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A Study of the Effect of Kaolin as a Fuel Oil Additive on the Corrosion Inhibition of Fireside Superheater Boiler Tubes

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Abstract

The objective of the present study is to determine the effect of Kaolin as a fuel oil additive to minimize the fireside corrosion of superheater boiler tubes of ASTM designation (A213-T22) by increasing the melting point of the formed slag on the outside tubes surface, through the formation of new compounds with protective properties to the metal surface. The study included measuring corrosion rates at different temperatures with and without additive use with various periods of time, through crucible test method and weight loss technique.

A mathematical model represents the relation between corrosion rate and the studied variables, is obtained using statistical regression analysis. Using this model, the best additive to ash weight ratio was specified. Then scanning electron microscopic images taken to the two treated and untreated samples with additive to study the difference in nature of slag formed on the metal surface to the two cases.

Keywords: *Kaolin effect on corrosion, corrosion in fireside boiler tubes, milting point of slag on outside tube surface.*

1. Introduction

Higher operating temperatures, the goal of every designer and user of Carnot cycle limited energy systems, are not being achieved today in power plants because of serious problems with materials of construction in flue gas atmospheres. The problem in central station boilers is one of finding the least expensive superheater alloys that can tolerate continuous exposure to hot flue gas carrying fuel ash, sulfur oxides and other undesirable components. Since economics limit the alloys that can be used, the problem becomes one of controlling the flue gas and the substances it carries so as to yield a reasonable life for moderately priced heat receiving surfaces. Three major factors are involved in external corrosion and in the formation of deposits [1]:

1. The temperature of metal surfaces and the gas stream.
2. The composition of substances in contact with metal surfaces and the nature of those surfaces.
3. Aerodynamic considerations involving gas and particle velocity and the size consist of deposited particles.

Metallurgical factors are important too, but only actions occurring at the outer exposed surface of metal will be considered here.

Several studies [2,3] , investigated the use of additives to control corrosion problems, the most effective materials for this purpose were (Al_2O_3, SiO_2) [4]. A detailed work is to be conducted by this research to suggest an available and cheap inhibiting material to suit the specified characteristics based on the mentioned materials.

2. Fuel Contaminates

It is the inorganic matter in fuels that leads to problems with corrosion and deposits. Crude oil may contain (1-500 ppm) of vanadium in pyrophyren complex form, depending on the source. Residual oil, a refinery concentrate, contains several times more vanadium than the crude from which it was derived. Combustion of such vanadium containing fuels produces very corrosive vanadium pentoxide deposits, which can destroy superheater boiler tubes, this hot corrosion is slow at 600 °C but the rate increases rapidly with temperature rise. Although vanadium removal from fuels is possible, the cost of such process cancels the economic advantage of using lower quality fuels. Therefore, vanadic corrosion must be controlled with chemical additives.

Sulfur varies widely in crude oils, ranging from elemental sulfur to thiophene and its homologues. Generally, the amount of sulfur in residual fuel is about twice that in crude oil from which it comes depending on refinery practice. Its content in hydrocarbon fuels is in the (1-3%) range.

Sodium on the other hand causes most trouble when it is present as the chloride, sulfate and soluble organic compounds in fuel. During combustion, sodium reacts with the sulfur to form sulfate, which deposited on boiler tubes surfaces causing high temperature corrosion.

3. Occurrence of Corrosion

Corrosion is categorized as high temperature if it is found where the gas temperature is above 540 °C, as with furnace wall tubes, superheaters, reheaters. Where the gas temperature is less than 540 °C as with air heaters and economizers, metal loss occurs by low temperature corrosion[5].

4. High Temperature Corrosion

At high temperature range (540-980 °C), sulfur in the fuel oil will convert mainly to SO_2. Conversion of SO_2 to SO_3 takes place in the furnace depending on sulfur content, excess air and flame temperature by the reaction of SO_2 with atomic oxygen which formed by dissociation of molecular oxygen in the flame zone.

