CORROSION PHENOMENA MANIFESTED TO THE HEAT EXCHANGERS THAT ASSURE THE COOLING OF THE REACTOR EFFLUENT FROM THE CATALYTIC REFORMING INSTALLATION

GEORGESCU LUCIAN[1], APOSTOLESCU MARIA[2], GEORGESCU OVIDIU[3], PETRESCU MARIUS GABRIEL[4], GEORGESCU ANA-DANIELA[5]

[1]Universitatea „George Bariţiu" Braşov, Centrul de Studii Ploieşti, Şoseaua Vestului 22, 100461, Ploieşti
[2]Universitatea Tehnică "Gh.Asachi", Facultatea de Chimie Industrială, B-dul. D. Mangeron 71A, 700050, Iaşi,
[3]SC GEXACOR COM SRL, Str. Înfrăţirii 5 A, 100202, Ploieşti,
[4]Universitatea Petrol şi Gaze din Ploieşti, Facultatea Tehnologia Construcţiei de *Utilaj Petrolier, B-dul Bucureşti nr. 39, 100680, Ploieşti*
[5]S.C. IPIP S.A., Str. Diligenţei nr. 19, 100575, Ploieşti

Abstract: *The heat exchangers that assure the effluent reactor cooling from the installation Catalytic Reforming installation are built from carbon steel. After a relative short work time, about 2,5 years, it was necessary the beam cleaning and the stuffing of the pipes and after another 1,5 years it was replaced the tubular beam.*
To the external part of the pipes beam where the carbon steel is in contact with the effluent and to the internal part of the pipes in contact with the recycled water there are point - like deposits and also deposits having aspects of oxide, metal sulphide layers and fouling under which it appears local corrosion forms.
In the paper there is studied the behavior of the carbon steel and brass to corrosion in the technological environments from the installation and it may be noticed that the brass presents advantages superior to the carbon steel for the construction of the tubular beam.

***Keyword*:** heat exchangers, Catalytic Reforming, corrosion, tubular beam

1. INTRODUCTION

The tendency of using brass instead of carbon steel for the construction of the heat exchangers' pipes where the water is the cooling environment became greater in the last years. The brasses are more resistant to corrosion and to the deposits forming on the surface in contact with water than carbon steel. Also, it is characterized by a superior heat transfer [1 – 3].

From mainly economic reasons, many times there is used stabilized brass for the construction of the heat exchangers beam and carbon steel for spacers, baffles, tubular plates and the heat exchangers hood. The result consists in the work time shortening. That is why all the heat exchanger components must be built from the same material or there must assure the electrochemical isolation of the materials with different potentials. Even that the stabilized brass pipes are more expensive with 2,5 – 3,5 than those of carbon steel, it represents superior characteristics of stability in the researched environments and less energy consumption for pumping [4, 5], that determines their utilization for the construction of the tubular beams. In this case, the maintenance expenses

decrease, there is prevented the accidental stop of the technological installation with big energetic and chemical products losses and there is increased the safety in work of the installation.

The heat exchangers that assure the effluent reactor cooling from the Catalytic Reforming installation are affected, during time, of corrosion phenomena and deposit inside and outside of the beam pipes, baffles, tubular plates and hoods.

2. THE EXPERIMENTAL PART

The reformed gasoline that gets out the R reactor of catalytic reforming (effluent) makes heat change with the hydro-fined gasoline in the heat exchangers S1 A, B and then it passes in the condensers with air A1, A2 and in the coolers S2 A, B, and after that it leads in the depentanizing column (figure 1).

The effluent from the reactor, formed by gasoline reformed with 6 % hydrogen, max. 3 ppm clor, under 1 ppm sulphides and max.100 ppm water, circulates through the inter-tubular space of the heat exchangers S2 A, B (coolers) and the recycled water form the cooling tower circulates through pipes. The component elements of theses coolers built from carbon steel are exposed to corrosion and deposit phenomena.

