USE OF HEXAMINE TO CONTROL PROPERTIES OF WATER CONDENSATE SYSTEM OF MEDICAL CITY HOSPITALS[+]

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Abstract

This research included use of Hexamine (Neutralizing a mines) to control the properties of conctensate systems water. pH and M-Al Kalinity values to prevent or reduce corrosion problems caused by CO_2 .

This system is the most important portion of steam Boilers system in ENGINEERING and MAINTENANCE department of MEDICAL CITY HOSPITALs (EMDOMCH), which is responsible for supplying the hospitals with pure saturated steam, an important substance for all types of medical operations.

Experiments were adapted to determine values of pH, M-AL Kalinity and corrosion rate before hexamine addition.

Many experiments were made using different concentrations and injection rates of hexamine to reach the optimum conditions to control the corrosion rate in this system.

المستخلص

تضمن البحث استخدام مادة الهكسامين أحد المركبات الأمينية ذات الطبيعة القاعدية للسيطرة على مواصفات مياه منظومة التكثيف وهي قيم PH وقيم M-Alkalinity لمنع او تقليل مشاكل التأكل المتسببة من وجود غاز CO_2 .

أجري البحث على منظومة التكثيف لمنظومة المراجل البخارية لقسم الهندسة والصيانة التابع لمجمع مستشفيات مدينة الطب . هذه المنظومة مسؤولة عن تجهيز المستشفيات بمادة البخار المشبع المهم جداً للعمليات الجراحية والتعقيم والطبخ .

التجارب التي اجريت تضمنت قياس مواصفات مياه منظومة التكثيف ومعدل التأكل قبل وبعد استخدام الهكسامين إذ تم استخدام الهكسامين بتركيزين 10% ، 14% وبمعدلات ضخ هي(0.5 , 1 , 2 , 3 , 4 , 5 ppm) وقد تم تحديد الظروف المثالية للتقليل من معدل التأكل الى اقل الحدود وكانت هذه الظروف المثالية هي 14 % ومعدل ضخ 3-5ppm .

Introduction

Problems caused by iron corrosion in condensate system are not restricted to piping and equipment damage or the loss of high-quality water and heat energy when condensate is lost.

Steam Condensing and Receiving System

Condensate system is one of important portions in steam boilers system. It consists of condensers, receivers, regulators, traps and piping. Normally considered a

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potential maintenance nightmare, a properly treated and operated condensate system can be a money maker for an industrial plant.

The following diagram shows the position of condensate system in boiler plant flow of ((EMDOMCH)).

Corrosion of steam condensate and return systems present a two fold problem to power-generating and steam-heating plants. Equipment damage and frequent replacement of lines, values and traps result in a serious maintenance problem. In addition, corrosion products frequently formed are carried back in to the steam-generating equipment and deposits there.

The result is plugging of lines, localized overheating and promotion of corrosion in the boiler system itself.

Corrosion in the condensate system manifests itself in certain typical forms, depending upon the corrosive factors involved. These factors are basically oxygen, carbon dioxide and condensed water. The attack due to dissolved oxygen is characterized by tuberculation, pitting and build up of iron oxide deposits. The mechanism involved is thought to be one of depolarization of the cathodic areas on the metal surface.

Collins and Henderson[1]made a detailed study of oxygen attack and arrived at the following conclusions:

1. Oxygen concentrations below 0.5 ppm cause negligible corrosion when the temperature is less than 70°C and the pH of the condensate is 6 or higher.
2. In the pH range 6 to 8 at oxygen concentrations of 0.5 to 4ppm the rate of attack for general corrosion is given by the equation

$$R = 24\,(C - 0.4)^{0.9}$$

where:

R : average rate of penetration in mdd

C : oxygen concentration in ppm[2].

Collins and Henderson[1] say that this equation is not valid for pitting corrosion and does not take into account the accelerating effect of temperature.

Skaperdas and uhlig[2] show that an increase in temperature from 60 to 90° C will double the rate of oxygen corrosion. Normally, one would expect a dual effect due to oxygen as a function of increasing temperature. On one hand, the corrosion rate should increase rapidly with temperature in accordance with normal kinetic considerations while on the other hand, the decreasing solubility of oxygen with temperature should decrease the attack.