Sodium in the fuel is mainly present as NaCl, readily vaporized during the combustion process, and react with H_2O to produce NaOH which react with SO_3 to give Na_2SO_4 as shown in the next equations [6]:

$$H_2O + NaCl_{(g)} \longrightarrow NaOH_{(g)} + HCl \quad \ldots(1)$$

$$2NaOH_{(g)} + SO_3 \longrightarrow Na_2SO_{4(g)} + H_2 \quad \ldots(2)$$

Sodium sulfate formation becomes increasingly favorable thermodynamically as the temperature decreases; its presence increases the oxidation rate. When the metal is in contact with the salt, a trigger reaction occurs involving a reducing agent (R) which could be constituent of alloy [7].

$$Na_2SO_4 + 3R \longrightarrow Na_2O + 3RO + S \ldots(3)$$

This step is followed by metal sulfide formation:

$$M + S \longrightarrow MS \quad \ldots(4)$$

The second stage comprised (autocatalytic destruction) reactions:

$$Na_2SO_4 + 3MS \longrightarrow 4S + 3MO + Na_2O \ldots(5)$$

$$4M + 4S \longrightarrow 4MS \quad \ldots(6)$$

Vanadium in fuel oxidized to V_2O_5 during combustion which reacts with Na_2SO_4 in many reactions (as shown bellow) to form products as low as 542 °C with a eutectic of (35 mol% Na_2O) molten at 530 °C. The low melting compounds are the most harmful corrosives in residual fuel [8].

$$Na_2SO_4 + V_2O_5 \longrightarrow 2NaVO_3 + SO_3 \quad \ldots(7)$$

$$Na_2SO_4 + 3V_2O_5 \longrightarrow Na_2O.3V_2O_5 + SO_3 \ldots(8)$$

$$Na_2SO_4 + 6V_2O_5 \longrightarrow Na_2O.6V_2O_5 + SO_3 \ldots(9)$$

5. Effects of Fuel Additives

Many additives function to control high temperature corrosion by their physical and chemical actions, and it is often not possible to separate the two actions.

Some mineral additives have been suggested and shown to bring positive effects to combat ash-related operational problems (e.g. slag formation), as a result of change in ash composition in the silicate oxide systems relevant for many biomass ashes and a subsequent change in melting temperatures [8,9]. The use of clay mineral (Kaolin) has shown to influence the ash chemistry by acting as a strong sorbent for sodium according to the following reactions suggested in earlier studies by Tran et al [10].

$$Al_2Si_2O_5(OH)_4 \longrightarrow Al_2O_3.2SiO_2 + 2H_2O \ldots(10)$$

$$Al_2O_3.2SiO_2 + 2NaCl + H_2O \longrightarrow 2NaAlSiO_4 + 2HCl \quad \ldots(11)$$

$$Al_2O_3.2SiO_2 + 2SiO_2 + 2NaCl + 2H_2O \longrightarrow NaAlSi_2O_6 + 2HCl \ldots(12)$$

$Al_2Si_2O_5(OH)_4$ Kaolinite is the dominating mineral in kaolin clay and $Al_2O_3.2SiO_2$ (meta-kaolinite) is an amorphous mixture of alumina and silica when kaolinite lesser water at high temperature. $NaAlSiO_4$ and $NaAlSi_2O_6$ are high melting Na-Al silicate minerals formed during fuel combustion [11].

Further studies [12,13], used kaolin as fuel additive during combustion of solid fuels having low melting point alkaline compositions, and found that it is particularly effective by producing high melting point alkali metal compounds during combustion.

6. Experimental Procedure

High temperature corrosion of the superheater alloy was studied in the presence of corrosive mixture (20 wt.% sodium sulfate + 80 wt.% vanadium pentoxide) using crucible testing method [١٤]. The effect of three variables (temperature, time and kaolin/ash weight ratio) on corrosion rate was investigated and analyzed using experimental design. Temperature was taken in the range (400-900 °C), while time was ranged in (2-10 hours) and additive to ash weight ratio (0-8wt.%). Selected ranges divided according to Box-Wilson experimental design with 21 coded values for each variable as shown in the first three columns of table (2). Equation (13) relates the coded and real values and then is used to calculate the second three columns of table (1) as shown.

Table 1,
Corrosion Rate Results According to Box-Willson Design.

