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Experimental Study on Boiler Scales Cleaning Using Hydrochloric and Citric Acids

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ABSTRACT

The effect of hydrochloric acid and citric acid was studied experimentally for boiler chemical cleaning to determine the dissolved scale by using carbon steel samples of water-side boiler tubes sections ,different concentrations of hydrochloric acid HCL and citric acid $C(OH)COOH(CH_2\,COOH)2.H_2O$ were used (2%,3%,4% and 5%) to calculate the weight loss of samples then determined the dissolved scale in gm/m^2. The more efficient acid for the chemical cleaning, was found to be HCL acid at 5% concentration by using 0.3% rodin inhibitor at temp. 60 °C and time 30 minute to obtain 248 gm/m^2 of dissolved scale while the citric acid at 5% concentration by using 0.3% hexamine inhibitor and temp.70 °C and time 240 minute to obtain 168 gm/m^2 of scale dissolved.

Keywords: boiler chemical cleaning, Hydrochloric acid, Citric acid

يدراسة مختبرية على تنظيف ترسبات المرجل باستعمال حوامض الستريك والهيدروكلوريك

الخلاصة

تمت دراسة تأثير حامض الهيدروكلوريك وحامض ألستريك باستخدام التجارب لإجراء عملية الغسل الكيماوي للمراجل وتحديد نسبة التكلسات المذابة باستعمال مقاطع من نماذج انابيب المرجل المصنوعة من كربون ستيل من نوع الجانب المائي , استعملت تراكيز مختلفة من حامض الهيدروكلوريك وحامض ألستريك هي(2% ,3% , 4% و 5%) لحساب فقدان الوزن للنماذج وتحديد نسبة التكلسات المذابة بوحدة الغرام /مترمربع . أكثر حامض كفاءة لعملية الغسل الكيمياوي تم تحديده ليكون حامض الهيدروكلوريك عندتركيز5% باستعمال% 0.3 رودين كمانع تأكل ودرجة حرارة 60 درجة مئوية ووقت 30 دقيقة لكي نحصل على 248 غرام /متر مربع من التكلسات المذابة بينما نحصل على 168 غرام/مترمربع من التكلسات المذابة لحامض الستريك عند تركيز5% باستعمال 0.3% هيكسامين كمانع تأكل ودرجة حرارة 70 درجة مئوية ووقت 240 دقيقة.

INTRODUCTION

Chemical cleaning is a process which primarily uses chemical solutions to remove fouling from inside plant and equipment. Metal equipment must be cleaned from time to time to prevent damage and maintain efficiency of operation. The chemical cleaning of metals has a number of advantages over mechanical cleaning methods. The greatest of these are that the metal equipment to be cleaned doesn't need to be dismantled and reassembled, and the cleaning doesn't damage the equipment, leaving areas that are more affect to corrosion than before,[1].

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Acid cleaning is essential after installation of a thermal power unit because the pipelines and other auxiliary equipment are contaminated by scale or corrosion, sediments, weld flash, different cutting, oil ad greases, atmospheric dust particles like mud , Sio_2 and clay. if much impurities are not removed from boiler these may cause further scaling or corrosion .

Poulson[2] has studied the possibilities of stress corrosion cracking during boiler acid cleaning operation. French [3] has used hydrofluoric acid for boiler cleaning and shenker has described an economical method of boiler cleaning. Phelan, Novitsky ,Yongshu ,flemming, Japan described different techniques for boiler chemical cleaning and corrosion protection.

In boilers of water-side the build-up of scale is a progressive, inevitable process. Even with stringent control of feed water and condensate chemistry, scale and deposition will occur. The main problems caused by boiler scales are:

1.Increase in tube wall temperature, hence, boiler tube ruptures.

2.Decrease in overall boiler efficiency, hence, increase in energy cost and loss of reliability.

