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EFFECT OF HOT CORROSION ON BOILERS PIPES IN NORTH BAGHDAD ELECTRIC POWER PLANT STATION

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ABSTRACT: - The high temperature external corrosion of boiler pipes was evaluated using weight loss technique. Samples of low carbon steel were supplied from north of Baghdad thermal station and used in current study. Locally supplied fuel ash was used as corrosion environment. Corrosion rates were determined as a function of time in the absence and presence of fuel ash. The results showed that the corrosion of boiler steel pipes was higher in the presence of fuel ash. Scanning electron microscope was also used to study the morphology of surface.

KEYWORDS: Corrosion, High Temperature, low carbon steel, fuel ash, boiler.

1- INTRODUCTION

One of the most important problems faced the heavy fuel oil boilers are hot corrosion result from ash and wastes of fuel combustion [1, 2].These wastes stick on the walls of the pipes exposed to flame, which contains a large proportion of the vanadium oxide (V2O5), as well as sodium sulfate (NaSO4) with a melting point relatively low ranging from (550-560)^{0}C [2-4].Materials and alloys used during exposure and in different circumstances to the hostile environment that is conducive to the formation of a layer on the metal surface. As a result, the interaction of this layer with the metal leads to formation of significant damage in these metals and alloys [5, 6]. Ash is the remnants of metal resulting from heavy fuel combustion process that stick on the fireside metal surface. Flam ash consists of a high percentage of sodium sulfate and vanadium. These materials consist of multi-fusible compound of $Na_2O.V_2O_5.5V_2O_5$ (Sodium Vanadayl Vanadate) of relatively low melting point. Corrosion is one of the problems of the steam boilers that operate using heavy fuel oil which operate at high temperatures and this type of corrosion called hot corrosion depends on several factors, including pipe components as well as the rise in temperature and the percentage of mineral waste (Ash) [6,7]. The present work was evaluated the external fireside corrosion of boilers steel pipe at different operating condition in absence and presence of fuel ash.

2- EXPERIMENTAL WORK

2.1 WEIGHT LOSS MEASUREMENTS

The samples of carbon steel have taken from the pipes of boiler, which used in the north of Baghdad Station for Electric Power Generation, the chemical composition of carbon steel given in Table 1:

Furthermore, the deposits were also locally collated, this fuel ash taken from pipe facing. The chemical composition of fuel ash is 71% Vanadium oxide (V_2O_5) and 29% sodium sulfate (Na_2SO_4).Carbon steel samples were cut by(metallurgical sample cutter QG-1

Germany) with surface area of 520 mm^2 and shaped in dimensions of (20 × 10 × 2) mm, these sample were grinding (belt surfaces grinder PQ China) annealed in furnace for 1 hr. at (250)^{0}Cin order to stresses removal, washed by distilled water, alcohol, gasoline and acetone oven drying at 50^{0}C for half-hour, then keep in desiccators until use. Before each test the sample was weight by balance (ACS 120-4 China) to fourth decimal of grams and dimensions measured by vernier to second decimal of millimeter. Solid fuel ash grinding in a mortar and mixed with acetone. Carbon steel sample were covered with ash- acetone and left half hour to form carbon steel –ash –acetone free sample. Corrosion rates obtained in absence and presence of fuel ash as a function of time (10-40) hr and temperature (600-900)^o C. Automatic Furnace with time and temperature controller (Maximum temperature 1200^{o}C type DLABTACH) was used in experimental work. After each test, the sample left to cool down gradually, then cleaned to remove corrosion products via pickling solution (30 ml hydrochloric acid, 10 gm ferrous ($FeCO_3$) and 120 ml of distilled water) for 10 minutes, this solution dose not attack the metal but dissolves and remove the corrosion products film, then the samples is washed using distilled water, alcohol, and acetone, left for half an hour to dry and then reweighted again. Mass loss per unit area was obtained using the following formula:

$$Mass\ loss\ per\ area = \frac{\Delta W}{A} \tag{1}$$

Where :
ΔW: is mass loss =W_1-W_2 (mg), the difference in mass before and after test.
A: surface area (cm^2).

2.2 SCANNING ELECTRON MICROSCOPY (SEM)

In order to observe the changes in surface morphologies of corroded samples in absence and presence of fuel ash the sever corrosion at 900^{0}C and 40 hwas examined using scanning electron microscope (Philip XL30).

