Hot corrosion Evaluation of Carbon Steel caused by Mixtures of Vanadium Oxide and Sodium Sulfate Simulating Ashes of Fuel Oils

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Abstract — *Ashes from the burning of fuel oils containing mixtures of vanadium, sodium, sulfur and chloride compounds in the form of molten salts or oxides can cause hot corrosion of the carbon steel tubes located in the furnace at high temperatures with extremely disastrous effects. In order to simulate the melting ash in the laboratory, mixtures of sodium sulfate and vanadium pentoxide were used in different proportions of Na_2O and V_2O_5 at temperatures of 500°C, 700°C and 800°C and in the exposure time of 12h, 24h and 36h using carbon steel coupons in the form of half-cane. The results were evaluated morphologically for the depth of the corrosive attack and the loss of mass using a confocal microscope where it was possible to evaluate the degree of corrosion caused by the action of the vanadate fluxes ($Na_2O.V_2O_5$).The deepest pitting occurred in the ratio $2Na_2O.V_2O_5$ at the three test temperatures. At the temperature of 800°C and in the time of 36 hours, the average thickness loss in the coupons was 11%.*

Keywords — **Hot corrosion, vanadate, vanadium oxide, sodium sulfate, fuel oil.**

I. INTRODUCTION

Hot corrosion in steam boiler tubes (furnace area) can be defined as the corrosion or degradation of carbon steel tubes resulting from the combined effect of oxidation and accelerated attack, at elevated temperatures, of ash from the burning of fuel oils containing mixtures of vanadium, sodium, sulfur and chloride compounds in the form of molten salts or oxides [1–3]. Rapp [4] considered that hot corrosion is associated with two temperature ranges. In the 650°C – 750°C range, it is of Low Temperature Hot Corrosion (LTHC), while a more severe corrosion is of High Temperature Hot Corrosion (HTHC) acting in the range 750°C – 950 °C.

The composition of boiler fuel oil consists of heavy hydrocarbons depending on the type of petroleum and the operations performed in the refineries, so that it meets the requirements of the specific standards for each type of steam boiler. Organics sulfurs are in the form of

mercaptans, sulfides, polysulfides and thiophenes. Additionally, impurities such as organometallic compounds, salts and metal oxides are also present in fuel oils in small amounts. Failure to comply with the norms that regulate the maximum levels of these compounds as well as the burning of fuels outside the operating standards and at high temperatures can be considered the main parameters responsible for this type of corrosion. However, it should be clear that impurity contents within the limitations of the standards do not completely eliminate the risk of corrosion.

Sodium may originate from sodium chloride (NaCl) from the oil produced water while vanadium is found in the form of porphyrins. Combined burning (oxidation) of the sulfur compounds with sodium chloride can generate sodium sulfate (Na_2SO_4), and burning the porphyrin in vanadium produces oxides such as VO, V_2O_3, VO_2 and V_2O_5. The V_2O_5 is mainly obtained in the function of oxidizing conditions and elevated temperature.

Several researches have shown the formation of vanadates ($Na_2O.V_2O_5$) resulting from the reaction between sodium sulfate and vanadium pentoxide in the function of temperature, stoichiometric ratios and of oxidizing conditions. The formation of these compounds with low melting point may dissolve the protective iron oxide layer on the surface of carbon and then attack the surface of the carbon steel itself [4–8]. In general, it is valid to admit that the lower the melting point of the constituents of an ash, the greater the probability of this ash becoming a flux and attacking the carbon steel. The reactions between sodium sulfate and vanadium pentoxide are shown below:

$$Na_2SO_4 + V_2O_5 \rightarrow Na_2O. V_2O_5 + SO_3$$
$$Na_2SO_4 + 3 V_2O_5 \rightarrow Na_2O. 3V_2O_5 + SO_3$$
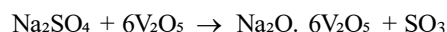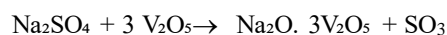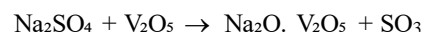$$Na_2SO_4 + 6V_2O_5 \rightarrow Na_2O. 6V_2O_5 + SO_3$$

Table 1 shows the low melting point of the vanadium and sodium compounds that can cause the attack on the carbon steel tubes, allowing the occurrence of catastrophic corrosion.

