

THE CORROSION OF TUBULAR FURNACES IN PLANTS. ATMOSPHERIC DISTILLATION OF CRUDE OIL AND IN VACUUM FOR FUEL OIL

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Abstract: The paper aims to investigate the corrosion of the furnace tube elements of intalatiile Atmospheric crude oil distillation and vacuum of oil. Such phenomena occur in the ceiling and accentuates intalatie distillation as we approach the staging area. Although the corrosion phenomena is not frequently met for the tubes from the furnace, it produces serious damage because when a tube reached limit corrosion in one spot it must be immediately replaced taking into account the fact that the remaining tube is in perfect condition.

Keywords: *corrosion, erosion, Sulfur compounds*

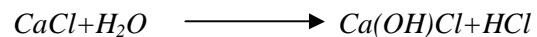
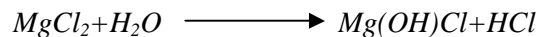
1. Introduction

For unsulphurous fuel oil, the pipes from the formance are made from steel P235GH, and for the sulphurous fuel oil, the pipes are made from steel with 5-9%Cr. The pipes are affected not only by the corrosion phenomena, but also by the erosion phenomenon at the end of the cycle in areas where the speed of the fluid increases. The same phenomena appears in the ceiling and increases as it get closer to the transfer area. Solid salt particles, sulphates and fuel, resulted from the water evaporation, are strongly hit by the meandres of introduction and by the ends of the tubes where the fluid changes it's course. At high speeds remarkable erosions are generated. At the first tubes entering the ceiling, where the speed of the fluid is 25m/s, the speed of corrosion is 0.2 mm/year and 1,5-2,5 mm/year for the tubes before leaving the furnace, where the amount of steam is bigger with a flow rate of cc78 m/s.

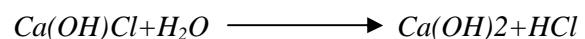
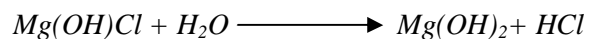
Although the corrosion phenomena is not frequently met for the tubes from the furnace, it produces serious damage because when a tube reached limit corrosion in one spot it must be immediately replaced taking into account the fact that the remaining tube is in perfect condition.

In the furnace, the fuel oil is heated up at 300-340°C, the temperature at which magnesium chloride hydrolyzes in proportion of 60-90%, and

the calcium chloride in proportion of 10%, hydrochloric acid being released.



Basic magnesium and calcium salts decompose at temperatures exceeding 3200C.



Hydrochloric acid in gas form is corrosive for carbon steel, meanwhile the sulfide hydrogen reacts even in the absence of water.

When processing the naphthenic oil with high chloride content, the transfer lines are sublimated to a combined effect of erosion-corrosion because of the naphthenic acids and crystallized salts. Naphthenic acids dissolve the protective layer of FeS and with the sodium hydroxide, introduced after salt removal, form sodium naphthenate, with detergent role which cleans the surface of the metal.

So the clean metal is subjected to the erosive action of the crystals (NaCl, CaCl, MgCl₂, Na₂SO₄).

2. Work technique

The experimental determinations regarding the corrosion behavior of ferrous metals as a result of the aggressive action of circulating oil in the furnace tubes were made with test-tubes of steel with chemical composition presented in **Table 2.1**.

No	Types of steel	The concentration of elements, %							
		C	Mn	Si	Cr	Ni	Ti	P	S
1	S235jR	0,19	0,63	-	-	-	-	0,050	0,070
2	P235GH	0,16	0,52	0,22	-	-	-	0,030	0,029
3	X6CrAl13	0,07	0,085	0,82	13,2	-	-	0,035	0,025
4	X6CrNiTi18-10	0,06	1,25	0,75	18,5	11,2	0,45	0,040	0,015
5	Section with breaking area	0,11	0,42	0,29	-	-	-	0,021	0,024

The samples were mechanically prepared then they were chemically etched with 5% HCl inhibited solution, washed with demineralized weak alkaline water and finally dried with acetone in a desiccator. After testing, individual observations were made on the condition of the surface and on the quantitative determination of corrosion.

From the pipe affected by corrosion, samples were taken and were chemically and microstructurally analyzed.

2.1 Experimental data analysis

Figure 1 shows a schematic diagram of the AD furnace with air heaters at the top, gas output.

