel, are up to 2 magnitude orders smaller than carbon steel, adviseing the changing of the material used in the heat exchanger HE$_1$. The laboratory test results are comparable with the results obtained in the installation, in real conditions. The costs for replacing the carbon steel pipes fascicle with austenitic stainless steel are paid off only after 20% of the exploitation time of the heat exchanger from the topside of the black oil vacuum distillation column.

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