



## STUDIES ON EQUIPMENT CORROSION IN CATALYTIC REFORMATION OF C<sub>1</sub> - C<sub>5</sub> FRACTION

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### Abstract

Observations and data regarding the intense corrosion and deposit phenomena of the carbon steel tube bundle of the heat exchanger are presented. The bundle ensures the cooling of the light fraction C<sub>1</sub> - C<sub>5</sub> from the top of the distillation column which carries out the removal of pentane and smaller derivatives into the RC equipment. Chemical and mineralogical analyses confirm the aggressive action of the fluids flowing through the exchanger. Tests have been done in order to replace the carbon steel with austenitic stainless steel into the manufacturing process of the tube bundle. The corrosion behaviour of the selected metallic materials in recycled cooling water and technological fluids was monitored.

*Key words:* austenitic stainless steel, corrosion, heat exchanger, tube bundle

### 1. Introduction

The metallic parts of the carbon steel equipment and also the heat exchanger from the top of the distillation column ensuring the removal of C<sub>1</sub> - C<sub>5</sub> fraction into the RC equipment are intensively affected by the corrosion and deposit phenomena. Subsequently the heat exchange process slows down and the functional time of the equipment decrease, together with lower safety in the operational process of the equipment. Another considered disadvantage could be the less purified technological fluid (C<sub>1</sub> - C<sub>5</sub> fraction). In order to solve the inconvenient the equipments should be manufactured from highly anticorrosive resistance materials like less alloyed steels and austenitic stainless steel (Chesa et al., 1984; Fontana and Greene, 1986; Trușculescu and Ieremia, 1983). The last one is characterized by good resistance to corrosion in aggressive environments containing hydrogen and H<sub>2</sub>S. The surface is also characterized by less roughness and more glossy,

where the depositions do not belong, involving easier cleaning methods and longer periods of time between maintenance procedures compared to the carbon steel. The costs involved present high differences, while the maintenance of austenitic stainless steel equipment is cheap and the carbon steel equipment permanent maintenance is expensive. For short periods of time the carbon steel is cheaper, while for longer times the stainless steel present obvious advantages, the costs expense liquidation is achieved in time (Chawla and Gupta, 1993).

### 2. Experimental setup

The heat exchanger S<sub>1</sub>, under monitoring for three years, ensures the cooling of the C<sub>1</sub> - C<sub>5</sub> fraction collected from the top of the column which condense the light hydrocarbons after passing through air condenser A<sub>1</sub> (Fig. 1). The composing elements of the heat exchanger S<sub>1</sub> are manufactured from carbon steel, the chemical composition being presented in Table 1.

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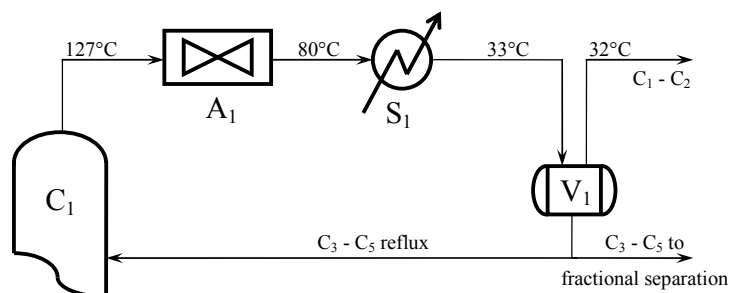


Fig. 1. The heat exchanger place,  $S_1$ , into the technological flux of the reforming catalytic equipment

Table 1. Chemical composition of the construction material

Heat exchanger constructive parts	Material	Concentration, %				
		C	Si	Mn	S	P
Tube bundle $\phi 20 \times 2$	OLT35K	0.13	0.27	0.66	0.025	0.026
Tube sheet	K460.2b	0.17	0.37	1.22	0.015	0.016
Shell, Plenum	K41-2b	0.11	0.20	0.62	0.041	0.014
Baffle	OL37-2K	0.13	0.34	0.60	0.030	0.032