3- RESULTS AND DISCUSSION

The mass loss data was obtained at different condition in absence and presence of fuel ash. Factorial experimental design was used to obtain the corrosion data through 32 testrun. Table (2) shows these result. It is clear that mass loss increased with time and temperature. The damage was larger in presence of fuel ash.

3.1 MECHANISM OF HIGH TEMPERATURE CORROSION

There are two types of corrosion in the high temperature (540-980^{0}C) range sulfidation and vanadic attack. Vanadic corrosion occurs when slugs containing vanadium and sodium and sulfur are deposited on the hot metal part at a temperature at which the song is molten. Vanadium pent oxide melts at about 680 ^{0}C and form sodium salts such as sodium meta vanadate ($NaVO_3$) which melts at 630 ^{0}C.Tacticsare formed with other components in the melts such as ferrous corrosion products and other minerals in fuel ash to produce liquid formation at 540^{0}Cor lower. Vanadic ($NaVO_3$) corrosion is extremely rapid and it is believed that it operates by a chain transfer process of oxygen from the melt surface to the metal interface.

3.2 MECHANISM OF FUEL ASH IN CORROSION PROCESS.

Three elements of fuel, mainly responsible for corrosion and deposits (sulfur, vanadium, and sodium) sulfur are the major offender and are involved most frequently. Vanadium troublesome as it is occurs appreciably only in same fuel oils. Sodium is found more frequently in liquid fuels. Sulfur is common to fuel oil and compounds of sulfur with iron, oxygen and the alkalis are the most offenders in the wastage of metals and frequently in the accumulation of deposits. It is convenient to discuss the roles of sodium and sulfur together since it is the compound (Na_2SO_4) which is involved in the hot corrosion reaction.

The sodium in the oil is mainly present as (NaCl) and is readily vaporized during the combustion process. There are a number of different mechanisms by which vaporization can take place, but once complete most the sodium exist in the vapor phase either NaCl or NaOH, their relative proportions being determined by the interaction of the type [2-4]:

$H_2O + NaCl_{(g)} \leftrightarrow NaOH_{(g)} + HCl$ (2)

(SO_3) in the fuel gases will react with this (NaOH) to form (Na_2SO_4) which will condense as such;

$2NaOH_{(g)} + SO_3 \leftrightarrow Na_2SO_4 + H_2O$ (3)

Vanadium and sodium and sulfate react to from products at low as540 ^{0}C with a eutectic of (35 mole %NaO) molten at 530^{0}C. The low melting compounds are the most harmful corrosion in residual fuel. Investigations indicated that three compounds were formed by reaction of sodium sulfate and vanadium pent oxide[1]:

$Na_2SO_4 + V_2O_5 \rightarrow 2NaVO_3 + SO_3$ (4)

$Na_2SO_4 + 3V_2O_5 \rightarrow NaO._3V_2O_5 + SO_3$ (5)

$Na_2SO_4 + 6V_2O_5 \rightarrow Na_2O.6V_2O_5 + SO_3$ (6)

All are highly corrosion. Mixtures of these compounds can also exist further they can dissociate for example at the freezing point

$Na_2O.6V_2O_6 \rightarrow Na_2O.V_2O_5.5V_2O_5 + 1/2\ O_2$ (7)

$Na_2O.6V_2O_5 + Fe \rightarrow Na_2O.V_2O_4.5V_2O_5 + FeO$ (8)

3.3 EFFECT OF TEMPERATURE

Table 2 and Figures1 and 2 show the relation between temperature and mass loss at different operating conditions. It is clear that mass loss increased with temperature. Generally, the reaction rate increased with rise in temperature. Equation 1 can be rearranged in term of corrosion rate as follows:

$$Corrosion\,rate\,(CR) = \frac{Mass\ loss}{time\ (t)} = \frac{\Delta W}{A.t} \quad (9)$$

So the corrosion rate data can be putted into an Arrhenius type equation [8]:

$$\text{Corrosion Rate } (\text{C.R.}) = \text{A Exp}\left(-\frac{\text{E}}{\text{R T}}\right) \quad (10)$$