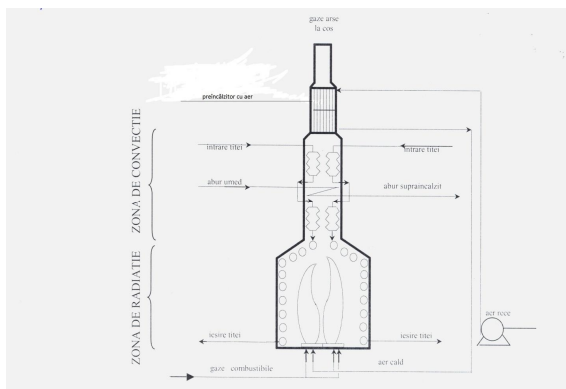


Figure 1: Schematic diagram of the AD furnace with air heaters

Tubular heat exchange elements are simultaneously subjected to both external corrosion due to combustion gases and internal corrosion due to technologic fluid and defense requirements, which vary from one facility to another.

Resulting corrosion products of the outer surfaces due to combustion gases and on surfaces within the same tube determined by the action of the technologic fluid, are acting simultaneously on the metall material. This simultaneously action not only determines modifications of the material structure, but also can have a negative influence on the main mechanical properties. Accurately assess of the changes occurring in the morphology of steel constituents and the nature of the subsided and differently dispersed phases allow more real appreciation of the possible use of such tubular elements.

Internal corrosion of the tubular elements of the furnaces from AD and VD plants is determined on one hand by the aggressiveness of the technologic fluid, and on the other hand by operating conditions. Processed raw material is made from paraffinic, naphthenic and aromatic hydrocarbons, sulphurous hydrogen, mercaptans, various chlorides, etc. For example, sulfur is dissolved in fuel oil at a rate of 0.20% to 0.24% and chlorides from 20 to 250 ppm. With technology operating at temperatures above 4000C and pressure of 20bar, fuel oil undergoes thermochemical decomposition reactions, resulting a surplus of unwanted corrosive agents, in addition to those existing in the crude oil, or those which are added as needed for processing it. The intensity of metal tubular elements degradation processes by corrosion is additionally influenced by the speed of the technologic fluid circulation and by their turbulence within the pipes in the oven and transfer lines. The fluid flow is biphasic, corrosion processes, as it consisted, depend not so much on the total acidity of crude oil, but on the total acidity of the non-vaporised residue from the system (Table 2). In order here to calculate the total acidity coefficient of the non-vaporised was determined residue efficiency in distilled fractions from native (TAC) of crude oil remaining after each fraction was removed.

The data presented in **Table 2.2** show that the total acidity coefficient of the non-vaporised residue reaches maximum of 2.56 mg KOH / g corresponding to the fuel oil exiting the furnace. The flow rate gradually increasing with the vaporization oil of a new quantity of hydrocarbs

determines a maximum of the total acidity coefficient, of flow rate and temperature. All these values are reached simultaneously at about exiting of the furnace. Given the severity of this condition the speed of the corrosion should be very high compared to the distilled fractions from the same crude oil. However, this fact was not determined in reality. This fact can be explained by assuming that in this case crude oil contains substances that ensure a protective layer of coke, as not in the case of distillates. This layer can be partially removed if the fluid's turbulence is high, fact that allows the installation of a localized corrosion attack.

Table 2.2: TAC Total acidity coefficient of distilled fractions and non-vaporised residue

Distillated fraction	Efficiency (%)	TAV fraction (mg KOH/g)	TAV calculated for non-vaporised residue (mg KOH/G)
Gasoline 70...100°C	12	0,03	2,21
Petroleum I 170...230	7	1,21	2,29
Petroleum II 230..280°C	6	1,25	2,38
Gas oil I 270...310°C	16	1,82	2,53
Gas oil II 310-350°C	3	1,99	2,56
Fuel oil > 350°C	56	3	0,55

Corrosion products resulting from the attack of naphthenic acids are soluble iron naphthens which can not provide protection as that of iron sulphide resulting from the interaction with hydrogen sulfide.

Along with naphthenic acid crude oil contains sulfur compounds, hydrogen sulphide, mercaptans, etc., whose attack on steel plant enhances the corrosion processes specially at high temperatures

Following this attack a layer of pores reducing the speed of corrosion of naphthenic acids is made.

Test-tubes from carbon steel S235JR and stainless steel X6CrAl13 and X5CrNi18-10 with and without sulphide layer were tested in solutions of naphthenic acids with TAC 145 mg KOH / g during 20 days at a temperature of 100°C (Table 3).