In order to research the behavior to corrosion of the carbon steel and other alloy for its eventual replacement, as for example the brass, there was taken proofs from the industrial installation and there was made corrosion tests with the device from the figure 2. The effluent from the reactor was tested normally or contaminated with 10 ppm HCl and for the removal of the corrosive agents there was made washings of the effluent from the reactor with demineralized hot water, to the temperature of 60^0C. The washing water having the pH = 6 was tested in the laboratory in order to determine its corrosive action on the metal test piece. The corrosion test pieces were made from carbon steel LT35K and brass CuZn28Sn1 having chemical composition presented in the table 1.

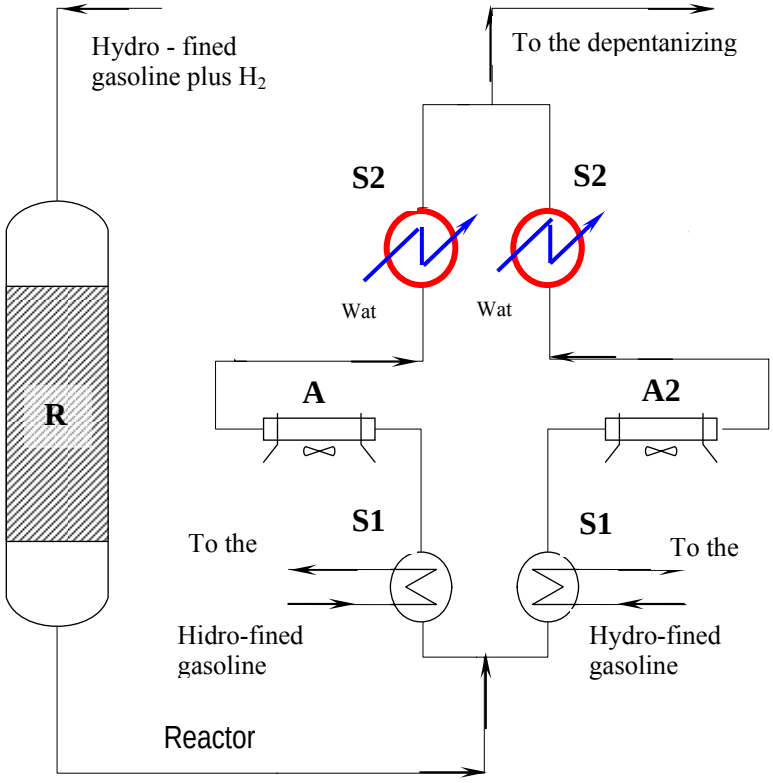
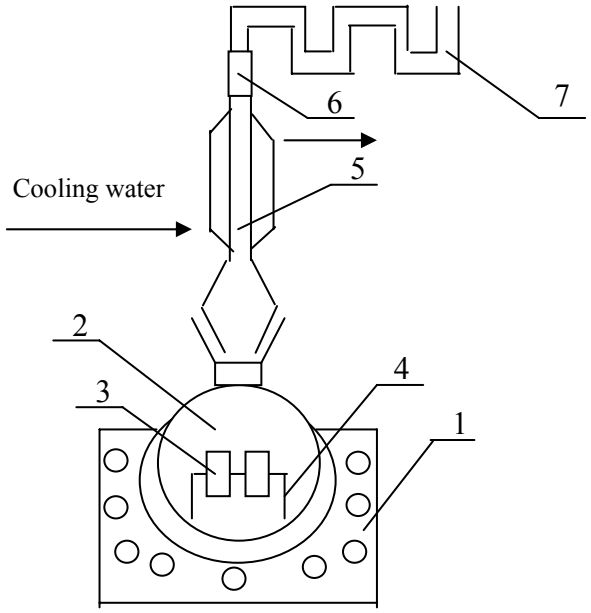


Fig. 1 – The position of the heat exchangers S2 A, B in the technological flux of RC installation.