Table 2. Chemical composition of the deposit samples from the heat exchanger

Deposition sample place	Composition, %			
	Iron oxides ( $Fe_2O_3$ )	Ca and Mg salts ( $CaCO_3$ )	Phosphates ( $PO_4^{3-}$ )	other components
Plenum	85.7 - 87.3	4.3 - 5.2	1.12 - 1.23	0.08 S; traces: Cu, Ni
Baffle, tube bundle	78.0 - 84.2	1.85 - 2.17	traces	0.3 Cr; 0.8 Zn; 0.032 S; traces: Ni, Cu, K
Tube sheet	84.9 - 86.5	2.91 - 3.18	traces	1.0 Zn; 0.5 Cr; 0.44 Na; 0.14 K; 0.12 Cu; 0.046S

During the monitoring period, the cooling water presented the following general characteristics: pH = 7.2 - 8.0; total hardness 326 - 493 mg  $CaCO_3/L$ ; alkalinity "m" 157 - 318 mg  $CaCO_3/L$ ; chlorides 80 - 120 mg/L; organic substances 20 - 68 mg/L and iron content 0.6 - 5.7 mg/L, indicating high probability to form large quantities of deposits.

The cooling tower water flows through the pipes of the fascicle, while the  $C_1 - C_5$  fraction and  $H_2$  (desorbed from reformed gasoline) with  $H_2S$  traces ( $< 1$  ppm  $S_T$ ) and chlorides (0.1 - 0.2 ppm) flow into the intertubular space. Deposition processes occur on tube bundle, tube sheets and baffles containing organic and inorganic substrates and promote local corrosion processes. Carbon steel getting in contact with sulphuric acid traces and the hydrochloric acid from hydrocarbons present into the inner tubular space is affected by corrosion processes and deposit formation. The phenomenon described above is not encountered in the case of austenitic stainless steel equipment. Salt deposits and microbiologic colonies are usually formed on the warm surfaces of the heat exchange, while the iron oxides resulted from the corrosion attack are supporting their accumulation and adhesion.

Microbiologic colonies are giving birth through their metabolic activity to corrosion effects due to their electrochemical activity with the metal but also due to the direct chemical attack of the metabolites

formed ( $H_2S$ ,  $SO_2$ ,  $NH_3$ ,  $NO_2$ ,  $CO_2$  etc.), which present highly aggressive behaviour against metals.

Visual inspections over the tube bundle and the inner tubular space show after three years use mud deposits, corrosion products, while some of the pipes are totally or partially closed (Fig. 2).

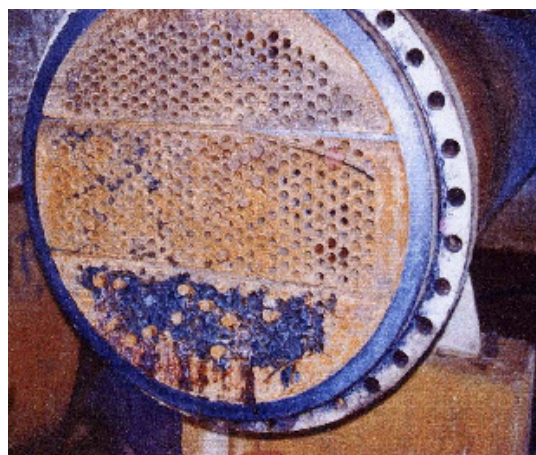


Fig. 2. Deposits on carbon steel tube sheet

At the upper part of the tube sheet, into the warm area, the main deposit is formed from biological mud.

Into the central part, between the baffles where the temperature is lower, the quantity of

biological mud decreases, while on the lower part of system and the technological fluid is evacuated, almost no mud is present but dark brown, iron oxides layers are noticed and also highly frequent clogged pipes.

The carbon steel plenum present grey-yellow- brown deposits and dark brown- black corrosion tubercle with 5 - 10 mm diameter scattered on the walls of the plenum. The corrosion tubercles are usually associated with corrosion plates measuring 10 - 20 mm in diameter.

The laboratory corrosion tests were performed using cooling water from the cooling tower and aqueous solutions resulting from washing the technological GPL (liquid petroleum gas) fluid with corrected pH. Other tests were done by placing samples in the operational heat exchanger.