Table.1 - Melting points of some constituents present in the ashes

Substance	Formula	Melting point (°C)
Sodium sulfate	Na_2SO_4	880
Vanadium pentoxide	V_2O_5	675
Sodium metavanadate	$Na_2O.V_2O_5$	630
Sodium pyrovanadate	$2Na_2O.V_2O_5$	640
Sodium orthovanadate	$3Na_2O.V_2O_5$	858
Ferric Oxide	Fe_2O_3	1565
Ferric orthovanadate	$Fe_2O_3.V_2O_5$	855
Ferric metavanadate	$2Fe_2O_3.2V_2O_5$	860

This type of corrosion has been observed in the inspections carried out on the carbon steel tubes of fire-tube boilers located in the furnace area (Figure 1). It is believed that this corrosion is associated with the burning of fuel oils.
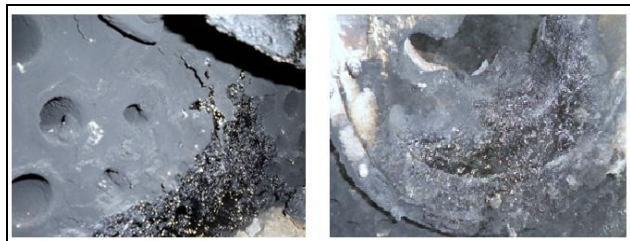

Fig. 1: Hot corrosion aspect of a fire-tube boiler

This work aims to present laboratory tests to evaluate the corrosion caused by mixtures of sodium sulfate and vanadium pentoxide at elevated temperatures on the carbon steel tube surface of fire-tube boilers.

II.   MATERIALS AND METHODS

Coupons were prepared through a carbon steel boiler tube with 3.8 cm diameter and 3 mm of thickness that was cut into a 2 cm wide cane. The carbon steel analysis is presented in Table 2 and is in accordance with the specification of the ASTM A178 [9].

Table.2. The chemical composition of of carbon steel tube

C (%)	Mn(%)	Si(%)	S%	P%	Fe(%)
0.030	1.80	0.35	0.009	0.017	Balance

In order to simulate the corrosive action of the ashes, it was decided that mixtures of V_2O_5 with Na_2SO_4 would be used to better approximate the original composition of the ashes produced in a real boiler operation as a function of the presence of sulfur. The V_2O_5 and Na_2SO_4 used in the laboratory tests are anhydrous and have a purity of 99.90%.

The representative samples of Na_2O and V_2O_5 in the proportions of 2:1; 1:1 and 1:2 were made from the mixtures of Na_2SO_4 and V_2O_5 macerated into a porcelain mortar and pestle. As much as 3 g of the representative sample of $Na_2O.V_2O_5$ was placed in a plastic syringe with nozzle, pressed with the plunger and later placed in the center of the half cane of the carbon steel tube and later placed in the electric furnace at the temperatures indicated. Test temperatures were 500, 700 and 800°C while the exposure times in the electric furnace were 12, 24 and 36 hours. Figure 2 shows the sequence of operations for performing the assay.
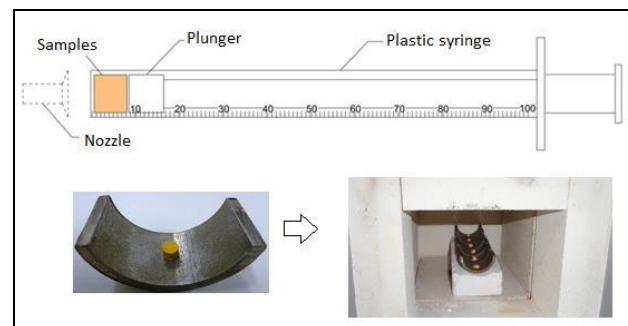

Fig. 2: Sequence of operations for carrying out the test with mixtures of Na_2SO_4 and V_2O_5.

The coupons removed from the electric furnace were cleaned. Initially, the ash layers were removed by lightly using a small spatula. The coupons were then immersed in a solution with 5% hydrochloric acid and 1% propargyl alcohol as a corrosion inhibitor for 30 minutes. Then they were washed with distilled water, alcohol and dried with hot air.