1 – Thermostat
2 – Berzelius vessel for testing
3 – Corrosion test pieces
4 – Corrosion support test pieces
5 – Ascendant refrigerant
6 – Molecular sieves
7 – Hydraulic closure vessel

Fig. 2 – Theoretical scheme of the corrosion testing device.

Chemical composition of the steels from which there where made the corrosion test pieces - Table 1

No.	Steel's mark	Component elements, %									
		C	Si	Mn	S	P	Cu	Zn	Sn	As	Pb, Fe
1.	OLT35K	0,11	0,25	0,7	0,018	0,032	-	-	-	-	-
2.	CuZn28Sn1	-	-	-	-	-	70,9	28	1,0	0,1	traces

3. RESULTS AND DISCUSSIONS

In the table 2 and the figure 3 there is presented the variation of the corrosion speed of the carbon steel and brass test pieces tested in reformed gasoline to the outlet from the reactor (effluent) that circulates through the coolers S2 A, B, to the environmental temperatures. The tests were made in the laboratory with gasoline taken from the industrial installation.

The corrosion speed of the test pieces tested in reformed gasoline effluent to the environmental temperature - Table 2

No.	Work environment	τ, Days/ hours	Carbon steel		Stabilized brass	
			K_g^-, g/ m^2h	P, mm/ an	K_g^-, g/ m^2h	P, mm/ an
1.	Gasoline S2 A, B	15/ 360	0,055	0,061	0,014	0,015
2.			0,061	0,068	0,011	0,012
3.		30/ 720	0,062	0,069	0,019	0,020
4.			0,068	0,075	0,022	0,023
5.		45/ 1080	0,072	0,080	0,031	0,032
6.			0,078	0,087	0,035	0,036
7.	Gasoline S2 A, B + 10 ppm HCl	15/ 360	0,084	0,094	0,020	0,021
8.			0,081	0,090	0,022	0,023
9.		30/ 720	0,092	0,102	0,027	0,028
10.			0,088	0,098	0,031	0,032
11.		45/ 1080	0,092	0,102	0,036	0,037
12.			0,106	0,118	0,044	0,045

In the reformed gasoline from the coolers S2 A, B with water traces (reactor effluent) the corrosion speed of the carbon steel is between 0,061 – 0,087 mm/ year, values that increase in the same time with the immersion time increasing and that of brass is of 2,4 ÷ 4,7 smaller than of the carbon steel. On the carbon steel test pieces surface there were deposits having dark brown color in a big quantity on about 90 % from the surface, non - uniform disposed, while the brass test pieces CuZn28Sn1 present very well, there do not present local corrosion forms. Introducing in gasoline effluent 10 ppm HCl, the corrosion speeds increase, more to the carbon steel than to the brass and the dark brown deposits are also on about 90 % from the surface of the carbon steel test pieces, but in a bigger quantity. The brass color became a little bit darker but on her surface there were not observed significant corrosion forms (figure 4).