It can be seen from the data presented in **Table 2.3** that the existence of a compact layer of iron sulfide reduces significantly the corrosion rate due to naphthenic acids.

Material	Protected with FeS layer	Corrosion rate	
		K _g ⁻ (g/m ² /h)	P (mm/year)
S235jR	No	0,092	0,102
	Yes	0,071	0,079
X6CrAl13	No	0,074	0,082
	Da	0,0092	0,0010
X6CrNi 18-10	No	0,014	0,016
	Yes	0,0053	0,006

But in industrial conditions, it is possible that in the presence of large amounts of naphthenic acids in crude oil, with a high-speed of technologic fluid, the FeS film can be damaged (broken) which allows the initiation and localization of new forms of localized corrosion. In these circumstances, inner and outer surfaces of the tubular element are highly stressed by the corrosion products.

The tube element from the AD furnace, which carries crude oil out of the furnace at a temperature of 340°C and pressure of 80 bar of P235 GH steel, after 60,000 hours of operation, had shown corroded areas with cracks.

The external diameter of the pipe, outside the cracked area is 10% higher than the minimum diameter, and in the fractured zone the remaining elongation is 12.4% with corresponding reduction of wall thickness to 0.9 mm and a reduction of 91% compared to nominal thickness of the tubular element.

In the breaking area, the tubular element shows an excessive oxidation due to local thermal overstressing. This is due to the deposit of corrosion products that reducing heat transfer, determined the appearance of cracks with a depth of 1.2-2.0 mm. The cracking and further material breaking were favored by the greater thickness of the decarbonized layer, caused by the mentioned thermal overstressing, respectively by exceeding its resistance capacity under the action of internal pressure (**Figure 2.2**)

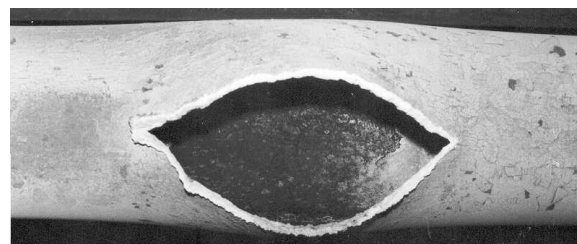


Figure 2.2. Cracks in the tube of the AD furnace

Metallographicall research conducted on processed cuts from both corroded and unaffected areas (2% solution of metal activation) revealed microstructural changes resulting from corrosion. In the unaffected area no changes were found in the ferritico-pearlitic layers, specific for P235GH steel (**Figure 2.3**) and the corroded area presents a modified ferritico-pearlitic structure with deformed grains.

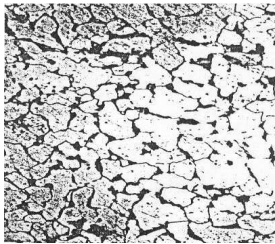


Figure 2.3. The material's microstructure from the unaffected area (x500)

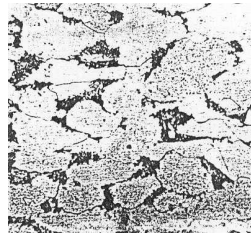


Figure 2.4. The material's microstructure from the breaking area (x 500)

Also from the analysis of metallographic cuts, it is revealed a spheroidizing of the carbides from the pearlite and a precipitation at their ferrite grains limits.

These specific types of precipitation are specific for the steel which is maintained at higher temperatures, compared to the recommended temperature range.

3. Conclusions

In the AVD plant which processes non-sulphurous oils, corrosion processes are determined primarily by naphthenic acidity and distilled from crude oil, expressed by total acidity coefficient (TAC), by the sulfur and chlorine compounds, and operating conditions.

Sulfur compounds present in crude oil have naphthenic corrosion braking action, as iron sulphide skin, as a product of the interaction between steel and sulfur compounds, is more compact and more adherent than iron naphthenate skin.

The flow rate of technologic fluid and its biphasic nature, corrode with the vaporization phenomenon to in balance and the start of the vaporos, liquid stages distress determines the intensification of the transfer lines corrosion and of the furnace pipes,

because in these parts of the installation there combines cavity, corrosion and erosion phenomena. The breaking of the AD furnace tube was due to exceeding the endurance limit of the steel as a result of local overheating due to corrosion products deposited layers, up to 8.2 mm thick. Overheating caused a pronounced decarburization and the emergence of cracks up to 2 mm grooves on the external surface of the pipe.

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