### 3. Results and discussion

The surface of the walls in the plenum, the tube sheet and the tube bundle present accentuated local corrosion forms, after the deposit have been removed with water under pressure (plague). Deposit samples have been dried (contain 20 - 29% water) at 105°C and the results of the analysis are presented. (Table 2).

The tubercles skeleton is thin, probably mostly consisting of ferro-ferric oxides, was a black soft-spongy deposit formed from hydrated ferric oxides and metal sulphides (Herro and Port, 1993). The sulphates are reduced to sulphurous acid by the action of the bacteria present in water, and subsequently their action against iron is leading to black ferrous sulphur. Onto the sulphur layer hydrated iron oxides layers are deposited, which are also including other impurities from water. Iron oxides can be considered in this case as the "germs" of subsequent appearance and accumulation of various deposits.

The wet deposits sampled from tube bundle and tube sheet have been submitted to further biological analysis. The results show high biological loads of this mud: total number of mezophile bacteria

W1.4541	50 / 1200	0.0008	0.00088
		0.0009	0.0010
		0.0025	0.0028
		0.0032	0.0036
W1.4571	50 / 1200	0.0007	0.00077
		0.0008	0.00088
		0.0012	0.0013
		0.0021	0.0023

The visual inspection of the surface of the carbon steel samples OLT35K emphasized soft deposits in a thin layer, scattered allocated, under which corrosion spots occurred, while the austenitic stainless steel samples present no deposits, and the general aspect was not changed.

Real condition tests were done in the plant by assembling samples on board into the industrial system on the tubular heat exchanger S<sub>1</sub>. The results

the shell, where the cooling water enters into the (which are developing at about 37°C) is 21·10<sup>9</sup> UFC/cm<sup>3</sup>; total coliform 240·10<sup>9</sup>/100 cm<sup>3</sup>; fecal coliformi 1609·10<sup>9</sup>/100 cm<sup>3</sup> and fecal streptococcus 542000/cm<sup>3</sup>.

Anticorrosive substances are added into the cooling water (inhibitors, bactericide, antifouling etc. (Apostolescu et al., 1999; Apostolescu et al., 2001; Constatinescu, 1976; Patton, 1995). Their efficiency is not high enough to prevent and reduce, considering the normal working parameters, the corrosion and deposition processes, which are strongly altering the heat exchange equipment.

In order to ensure optimal and safe functionality of the heat exchanger S<sub>1</sub>, under the given conditions, the replacement of the carbon steel with austenitic stainless steel was proposed. Two sets of tests were run considering the corrosion behaviour of the materials into the fluids flowing through the heat exchanger. The values of the corrosion rate, P (mm/an) were determined by gravimetric method (Constatinescu, 1976).

The first set of laboratory tests were performed on the cooling water from the cooling tower, using metallic samples (25×40×1.5 mm) manufactured from carbon steel OLT35K and austenitic stainless steel W1.4541 (10TiNiCr180) and W1.4571 (10TiMoNiCr175) properly prepared (Constatinescu, 1976). Tests were run in laboratory facility in closed system, samples being totally emerged into water. Fluid volume/ metallic surface ratio were 15 mL/cm<sup>2</sup>. The experimental results are presented in Table 3.

**Table 3.** Laboratory corrosion speeds of the metallic samples in cooling water from the cooling tower basin

Materials	Immersion time, days / hours	Corrosion speed	
		K <sub>g</sub> , g/m <sup>2</sup> h	P, mm/an
OLT35K	50 / 1200	0.066	0.073
		0.067	0.074
		0.072	0.080
		0.086	0.096

are indicative of corrosion speeds greater than those determined in laboratory for carbon steel, namely 0.16 to 0.19 mm/year and 0.0042 to 0.0050 mm/year for austenitic stainless steel.

The second set of tests was conducted in aqueous solutions resulting from washing the technological GPL (liquid petroleum gas) fluid, taken out of the ebb vessel V<sub>1</sub>. The GPL fluid was washed with hot water to extract the corrosive agents contained; a solution with pH = 6.8 resulted. In order to increase the corrosivity of the solution, a part was treated by adding sodium hydroxide up to pH = 9.0, and into the other acid was added to reach pH = 3.5.