X_1 Cod.	X_2 Cod.	X_3 Cod.	Tem. (^oC)	Time (hr)	Add./ash (wt)	C.R. gmd
+1	+1	+1	794	8.3	6.3	93.24
-1	+1	+1	506	8.3	6.3	32.58
+1	-1	+1	794	3.7	6.3	77.76
-1	-1	+1	506	3.7	6.3	17.64
+1	+1	-1	794	8.3	1.7	157.5
-1	+1	-1	506	8.3	1.7	117
+1	-1	-1	794	3.7	1.7	117.9
-1	-1	-1	506	3.7	1.7	72
$\sqrt{\alpha}$	0	0	900	6	4	216
0	$\sqrt{\alpha}$	0	650	10	4	99
0	0	$\sqrt{\alpha}$	650	6	8	54
$-\sqrt{\alpha}$	0	0	400	6	4	13
0	$-\sqrt{\alpha}$	0	650	2	4	50.58
0	0	$-\sqrt{\alpha}$	650	6	0	130.5
0	0	0	650	6	4	63
1	0	0	794	6	4	93.6
0	1	0	650	8.3	4	70.2
0	0	1	650	6	6	54
-1	0	0	506	6	4	45
0	-1	0	650	3.7	4	59.4
0	0	-1	650	6	1.7	83.7

$$X_{Real} = X_{Coded}\left[\frac{X_{Center} - X_{Min.}}{\sqrt{\alpha}}\right] + X_{Center} \qquad ...(13)$$

where:

X_{Real} is the variable real value.

X_{Coded} is the coded value according to Box-Willson Exp. Design.

X_{Center} is the median real value.

$X_{Min.}$ is the minimum real value.

α is the number of variables.

The superheater tube alloy of ASTM designation (A213-T22) is used with the composition (taken from Al-Dora Power Station in Baghdad) as shown in table (2):

Table 2,
Elemental Ratios of Boiler Steel Tube.

Element	C	Si	Mn	Cr	Mo
% Wt.	0.1	0.5	0.4-0.7	2-2.5	0.9-1.2

The tube cut into cylindrical pieces of dimensions (5mm height, 38mm outer diameter and 25mm inside diameter).

Specimens were degreased, annealed and stored in desiccators, and then abraded under tap water. Dimension of each specimen measured and weighed to the fourth decimal of gram.

Artificial ash was then prepared by mixing and grinding sodium sulfate with vanadium pentoxide at weight ratios of (80%V_2O_5 + 20%Na_2SO_4) using electrical mortar (type RETSCH-BB1A). Similarly the mixture of ash with additive (Kaolin) was prepared to have the proposed (additive/ash) weight ratios as shown in column 6 of table (1). The cleaned specimens were then immersed in the ash and put in a high resistance crucible and placed in the muffle furnace (Type NABERTHERM-N20/H) under controlled temperature and time. When experimental run finished samples are taken to clean and weighed to calculate weight loss and corrosion rates as shown in column 7 of table (1). Two photos of the treated and untreated slag of fractured samples were then taken using 1000x magnification scanning electron microscopy (type Hitachi S-3000N Japan) in the University of Sulaimania, Kurdistan to compare the effect of additive on the structure of the formed slag.

7. Results and Discussion

From the practical results of corrosion rates shown in column7 table (1), a regression analysis is applied to get the polynomial of equation (2) using STATISTICA ® kernel release 6.0. This equation represents the best form of mathematical model that relates corrosion rate (C.R.), with the three studied variables (temperature, time and additive/ash weight ratio). Value of correlation coefficient was 0.9407. This model is used to plot graphical figures between corrosion rates versus each variable, and to evaluate the suitable additive/ash weight ratio.

$$\begin{aligned} \text{C.R.} = {} & 273.57 - 0.7715T + 2.459t - 26.51A - \\ & 0.001822Tt + 0.01289TA - 1.26977tA \\ & + 0.000767T^2 + 0.789933t^2 + 1.847988A^2 \end{aligned} \qquad \ldots(14)$$

where:

C.R.= Corrosion Rate (gmd)

T=Temperature (^{o}C)

t= time (hr.)

A=Additive to ash weight ratio (gm/100 gm ash)

Figure (1) shows the effect of additive/ ash weight ratio on the corrosion rate at different temperatures and at a time period of 5 hours according to equation (14). It is clearly found that increasing ratio of additive with ash mixture reduces corrosion rate and this effect appears efficiently at weight ratio (6wt %). Explication of this case is due to the physical and chemical role of alumina and silica in kaolin.

Effect of alumina combined with silica is found to be due to the reaction with sodium sulfate and sodium chloride to produce a protective high melting point compact scale of ($Na_2O.Al_2O_3.2SiO_2$)[1] and (NaAlSiO4, NaAlSi2O6)[10] which prevents the transport of oxygen from the melt surface to the metal interface.