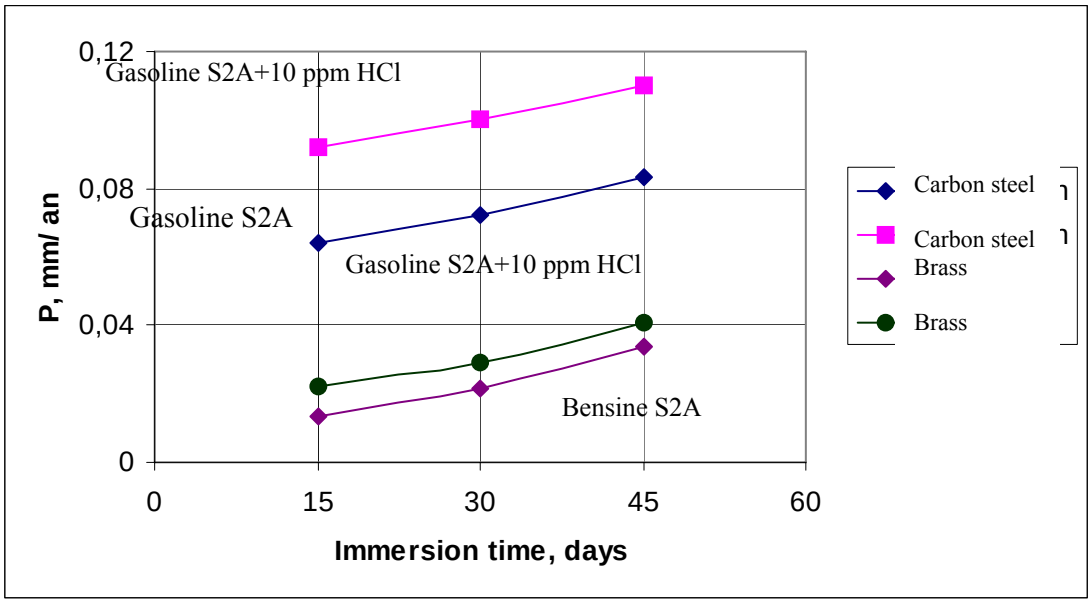


Fig. 3 – Variation of the corrosion speed of the test pieces from carbon steel and brass, with the immersion time, in reformed gasoline effluent to the environmental temperature.

Fig. 4 – Corrosion in points and spots pronounced to the carbon steel (a) and generalized insignificant corrosion to the stabilized brass CuZn28Sn1 (b) in gasoline S2 A, B + 10 ppm HCl.

In order to eliminate the corrosive agents from the gasoline S2 A, B there were washed 1000 ml of gasoline with 200 ml of distilled water to the temperature of 30^0C. The resulted washing water had the pH = 6,0.

The corrosion tests were made to the temperatures of 20^0C, 40^0C and 60^0C, the obtained results being presented in the table 3 and the figure 5.

Corrosion speed of the carbon steel and brass CuZn28Sn1test pieces in the washing water of the gasoline S2 A, B. - Table 3

Work environment	Immersion time, days/ hours	Temp, ^{0}C	Carbon steel		Stabilized brass	
			K_g^-, g/ m^{2}h	P, mm/ an	K_g^-, g/ m^{2}h	P, mm/ an
The washing water of the gasoline from S2A, B	15/ 360	20	0,091 0,107	0,101 0,119	0,010 0,013	0,010 0,014
		40	0,108 0,124	0,120 0,138	0,012 0,018	0,013 0,019
		60	0,145 0,163	0,161 0,181	0,019 0,025	0,020 0,026
	30/ 720	20	0,110 0,132	0,122 0,147	0,019 0,021	0,020 0,024
		40	0,159 0,197	0,177 0,219	0,020 0,028	0,021 0,029
		60	0,262 0,304	0,291 0,338	0,031 0,035	0,032 0,038