With these three aqueous solutions, laboratory tests have been conducted at 50°C for 480 hours. The results are presented in Table 4. Austenitic stainless steel present also in these aqueous solutions corrosion speed values with two orders size smaller

than the carbon steel, and the tested samples surface do not present signs of corrosion or deposits.

All these calls for austenitic stainless steel heat exchanger manufacturing of the tubular fascicle S<sub>1</sub>.

**Table 4.** Corrosion rates for the carbon and austenitic stainless steel samples in aqueous solution extracted from GPL

Working conditions	Material	Corrosion rate	
		K <sub>g</sub> <sup>-2</sup> , g/m <sup>2</sup> h	P, mm/an
Aqueous solution with pH corrected at 9.0	OLT35	0.0770	0.0850
	W1.4541	0.0019	0.0021
	W1.4571	0.0009	0.0010
Aqueous solution with pH corrected at 6.8	OLT35	0.0920	0.1020
	W1.4541	0.0022	0.0024
	W1.4571	0.0013	0.0014
Aqueous solution with pH corrected at 3.5	OLT35	2.8900	3.2100
	W1.4541	0.0056	0.0062
	W1.4571	0.0031	0.0034

**Table 5.** Heat exchangers costs\*

	The name of the items of expenditure	Value, EUR	
		carbon steel	austenitic stainless steel
1.	Materials value	2970	14600
2.	Supply costs (10% from 1)	297	1460
3.	Labour value	974	1100
4.	Overhead cost (135% from 3)	1315	1485
5.	Price cost (1 + 2 + 3 + 4)	5556	18645
6.	Profit (8% from 5)	444	1492
7.	Total value (5 + 6)	6000	20137

\*ensure the cooling of the C<sub>1</sub> - C<sub>5</sub> fraction from the top of the column into the RC equipment

Besides testing the corrosion behaviours of the two metallic materials, the costs were summarized, both for manufacturing the tubular fascicle with W1.4571 austenitic stainless steel and carbon steel (Table 5). Additional costs were calculated for the maintenance during 3 years run of the carbon steel heat exchanger (Table 6).

Although the stainless steel tube bundle is 3.35 times more expensive than carbon steel, the maintenance costs of the carbon steel heat exchanger over 3 years overstep significantly the cost of the stainless steel equipment. Thus, the recovery of manufacturing and mounting costs of the austenitic stainless steel exchanger is made in only 7 to 8 months of operation.

#### 4. Conclusions

During 3 years monitoring of the heat exchanger whose tube bundle is carbon steel OLT35K, it was noticed that the two fluids, C<sub>1</sub> - C<sub>5</sub> fraction circulating intertubular and the cooling water

generate intense corrosion and deposit phenomena, which requires large expenses for equipment maintenance.

**Table 6.** Expenses for by the heat exchanger from the top of the C<sub>1</sub> - C<sub>5</sub> removal column

Make-up costs	Value, EUR
<b>Fascicle cleaning and pipe cancelling (every 7 - 8 months)</b>	
a. Pipes and plenum disassembling, cleaning, washing, closing broken pipes, pressure tests, plenum closure, pipes connection.	8150
b. Stop / start installation, production losses	16300
<b>Technical solution study</b>	1630
<b>Tubular carbon steel fascicle replacement (every 36 months)</b>	
a. Pipes and plenum disassembling, old tube bundle disassemble, new tube bundle assembling, pressure tests, plenum closure, pipes connection.	13580
b. Stop / start installation, production losses	16300
<b>TOTAL EXPENSES</b>	
<b>4 stops every 7 - 8 months for fascicle cleaning and pipe cancelling: 4 × (8150 + 16300)</b>	97800
<b>1 stop every 36 months for fascicle replacement</b>	29880
<b>Technical solution study</b>	1630
<b>Full costs for 36 months operation (carbon steel)</b>	<b>129310</b>

Chemical and microbiological analyses carried out on deposition taken in the heat exchanger confirm the aggressiveness of the two fluids.

The corrosion reaction rate of austenitic stainless steel, in both fluids are up to two orders of magnitude smaller compared with the carbon steel case, arguing their use in manufacturing of the tubular fascicle.

Construction costs for the tube bundle austenitic stainless steel equipment could be recovered in 7 to 8 months of operation.

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