In this research, the confocal optical microscope, model Olympus LEXT OLS 4000 Confocal Laser Microscope, was used to punctually identify the morphology of the corrosive attack on the metallic surface. The increase in the analysis of the images was limited to 420 times as a function of the geometry of the curve of the coupons, restricting the area of study in the dimensions 0.64 mm x 0.64 mm in the area of interest.

As shown in Figure 3, the pitting are identified by red circles in the micrograph, and by means of proprietary software installed in the confocal optical microscope, a rectangle triangle is generated that determines the depth of each pitting as shown in the 3D image.

In the evaluation of pitting corrosion, the concepts of the ASTM standard G46-94 [10] were used while measuring the deepest pitting and expressing the degree of corrosion in terms of maximum depth or the mean of the 10 pitting with the highest penetration.
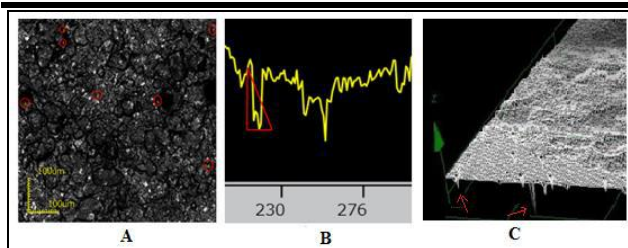
Fig. 3: A) Identification of pitting the micrograph; B) Profile of pitting with depth; C) Pitting in 3D.

III. RESULTS AND DISCUSSION

Figure 4 shows the appearance of the coupons after removal from the electric furnace. Considering that the fluxing mass (Na_2SO_4 and V_2O_5 mixture) was placed at the center of the cane-shaped coupon, it has been observed that the corrosion was localized and more intense, resulting in a depression and localized mass loss of carbon steel. Furthermore, the appearance of the molten mixture has also been observed.

Fig. 4: Appearance of the coupons after removal from the electric furnace

After cleaning the coupons, the thickness determination was performed by means of a digital micrometer in the centralized area of the coupon where the corrosive attack of the melt mixture of Na_2SO_4 and V_2O_5 occurred. The results are presented below:

a) at a temperature of 500°C and for 12 hours, there was an average thickness reduction of 1.8%;

b) at a temperature of 700°C and for 24 hours, there was an average thickness reduction of 4.6%;

c) at a temperature of 800°C and for 36 hours, there was an average thickness reduction of 11%.

The results of mass loss in the area of attack with the flux mixture tended to increase with increasing temperature and time of exposure. Consequently, the mass losses involve the reduction of thicknesses in the specimens.

In the micrographs shown in Figures 5, grooves, excavations, pitting and uniform corrosion on the surface of the exposed coupons at 500°C with mixtures of Na_2SO_4 and V_2O_5 were observed. Additionally, these observations were mentioned in the research studies conducted by Lai [11] and Khadom [12] as a characteristic of the dissolution of the oxidation film.
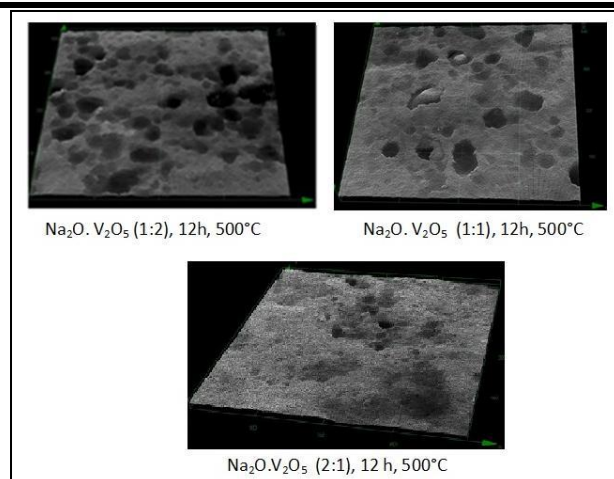

Fig.5: Aspect of surfaces in 3D after the tests at 500 °C and 12 h of exposure.