Silica is found to be effective due to the reaction with sodium compounds to form a series of silicates such as ($Na_2O.SiO_2$) which melts at (1000 ^{o}C)[1].

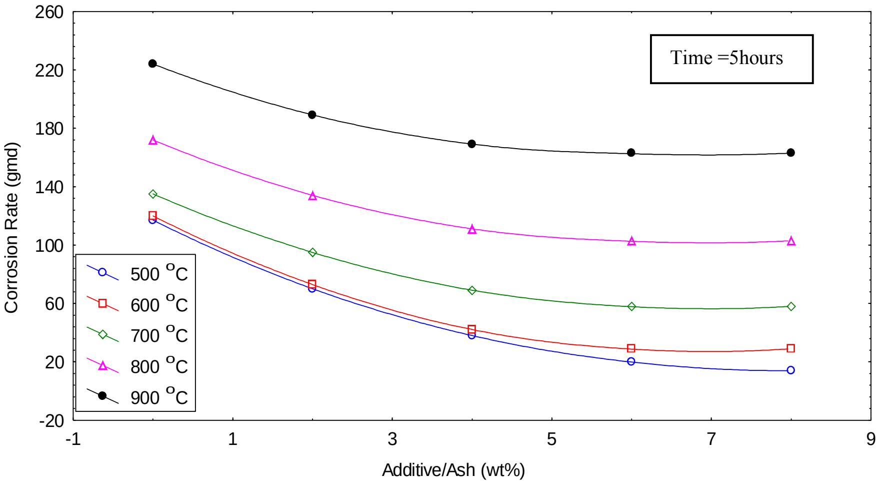

Fig.1. Effect of Additive Ratios on Corrosion Rate at Various Temperatures.

Figure (2) clarify the effect of additive on corrosion rates with time, it was found that the efficiency of additive increases with time especially after the eighth hour from the experiment beginning. That means the growth of a protective layer on the metal surface with time helps to preserve it from severe oxidation.

Figure (3) represents the relation between temperature and corrosion rate according to equation (14). It is clearly shown that increasing temperature range leads to higher corrosion rate, and this increase confirm the exponential relationship. Efficiency of additive decreases when the temperature exceeds (600 ^{o}C) due to formation of ($NaVO_3$, $Na_2O.3V_2O_5$, $Na_2O.6V_2O_5$) according to chemical reactions (4, 5, 6), these compounds catastrophically oxidize the alloy parts by acting as oxygen carriers and metal oxide distorts.

Figures (4) and (5) show the change in corrosion rate with time. In the two figures a similar behavior noticed with and without additive use and the difference appeared only in the range of temperature. In case of additive use a rate plot follows logarithmic equation is obtained, while without additive use an exponential equation is found; i.e. two types of scale are formed.

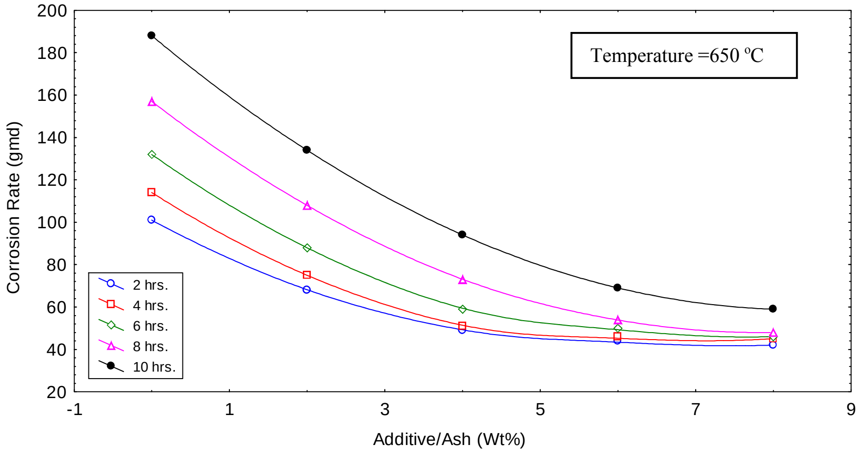

Fig.2. Effect of Additive Ratios on Corrosion Rate at Different Time Periods.

