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 Na₂O and V₂O₅ 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 (Na₂O·V₂O₅). The deepest pitting occurred in the ratio 2Na₂O·V₂O₅ 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 (Na₂SO₄), and burning the porphyrin in vanadium produces oxides such as VO, V₂O₅, VO₂ and V₂O₅. The V₂O₅ is mainly obtained in the function of oxidizing conditions and elevated temperature.

Several researches have shown the formation of vanadates (Na₂O·V₂O₅) 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:

\[ \text{Na}_2\text{SO}_4 + 3\text{V}_2\text{O}_5 \rightarrow \text{Na}_2\text{O} \cdot 3\text{V}_2\text{O}_3 \]
\[ \text{Na}_2\text{SO}_4 + 3\text{V}_2\text{O}_5 \rightarrow \text{Na}_2\text{O} \cdot 3\text{V}_2\text{O}_3 \]
\[ \text{Na}_2\text{SO}_4 + 6\text{V}_2\text{O}_5 \rightarrow 2\text{Na}_2\text{O} \cdot 3\text{V}_2\text{O}_3 \]

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          | Na₂SO₄      | 880                |
| Vanadium pentoxide      | V₂O₅        | 675                |
| Sodium metavanadate     | Na₃O.V₂O₅   | 630                |
| Sodium pyrovanadate     | 2Na₃O.V₂O₅  | 640                |
| Sodium orthovanadate    | 3Na₃O.V₂O₅  | 858                |
| Ferric Oxide            | Fe₂O₃       | 1565               |
| Ferric orthovanadate    | Fe₂O₃.V₂O₅  | 855                |
| Ferric metavanadate     | 2Fe₂O₃.2V₂O₅| 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 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 V₂O₅ with Na₂SO₄ 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 V₂O₅ and Na₂SO₄ used in the laboratory tests are anhydrous and have a purity of 99.90%.

The representative samples of Na₂O and V₂O₅ in the proportions of 2:1; 1:1 and 1:2 were made from the mixtures of Na₂SO₄ and V₂O₅ macerated into a porcelain mortar and pestle. As much as 3 g of the representative sample of Na₂O.V₂O₅ 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 Na₂SO₄ and V₂O₅.

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.
III. RESULTS AND DISCUSSION

Figure 4 shows the appearance of the coupons after removal from the electric furnace. Considering that the fluxing mass (Na₂SO₄ and V₂O₅ 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.

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 Na₂SO₄ and V₂O₅ 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 Na₂SO₄ and V₂O₅ 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.
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 Na₂O in the melt mixture, and pitting with greater depth (65.36 µm) occurred at 800°C.

**Table 3: Maximum depth of pitting (µm)**

| Mixture | 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 Na₂O 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 Na₂SO₄ 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 Na₂O and V₂O₅ in the tests.

**IV. CONCLUSIONS**

High temperature corrosion tests with mixtures of Na₂SO₄ and V₂O₅ 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 2Na₂O:V₂O₅ 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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