Where is A = Frequency factor, E = Activation energy, R = Gas constant (8.314 J/mole.K), and T = Absolute temperature (K). Taking the logarithms of the previous equation then:

$$\log\,(\text{C.R.}) = \log\ \text{A} - \frac{\text{E}}{2.303\ \text{R T}} \quad (11)$$

So that log (C.R.) gives a straight line when plotted vs. (1/T) with a slope of (-E/2.303 R). Many thermally activated processes behave in a similar way and an Arrhenius plot enables us to determine the activation energy. Equation 11 was drawn in Fig. 3, for 40 h exposure time. Similar figures can be obtained at other times. Values of activation energies were listed in Table 3. The values of activation energy was higher in absence of ash, this indicate that the corrosion process needs more energy to occur, while in presence of ash, the corrosion reaction become easier.

3.4 EFFECT OF TIME

Exposure time effect was shown in Table 2and Fingers4 and 5.Mass loss increased with time. The effect of mass loss was higher in presence of fuel ash. The kinetics of oxidation of metals and alloys usually track several reaction rates. Most reactions obey a parabolic rate. Some reactions follow a linear rate. Some other reaction kinetics may contain logarithmic and inverse logarithmic rates. Parabolic rate occur when the oxide scale forms on the metal surface, the oxidation reaction is organized by the diffusion of ions through the oxide film, which is in turn controlled by the chemical potential gradient as a driving force.

As the width of the oxide scale increases, the rate of oxidation decreases with increasing time due to the increasing diffusion distance for ions. The linear rate occur When the oxide scale creating on the metal surface delivers no protection blockade due to oxide cracking, unstable oxides, and molten oxidation products, the oxidation rate generally remains constant with increasing time. At very low temperatures when the oxide film forms on the metal surface, the oxidation rate usually follows either a logarithmic or an inverse logarithmic rate [9].Fingers 4 and 5 show, approximately, a linear relation between mass loss and time.

3.5 METALLOGRAPHIC EXAMINATION (SEM)

The scanning electron microscopy (SEM) was of valuable assistance in providing more information about the surface morphologies of surface. Fig. 6a shows the metal surface before exposing to corrosive environment. Fig. 6b shows the metal surface after exposing to sever corrosion condition of 900˚Cand 40h in absence of fuel ash. While, Fig. 6c shows the metal surface after exposing to sever corrosion condition of 900˚C and 40h in presence of fuel ash. Carbon steels are the most widely used engineering materials and are used widely for high-temperature applications in power generation, chemical and petrochemical industries. At temperatures below 570 °C, iron oxidizes to form Fe_3O_4 and Fe_2O_3. Above 570 °C, it oxidizes to form FeO, Fe_3O_4, and Fe_2O_3 [10]. The oxides can be seen clearly in Fig. 6 a and b. the damage was greater in presence of fuel ash.

4- CONCLUSION

Corrosion in boilers and associated equipment is causing severe economic and operational difficulties in power plants, through experiments show that contaminants of mineral impurities (Ash) significantly affect the course of corrosion. The mass loss of steel pipes increased with both temperature and time of the experiment. Presence of fuel ash has a great effect on metal surface.

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Table (1): Chemical Composition (wt. %) of testing samples.

S	**Si**	**P**	**C**	**Mn**	**Cr**	**M**	**Fe**
0.06	**0.5**	**0.007**	**0.066**	**0.18**	**1.9**	**0.53**	**Remain**

Table (2): Mass loss data at different conditions.

No.	Temperature ^0C	Time (Hours)	Mass loss(mg /cm^2)	
			Without ash	With ash
1	600	10	0.0000	0.0078
2	700		0.0018	0.0108
3	800		0.0028	0.0138
4	900		0.0033	0.0149
5	600	20	0.0008	0.0102
6	700		0.0029	0.0116
7	800		0.0036	0.0147
8	900		0.0041	0.0156
9	600	30	0.0019	0.0108
10	700		0.0039	0.0123
11	800		0.0042	0.0147
12	900		0.0049	0.0161
13	600	40	0.0022	0.0117
14	700		0.0048	0.0128
15	800		0.0051	0.0161
16	900		0.0056	0.0169

Table 3.Activation energy for the corrosion of steel alloy in absence and presence of fuel ash.