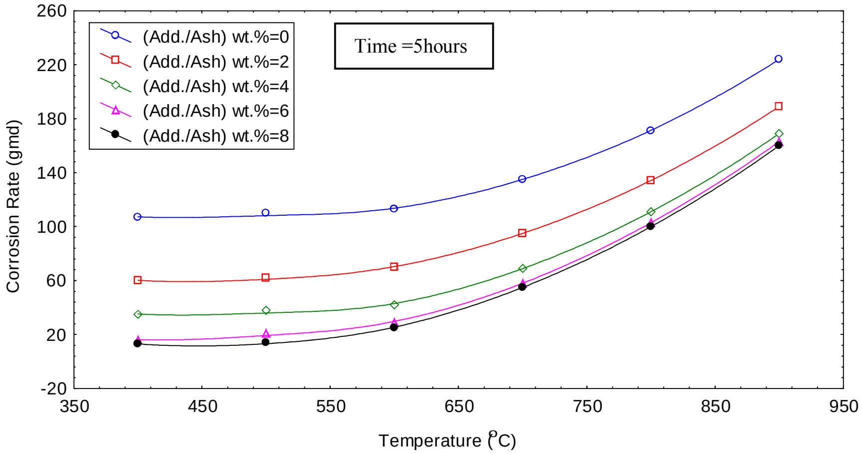

Fig.3. Effect of Temperatures on Corrosion Rate at Different Additive Ratios.

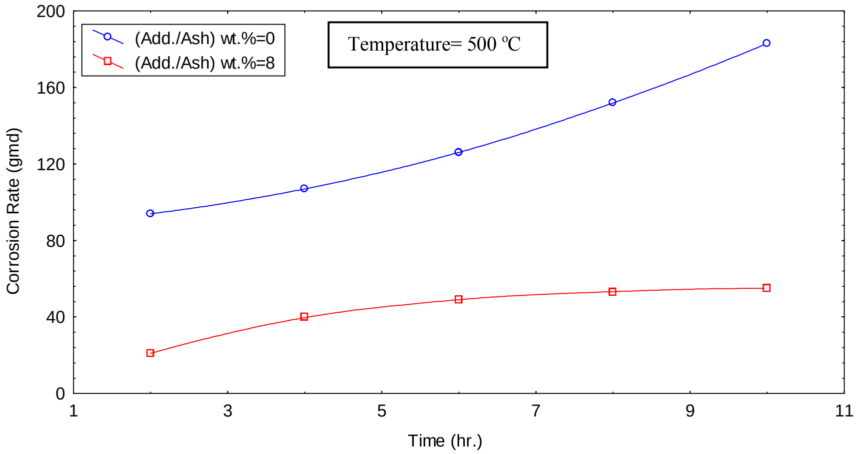

Fig.4. Change in Corrosion Rate versus Time with and without Additive.

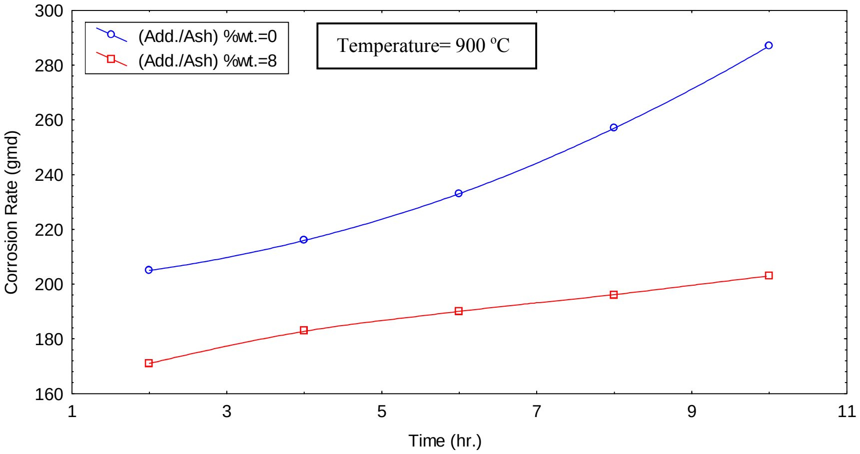

Fig.5. Change in Corrosion Rate versus Time with and without Additive.