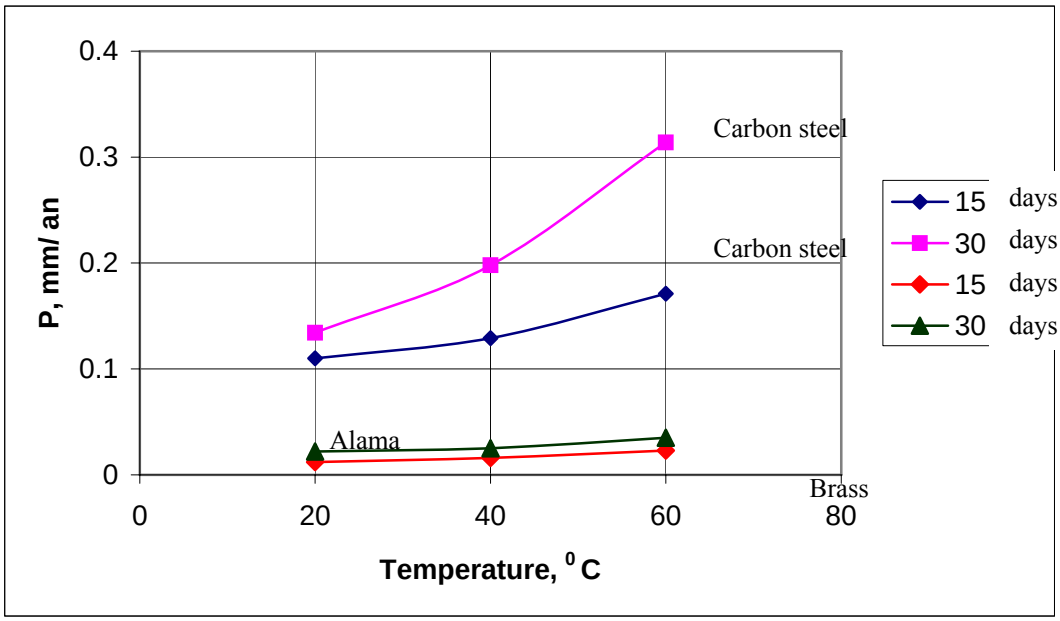


Fig. 5 – Variation of the corrosion speed of the carbon steel and brass with temperature test pieces, after 15 and 30 days in the washing water of the reformed gasoline.

In all researched cases, the corrosion speed increases in the same time with the temperature increasing, more to the carbon steel than to the brass. In the washing water of the gasoline from S2A, B, the corrosion speed of the carbon steel is 0,11 mm/ year respectively 0,135 mm/ year to the environmental temperature and 0,171 mm/ year

respectively 0,315 mm/ year to the temperature of 60^0C. These values represent the values average of the two corrosion test pieces. On the test pieces surface there were deposits of black color metal oxides disposed point - like. After there elimination there were distinguished the corrosion points. The same notices were made in the installation where the pipes from carbon steel were covered by metal oxides and were affected by the local corrosion.

In exchange, the test pieces made from stabilized brass (pipe of CuZn28Sn1) had corrosion speed of 6 – 9 times smaller than the carbon steel and there were not affected of local corrosion forms; there was not produced the brass zinc unalligation.

The results of the laboratory researches were confirmed by the notices made in the industrial installation where to the tubular beam of these heat exchangers it appears deposit and corrosion phenomena.

To the external part of the pipes where the carbon steel is in contact with the effluent there are point - like deposits and under the form of oxides and metal sulphides layers. Also, in the zone of baffles there are deposits adherent to the metal and run out of pipes and under them it appears local corrosion forms (points and spots) (figure 6).

Fig. 6 – Deposits on the tubes in a **U** form of the heat exchangers S2 A (the effluent part).

The internal part of the pipes is in contact with the recycled water through the cooling tower, being affected by deposits, under which there were distinguished corrosions having the form enough pronounced of points, spots and caverns (figures 7 and 8).

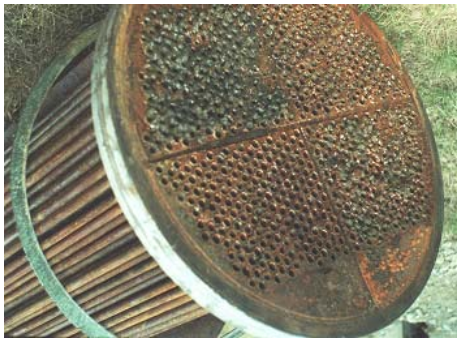


Fig. 7 – Deposits on the tubular plate (the cooling water) and the pipes exterior (the effluent) from carbon steel to the heat exchanger S2A.