Time (h)	Activation energy (kJ/mole)	
	Without ash	With ash
10	29.08	18.92
20	45.31	11.37
30	25.66	11.69
40	25.41	11.32

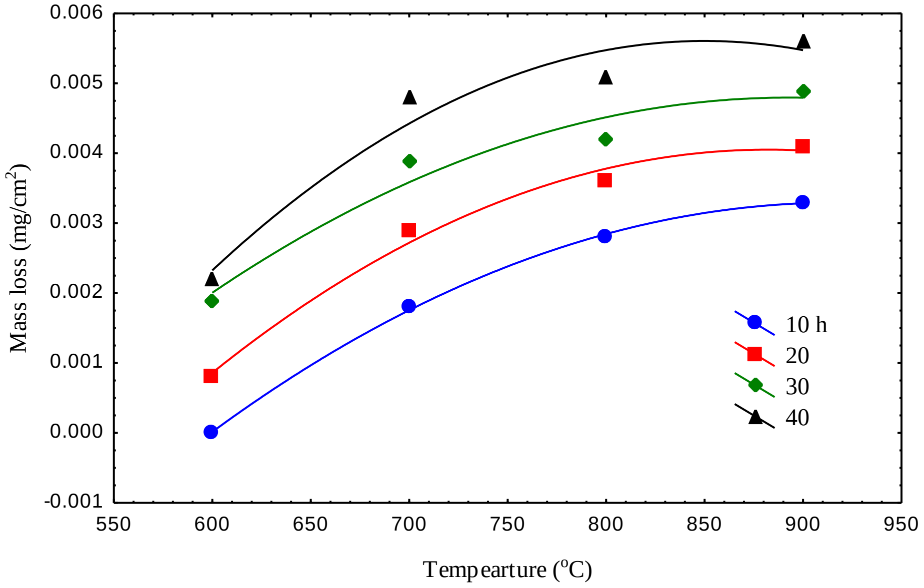


Fig. 1 Effect of Temprature on mass loss of steel alloy in absence of fuel ash at different times.

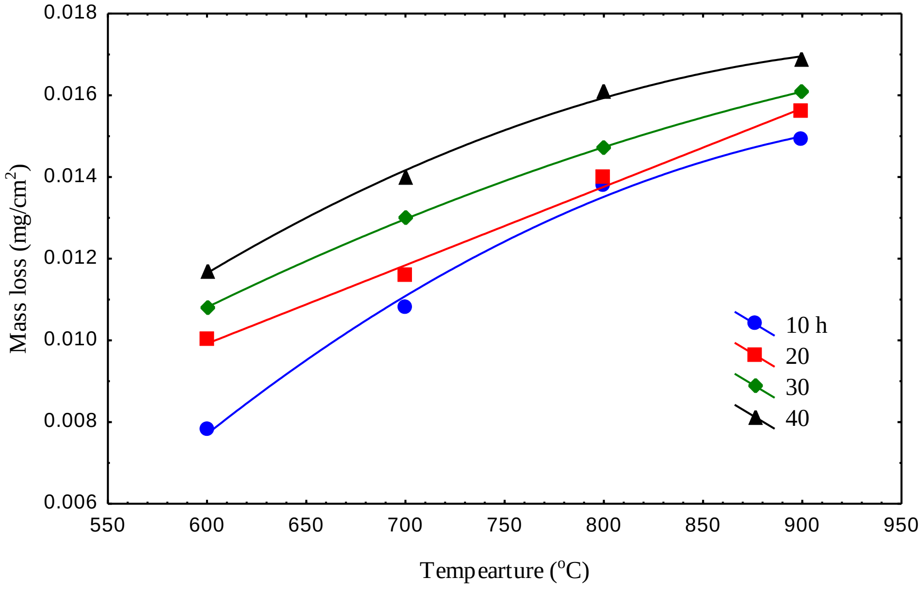


Fig. 2 Effect of Temprature on mass loss of steel alloy in presence of fuel ash at different times.