The increase in tube wall temperature is a result of the low thermal conductivity of scales as compared to metal. The reduction in heat-transfer can lead to the design temperature of the tube wall being exceeded, which in turn may lead to failure of the tube by creep rupture. Overall efficiency can be defined as the ratio of steam output to the fuel consumption ratio. Again, since scaling impedes heat transfer, more fuel is required to produce a given amount of steam, thus reducing overall efficiency and loss of energy. [4,5]

If fouling is allowed to continue, in some cases catastrophic failure of plant can occur resulting in complete and extended loss of use. This is the main concern with magnetite (Fe3O4) foulings in steam generator plants such as those in power station boiliers. As the magnetite scale grows with service time it increases the thermal resistance of the generator tube to the imposed heat flux. Once the magnetite gets thicker than 50 m this can result in the metal temperature of the generator tube exceeding the yield temperature for the given stress conditions.

In Figure(1) show Tube failure results and hundreds of thousands of dollars per day of power generation capacity is lost in downtime.

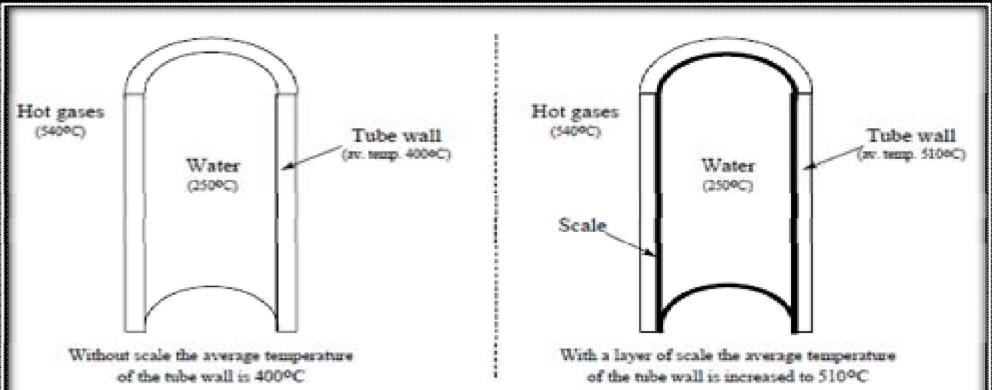

Figure 1 - The effect of scale on tube temperature

The primary constituent of boiler scales is magnetite (Fe_3O_4), which is formed as a result of the reaction of metallic iron with high-temperature steam. Copper is present due to corrosion of the copper alloy, aluminum bronze feed water condensers and pre heaters, often because of oxygen ingress into these systems. Copper is transported through the steam cycle where it forms on the boiler internals. Table (1) shows the compounds generally found and transported through the steam cycle and deposited on boiler internals either from contaminants contained in the boiler feed water system or from use of outdated phosphate-based water treatment chemicals. In addition to these crystalline inorganic compounds, there may be organic residuals present in the scale.[4]

Table (1) The Compounds Found in Boiler Scales

Compound	Formula
Anhydrite	$CaSO_4$
Aragonite	$CaCO_3$
Brucite	$Mg(OH)_2$
Copper	Cu
Calcite	$CaCO_3$
Hematite	Fe_2O_3
Hydroxyapetite	$Ca_{10}(OH)_2(PO_4)_6$
Magnetite	Fe_3O_4
Quartz	SiO_2
Thenardite	Na_2SO_4
Wollastonite	$CaSiO_3$

Selection of the acid is primarily dependent on scale (deposit) type, although the physical turbulence available, solution temperature, and the metallurgy of the equipment are also of importance. Generally there are two types of acids : minerals and organic . Mineral acids are cheaper and, because of their high ionization, can be used at room temperature, such as H_2SO_4 Sulphuric , HNO_3 nitric**,** HCl hydrochloric**,** H_3PO_4 phosphoric and NH_2SO_3H sulfamic**,** whereas organic acids, being much less strongly ionized, are used at temperatures around 90^{o}C to affect their chelating (complexforming) properties on the scale,such as HCOOH formic, Oxalic, EDTA and Citric .Organic acids are only used when there is a probability of corrosion damage by a mineral acid.