As the temperature increases from 500°C to 700°C and then to 800°C, there is a transformation of the corrosion located in uniform corrosion and consequently, there is a greater loss of mass of the carbon steel coupons as shown in Figures 6 and 7.
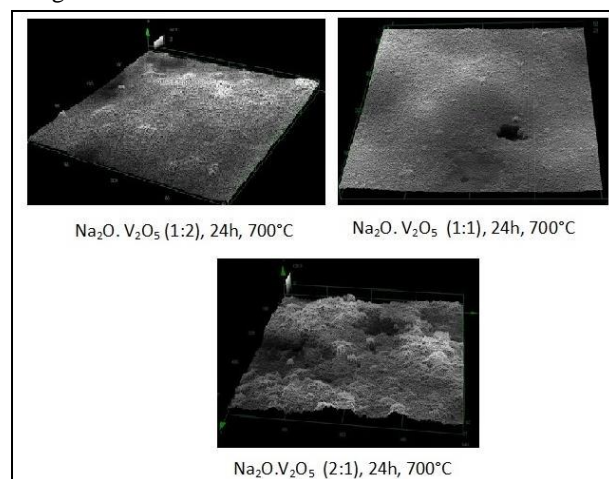

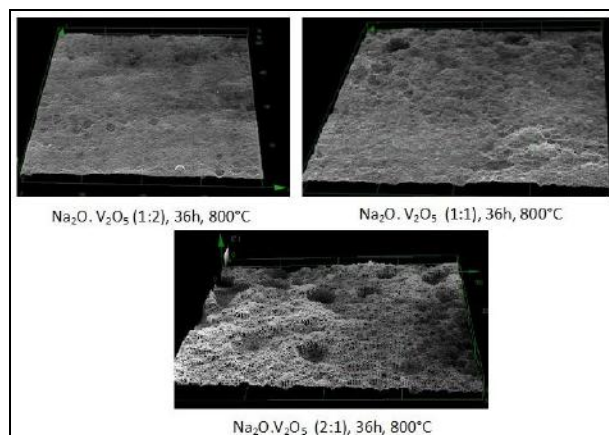*Fig. 6: Aspect of surfaces in 3D after the tests at 700 °C and 24 h of exposure.*

Fig. 7: Aspect of surfaces in 3D after the tests at 800 °C and 36 h of exposure.

As shown in Table 3, at all the three test temperatures (500°C, 700°C and 800°C), it is noted that deeper pitting increases with temperature and with increasing Na_2O in the melt mixture, and pitting with greater depth (65.36 μm) occurred at 800°C.

Table 3: Maximum depth of pitting (μm)

Mixture $Na_2O.V_2O_5$	T,°C	Exposure time, h	Number of pitting	Maximum depth of pitting (μm)
1.1	500	12	7	35.94
1.2	500	12	11	20.64
2.1	500	12	2	64.63
1.1	700	24	8	24.76
1.2	700	24	7	37.00
2.1	700	24	8	52.46
1.1	800	36	13	34.11
1.2	800	36	13	25.48
2.1	800	36	7	65.36

Pitting corrosion in the presence of ash is cited by Singh et al.[1] and Khadom et al. [12]. Generally, the deposits of ash rich in Na_2O have a characteristic pitting attack [13]. With increasing temperature, the oxidation film tends to grow and fracture by increasing the diffusion of the sulfur present in the Na_2SO_4 rich fluxes. This results in a corrosive attack by sulphation, which may be pitting [11]. Such facts may indicate that pitting may be one of the initial stages that progresses toward generalized corrosion, as the oxidation film is dissolved over time and in the proportions of Na_2O and V_2O_5 in the tests.

IV. CONCLUSIONS

High temperature corrosion tests with mixtures of Na_2SO_4 and V_2O_5 simulate the ash action from the combustion of fuel oils, providing results in which the following conclusions can be drawn:

- The microscopic evaluation showed that the action of the vanadates fluxes on the surface of the carbon steel resulted in uniform corrosion and corrosion by pitting in rounded form (excavations) and deep pitting;
- The deepest pitting occurred in the ratio $2Na_2O.V_2O_5$ at the three test temperatures.
- Microscopic evaluation suggests that from 700°C, localized corrosion progresses to uniform corrosion.
- At the temperature of 800°C and in the time of 36 hours, the average thickness loss in the coupons was 11%.

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