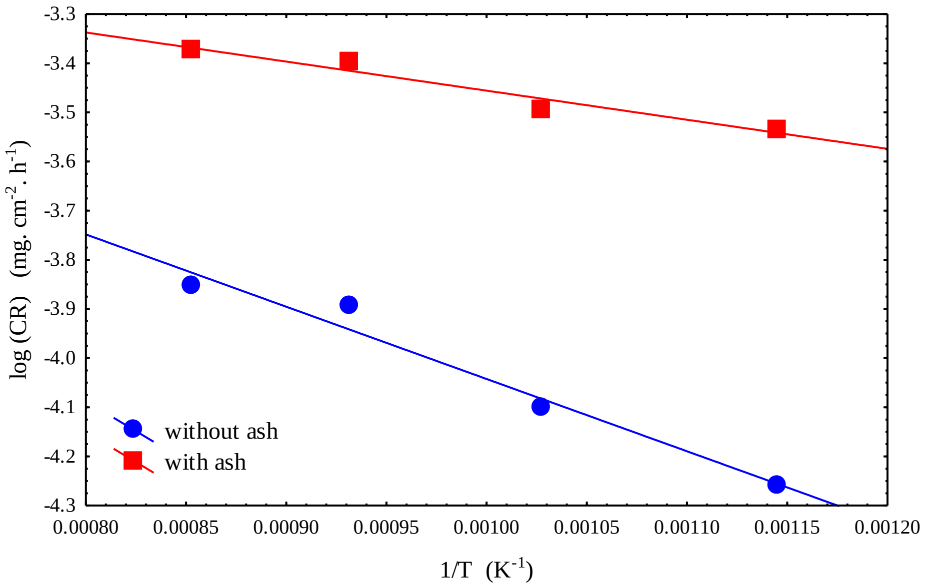


Fig. 3 Arrhenius type plot for high temparture corrosion of steel alloy in absence and presence of fuel ash for 40 h.

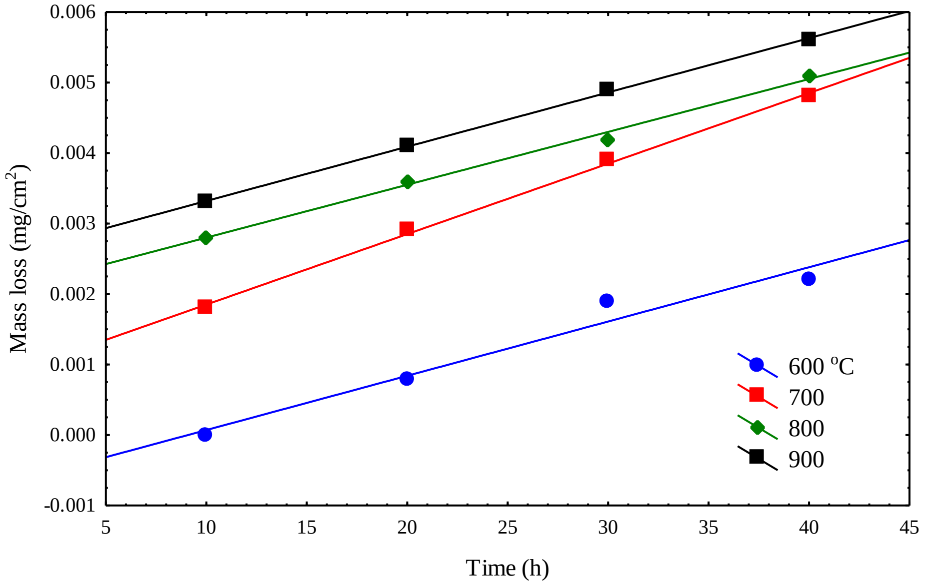


Fig. 4 Mass loss as a function of time at different temperature in absence of fuel ash.