The soft deposits from the pipes and from the tubular plate were analyzed from the biological point of view, observing that they have a great microbiological charge:

- The total number of meseophile bacteria that develop to the temperature of 37^0C is of $2{,}1 \cdot 10^{10}$ UFC/ cm^2
- total coli forms = $240 \cdot 10^9$/ 100 cm^3
- excrements coli forms = $1609 \cdot 10^9$/ 100 cm^3
- excrements streptococci = 542 000/ 100 cm^3

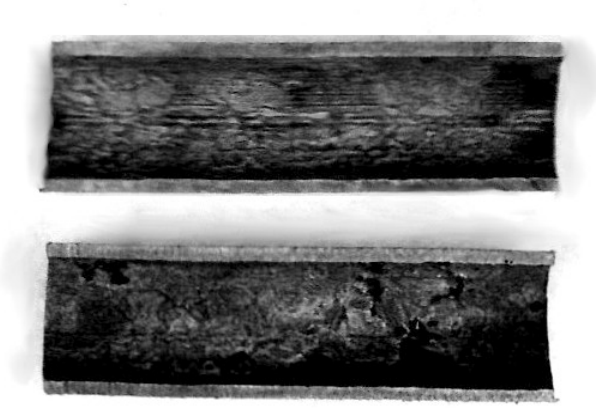


Fig. 8 – Local corrosion forms (points, spots, caverns) under the deposits formed inside the carbon steel pipes through it circulates the cooling

The first corrosion layer which is in contact with the metal has a black color because of the ferroferric oxide (loadstone) and iron sulphide formed as a consequence of the sulphates conversion from the water in the hydrogen sulphide, respectively ferrous sulphide ($H_2S + Fe \rightarrow FeS + H_2$), under the action of the water bacteria (desulfovibrio desulfuricans). Other this layer there are deposited other feeric oxide layers having the red brown color in which there are also water impurities. The oxides and the iron sulphides that form are germs for the apparition and the accumulation of other deposits.

In the case of using brass instead of carbon steel, these disadvantages are eliminated in a large measure and also the brass assures a superior heat transfer.

4. CONCLUSIONS

As a result of the researches made it may be presented the following conclusions:

- the visual examination of the external surface of the carbon steel pipes to the heat exchangers that assure the effluent reactor cooling from the Catalytic Reforming installation emphasized the presence of certain layers of oxides and metal sulphides deposits under which there were local corrosion forms. These were confirmed also in the laboratory tests made with carbon steel test pipes immersed in the environments of the industrial installation.
- the washing water pH of the gasoline from S2 A, B is 6,0.
- in the reformed gasoline that gets out the reactor (effluent) with water traces, the corrosion speed of the carbon steel determined in the laboratory is of 0,061 – 0,0087 mm/ year and that of the stabilized brass is of 2,4 – 4,7 times smaller than of the carbon steel. On the carbon steel test pieces it appears many deposits under which there are local corrosion forms, toward the brass test pieces that present very well.
- in the presence of 10 ppm HCl in the gasoline, the corrosion and deposits phenomena increase.
- for the construction of the tubular beams it is recommended the stabilized brass CuZn28Sn1, having an arsenic content of 0,02 – 0,06 % in order to prevent the unalligation (zinc unalligation) process.

REFERENCES

[1] Dabosi F., Beranger G., *Corrosion localisée*, Les édition de physique, France, 1994.
[2] Desjardins D., Oltra R., *Corrosion sous contrainte. Phénoménologie et Mécanime*s, Les éditions de physique, France, 1990.
[3] Georgescu L., Apostolescu Maria, *Studiul privind posibilităţile de înlocuire a materialelor metalice cu nemetale din punct de vedere al cheltuielilor de producţie*, Referat nr. 3 la Teza de Doctorat, Universitatea Tehnică "Gh. Asachi" Iaşi, 2006.
[4] Rue J. R., Naeger D. P., *CORROSION/ 90,* Paper # 211, NACE, Houston, Texas, 1990.
[5] Patton C. C., *Applied Water Technology*, Second Edition, Campbell Petroleum Series, Oklahoma, USA, 1995.