Most internal deposits can be removed with mineral acid and organic acid .The most widly used solvent is a 5% hydrochloric acid solution with inhibitor and complexes. Phosphoric,sulfuric and sulfamic acid are also used in boilers that operate at 2000psig. Inhibited ammonium citrate and a combination of hydroxyacetic and formic acids are commonly used organic .Salts of EDTA (ethylene-diamin-tetraacetic acid) have been used for both off-line and on-line cleaning. [1,6]

The need to chemically clean an operating boiler is usually determined from an inspection of a particular unit performed during planned inspections. Other factors influencing the decision of whether or not to chemically clean include:

1. overall efficiency
2. hot spots - as evidenced by infrared inspection
3. tube failure during normal operation

Tube samples should be removed from locations where heavy scaling is suspected. The tube sample should be at least three feet long so the method of removal (cut-off wheels and cutting torches) does not contaminate the scale at the center of the sample with slag or filings.

The scale is then analyzed using several different techniques in order to determine its composition. The scale density is determined gravimetrically after dissolution of scale in inhibited HCL . Loss of weight on firing in a furnace will measure the percentage of hydrocarbons present, which then determines the need for alkaline degreasing. The need to clean is based on the scale density. Table(2) shows the range of scale density encountered, along with the appropriate action required.

Table(2): Scale density ranges and required action

Scale density g/ft^2 or mg/cm^2	Recommended action
< 23 (25)	No action required
23 – 70 (25-75)	Chemically clean within one year
70 – 93 (75 -100)	Chemically clean with three months
> 93 (100)	Chemically clean before further operation

EXPERIMENTAL PROCEDURE

A laboratory test used in this investigation in Al-Dhoura power station , Different carbon steel specimens of boiler water side tubes (pressure 80 bar and Temp.350 °C) were obtained and coated with scale of hematite ,magnetite and copper type. as shown in fig.(2) and fig.(3).

<u>Acid solution preparation</u>:

1. 2% concentration of Hydrochloric acid HCL with 0.3% of Rodin as corrosion inhibitor, using $c_1\ v_1 = c_2\ v_2$

   $$37\% * v_1 = 2\% * 300ml \rightarrow v_1 = 16.2ml \text{ for 2\% HCl}$$

   Then calculated 3%, 4%,5% and obtained (24.3, 32.4 and 40.5ml) respectively.

   -0.3 gm for 100 ml then → 0.9 $\sim 1gm$ for 300ml for rodin.

2. 2% concentration of citric acid $C(OH)COOH(CH_2\,COOH)2.H_2\,O$ with 0.3% of hexamine were prepared as for HCL acid.

Cleaning by HCL

Weighing the specimen (1) and record w_1 ,then immersed in 2% HCL with 0.3% Rodin inhibitor in water bath at temp. 60℃ and for 60 min. ,then after 60 min. the specimen was removed and rinsed with distilled water then dried in oven and cooled in discator then record the w_2 ,repeat the procedure by using 3%,4% and 5% then calculated the dissolved scale in (gm/m^2) by using the following equation:

$$Dissolved\ scale = \frac{\Delta w}{area} * 10000 \quad ...(1)$$

As shown in table (4).

CLEANING BY CITRIC ACID:

Weighing the specimen (5) and record w_1 ,then immersed in 2% citric acid with 0.3% hexamine in water bath at temp. 60℃ and for 60 min. ,then after 60 min. the specimen was removed and rinsed with distilled water then dried in oven and cooled in discator then record the w_2 ,repeat the procedure by using 3%,4% and 5% then calculate the dissolved scale (gm/m^2) as shown in table (5) .

Repeat the procedure of citric acid and take specimen(9) then change the immersion time from (90,120,180 and 240 min.) at temp. 70℃ then calculate the dissolved scale as shown in table(5) .

Figure (2) Sample before acid cleaning

Figure (3) Samples with boiler scales

RESULTS AND DISCUSSION

HCL cleaning:_HCL is the most commonly used for cleaning tubes made of carbon steel ,The samples of water-side boiler tubes coated with hematite and magnetite and when immersed in HCL acid solutions, the reactions that occur through the chemical cleaning with HCL are shown in the following equations:[1]

(a) $Fe3O4 + 8HCl \rightarrow FeCl2 + FeCl3 + 4H2O$

(b) $Fe^{3+} + Cu° \rightarrow Fe^{2+} + Cu^{+}$

(c) $Fe^{3+} + Cu+ \rightarrow Fe^{2+} + Cu^{2+}$

(d) $2Fe^{3+} + Fe° \rightarrow 3Fe^{2+}$ (corrosion)