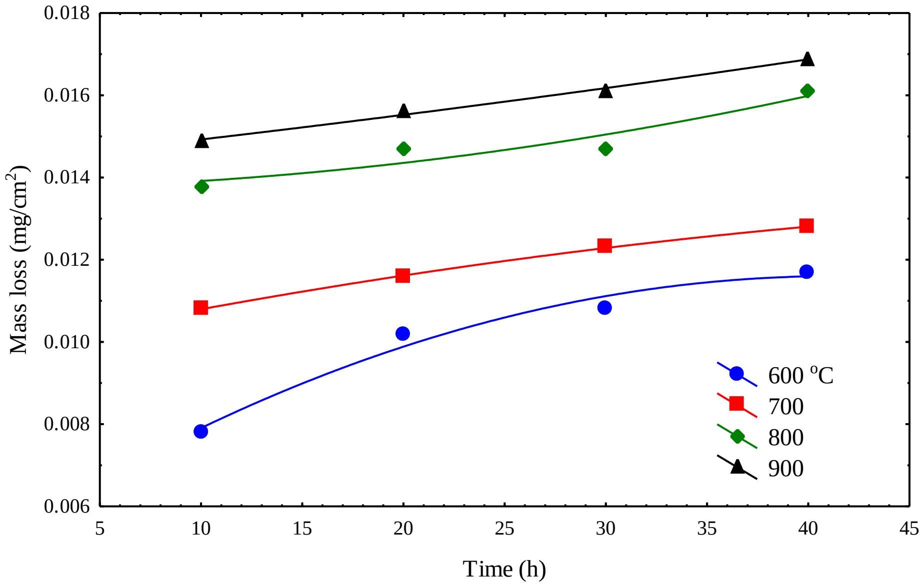
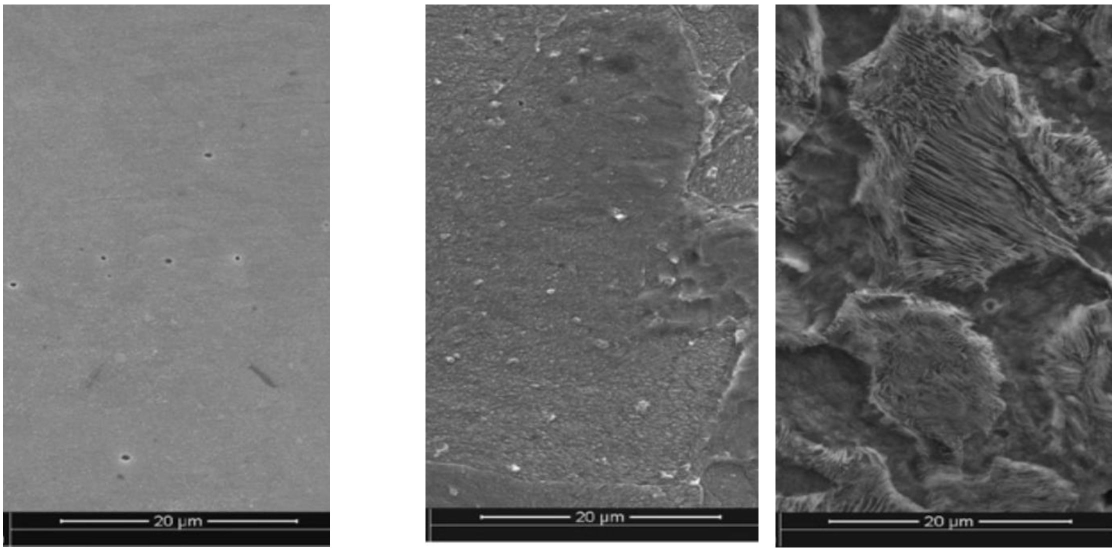


Fig. 5 Mass loss as a function of time at different temperature in presence of fuel ash.



a. Before test

b- After test – without ash

c- After test – with ash

Fig. (6): Scanning electron microscopy (SEM) for steel surface at 900 °C and 40 h.

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تأثير التآكل الساخن على أنابيب المراجل محطة شمال بغداد لتوليد الطاقة الكهربائية

الخلاصة:

في هذا البحث تمت دراسة التآكل الساخن للجزء الخارجي لأنابيب المراجل البخارية باستخدام تقنية الفقدان بالوزن. تم استخدام نماذج للحديد الكاربوني من محطة شمال بغداد لتوليد الطاقة الكهربائية و أيضا تم استخدام رماد موقعي من المحطة كوسط تآكل. تم إيجاد معدلات التآكل بوجود و عدم وجود الرماد. حيث أظهرت الدراسة أن التآكل يزداد بوجود الرماد. و تم استخدام الطرق المجهرية لغرض دراسة التغيرات التي تطرأ على سطح المعدن.

الكلمات الدالة: التآكل, درجة الحرارة العالية, الحديد منخفض الكاربون, رماد الوقود, المرجل