In case of oxidation without additive treatment a porous scale is formed; the transport occurs by an outward migration of metal by the vacancy mechanism, vacancies may collect to form cavities and pores at the metal-oxide interface and produce appreciable porosity in the oxide scale after more extended reaction, and the cavities may act as carriers to the solid state diffusion process. Fig. (6) depicts a sample of slag removed from the metal surface in case without additive.

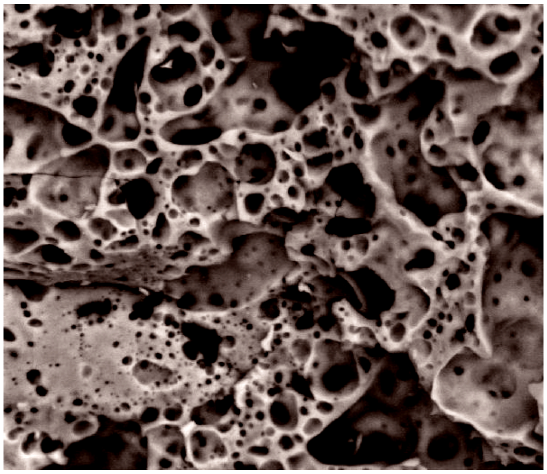

Fig.6. Untreated Slag Sample.

While in the case of additive treatment a compact scale is formed due to the reaction of additive materials (Al_2O_3, SiO_2) with the corrosive materials to produce high melting point compounds, this scale acts as a barrier which separates metal from oxygen gas. Rate of oxidation at high temperatures is limited by a solid state diffusion through the compact scale. As the diffusion distance increases by increasing oxide layer thickness, the rate of reaction decreases with time. Thus compact scale offers useful protective properties from practical point of view on the important features of metals oxidation. Figure (7) shows a sample of slag formed on the metal surface with additive treatment; the structure of this material is lighter, softer and is easy to crumble. Structurally, the material, as seen in the highlighted area, has holes (pores) that are noticeably larger than those in figure (6). This explains why the material is much weaker and lighter than the baseline untreated material. Smooth and dense areas can still be seen, but the pores are generally larger and add to the lightness and friable nature of this sample.

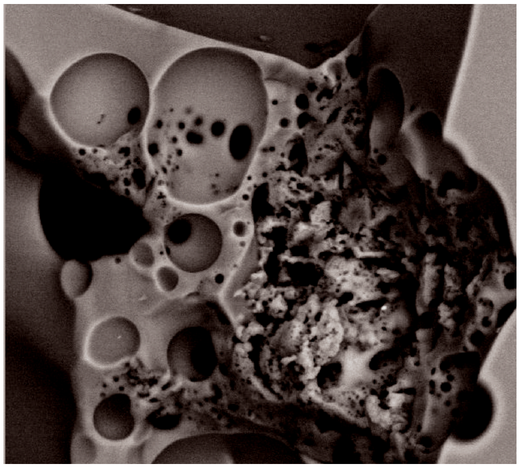

Fig.7. Treated Slag Sample.

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دراسة تأثير الكاولين كمادة مضافة لزيت الوقود على منع التآكل بجانب الاحتراق الخارجي لانابيب المرجل البخاري المحمص

علاء مشجل علي
قسم الهندسة الكيميائية/ الجامعة التكنولوجية

الخلاصة

الهدف من هذه الدراسة هو تحديد تأثير استخدام مادة الكاولين كمادة مضافة الى زيت الوقود للتقليل من التاكل بجانب الاحتراق الخارجي لانابيب المرجل المحمص ذات المواصفات القياسية (ASTM A213-T22) برفع درجة انصهار الخبث المتكون على السطح الخارجي للانابيب من خلال تكوين مركبات جديدة ذات مواصفات واقية لسطح المعدن. تضمنت الدراسة قياس معدل التآكل بدرجات حرارة مختلفة باستخدام وبعدم استخدام المادة المانعة للتآكل وبفترات زمنية مختلفة من خلال طريقة قياس البودقة وتقنية الفقدان بالوزن.

تم الحصول على موديل رياضي يمثل العلاقة بين معدل التآكل والمتغيرات المدروسة باستخدام التحليل الاحصائي. تم استخدام هذا الموديل لتحديد افضل نسبة وزنية (المادة المضافة/الرماد). كما تم أخذ صور بالماسح المجهري الالكتروني للعينتين المعاملة وغير المعاملة بالمادة المضافة لدراسة الفرق في طبيعة الخبث المتكون على سطح المعدن للحالتين.