(e) $Cu^{2+} + Fe^{o} \rightarrow Fe^{2+} + Cu°$ (corrosion)

(f) $2H^{+} + Fe° \rightarrow Fe^{2+} + H2(g)$ (corrosion)

In (a) the magnetite is two-thirds Fe^{3+} (ferric) and one-third Fe^{2+} (ferrous). However, as the scale is removed to reveal bare metal, the metal rapidly reduces the ferric ion while further corroding itself (d). Any copper present will be oxidized by the Fe3+ acting as an oxidant (b,c). Cupric ions are also unstable with respect to bare steel, and so they replate as metallic copper before the acid solution can be drained (e).

The classic acid corrosion mechanism (f) can occur when the base metal underneath the scale is uncovered. This reaction is easily minimized (up to a 99% rate reduction) by addition of a corrosion inhibitor blend. These inhibitors (often cationic) tend to adsorb to the electronegative metal surface to form a thin film that inhibits attack.

Ferric and cupric ions from the dissolved scale attack the bared steel surface by pitting corrosion (d,e). This can sometimes result in localized damage and greater weight losses than the inhibited acid corrosion. To overcome this, reducing agents can be added to the cleaning solution to reduce the ferric ions before they attack the base metal.

According to table(3) the weight loss of samples effected by increasing HCL concentration with inhibitor rodin (i.e.) the dissolved scale increased from (117.4 – 248) gm/m^2 at 2% - 5% concentration of HCL and a linear relation shown in fig.(6). The scale completely remove after acid immersion as shown in fig. (4) .The result show the 5% of HCL is more efficient to remove the scales at temp. 60 ℃ and 30 minute and the value 248 gm/m^2 recommended to clean the boiler within one year according to table(3) .

Citric acid cleaning:_According to table(4) the weight loss of samples effected by increasing the concentration of citric acid with 0.3% hexamine as a corrosion inhibitor, the dissolved scale increased from 30.8 to 58.82 gm/m^2 at 60 minute and at temp. 50℃ . This result show that the dissolved scales are very little at this time (60) min. as shown in fig.(5)

While table (5) and fig(8) show the dissolved scale increased from 85. 6 to 168.06 gm/m^2 as time from 90min. to 240min respectively at 5% concentration of citric acid 0.35 hexamine and temp.70 ℃ .Because of citric acid as organic acids and less strongly ionized and used at temp. around 90℃ to effect their chelating (complex forming) properties on the scale and used more time (i.e.240 min.) so citric acid is less efficient for chemical cleaning.

Another results that obtained, the effect of 5% HCL concentration on weight loss of the sample to dissolve 4.7gm of scale at 60 minuet.[7]

CONCLUSIONS

The over all experimental results show that the HCL acid work more efficiently than citric acid because the one is cheap and easily to ionized . Since the solubility of the scale is increasing with concentration ,It is reported that the optimum concentration is 5% for scale removal to be 248 gm/m^2 at time 30 minuet , while the citric acid need more time for scale removal to be 58.82gm/m^2 at time 60 minuet.

Table (3) Dissolved scale for different conc. of HCL with 0.3% Rodine at temp. 60 ℃ and time 30 min.

Sample	Conc.%	W_1 gm	W_2 gm	ΔW gm	Area/cm^2	Dissolved scale(gm/m^2)
1	2	115.5	115.2	0.3	25.55	117.7
2	3	125.8	125.3	0.5	27.69	180.5
3	4	130.7	130.08	0.62	29.6	209.4
4	5	127.8	127	0.8	32.2	248

Table (4) Dissolved scale for different conc. of Citric acid with 0.3% hexamine at temp. 50 ℃ and time 60 min.

Sample	Conc.%	W_1 gm	W_2 gm	ΔW gm	Area/cm^2	Dissolved scale(gm/m^2)
5	2	120.28	120.2	0.08	25.9	30.8
6	3	118.9	118.8	0.1	26.64	37.5
7	4	129	128.85	0.15	30.34	49.4
8	5	134.2	134	0.2	34.0	58.82

Table (5) Dissolved scale for 5%conc. of Citric acid with 0.3% rodine at temp. 70 ℃ and different times.

Sample	Time/min.	W_1 gm	W_2 gm	ΔW gm	Area/cm^2	Dissolved scale(gm/m^2)
9	90	130.5	130.25	0.25	29.2	85.6
10	120	125.6	125.3	0.3	27.2	110.2
11	180	126.8	126.43	0.37	27.4	135
12	240	117.6	117.2	0.4	23.8	168.06

Figure (4) The samples after the cleaning by HCL acid

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Figure (5) The samples after cleaning by citric acid

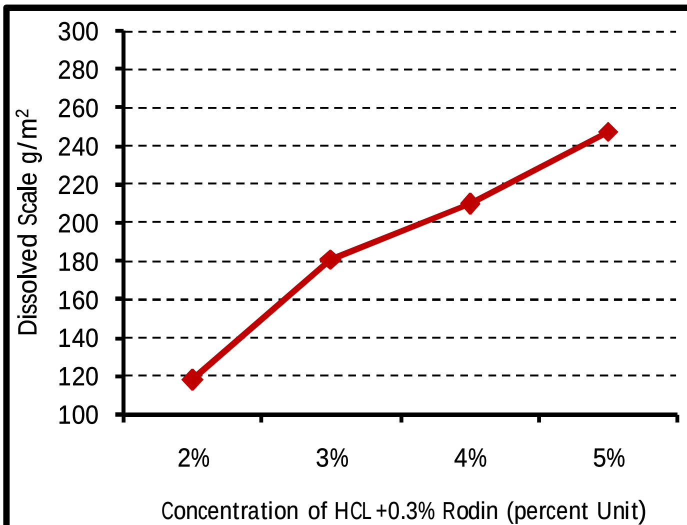

Fig. (6) Effect of HCL concentrations on the scales in presence of 0.3% rodin

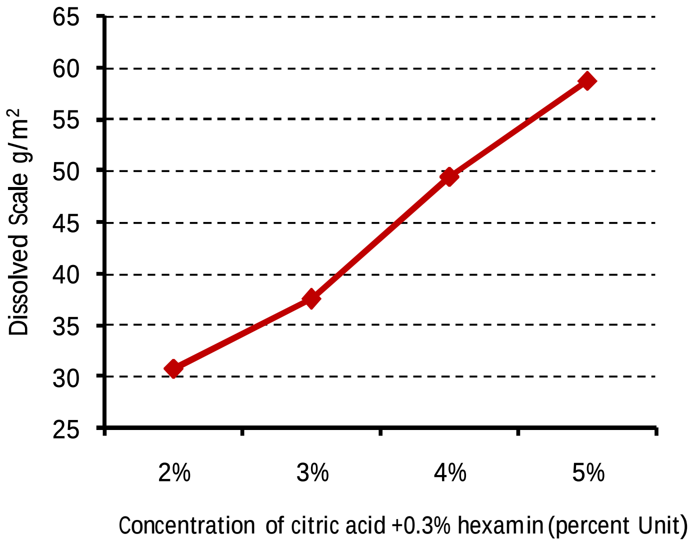

Figure (7) Effect of Citric acid concentrations on the scales in presence of 0.3%hexamin

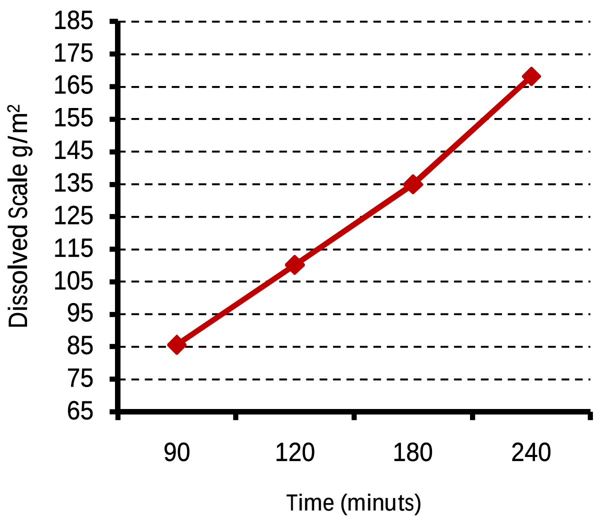

Fig. (8) The relation between dissolved scale and Time

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