Carbon dioxide attack manifests itself by thining and grooving the metal walls failure occurring most readily at threaded connections. The walls are relatively clean, in contrast to the masses of corrosion products which cover the areas of oxygen attack. Collins[1] has also studied the corrosion rate of carbon dioxide and developed the equation

$$R = 5.7\,W^{0.6}$$

where:

R : rate in mdd

W: carbon dioxide concentration in condensate in ppm multiplied by 0.1

Here again the temperature effect is not considered. Skaperdas and Uhlig[2] have found that an increase in temperature from 60 to 90^{o}C raises the attack rate of carbonic acid on low carbon steel by a factor of 2.6.

It is interesting to note that steam , which usually is thought of as being pure distilled water and relatively inoffensive , is instead highly corrosive and contains considerable quantities of CO_2 and O_2 . The principal source of these two gases is the boiler feed water. The carbon dioxide results mainly from the decomposition of the bicarbonates and carbonates in the boiler with the resultant liberation of free CO_2 [3].

The nature of the condensed water also affects the type and amount of corrosion. The presence of droplets leads to localized pitting attack. A uniform film on the other hand , causes more general corrosion . Brit[4] report this phenomenon in some detail .

Corrosion Control Practices of Condensate Systems

Condensate systems can be chemically treated to reduce metal corrosion . pH control in preboiler systems involves the use of ammonia or other amines (Neutralizing a nines) studied by many investigators[5,6] . This is necessary in systems operating above the 900 to 1200 psig range with high purity water.

These weak bases permit a more closely controlled regulation of pH .

Calise and Duft[5] give the following values in ppm for the amount of material necessary to give pure water a pH of 9.0

1- Ammonia – less than 0.5
2- Cyclohexylamine – 2.0
3- Morpholine –4

They found[5]that general corrosion is frequently prevented by pH control and maintenance of 9.0 pH reduces general corrosion appreciably[7,8].

Tash and klein[9] found morpholine to be an effective inhibitor while Grabowski[10] found that the volatile amines can be effective and claim that NH_3 in the pH range of 8.5 to 9.5 reduced the corrosion of copper.

They state that to keep the copper and iron surfaces from corroding, the O_2 , CO_2 and SO_2 gases must be kept a low value while the proper pH is being maintained.

Homig and Richter[11] found that morpholine is superior to ammonia or cyclohexylamine for iron inhibition, but here again it is essential that the O_2 and CO_2 content be kept at a minimum.

A more recent approach to pH and alkalinity control in condensate system includes filming amines , and oxygen scavenger – metal passivators[12] . Filming amines form a protective film on metal surfaces.

This approach has come into widespread use with the development of suitable products containing long- chain nitrogenous materials.

Theory:

Steel in contact with water tends to dissolve (i.e corrode) spontaneously. Iron put into solution this way immediately reacts with water, producing an insoluble oxide coating which will prevent rapid continuation of the corrosion process. If it were not for this protective oxide coating, the iron would go completely into the solution in a relatively short period of time[13]. Corrosive agents are simply those materials that have an ability to remove or prevent the formation of a protective oxide coating over the metal. Pure water itself is corrosive to steel while the protective

coating is in the process of formation . Corrosion will tend to continue unless the pH value of the water is increased by the addition of an alkaline substance[13].

□ Carbon Dioxide Corrosion

Carbon dioxide can enter a condensate system as a dissolved gas or it can be chemically combined in the bicarbonate or carbonate of the feed water. Generally dissolved carbon dioxide is removed in the deaerating heater. The following reactions show the break down of naturally occuring bicarbonate and carbonate alkalinity to carbon dioxide[12].

Reaction 1 : $2NaHCO_3 + \text{heat} \Leftrightarrow Na_2CO_3 + CO_2 + H_2O$ …….. (1)
Reaction 2 ; $Na_2CO_3 + H_2O + \text{heat} \Leftrightarrow 2NaOH + CO_2$ …….. (2)

Reaction 1 proceeds to complete . Reaction 2 is only about 80% complete[13]. Steam condensate which contains free carbon dioxide is corrosive to steel because it removes and prevents the formation of a protective oxide coating

* Oxygen Corrosion

Dissolved oxygen replaces hydrogen ions in the reduction reaction.
The reaction are as follows[12]:
Oxidation :

$$\underset{\text{Iron}}{Fe} \rightarrow \underset{\text{ferrous ion}}{Fe^{2+}} + \underset{\text{electrons}}{2e^-} \quad \text{……} \quad (3)$$

Reduction :

$$\frac{1}{2}O_2 + 2e^- \rightarrow O^{2-} \quad \text{……} \quad (4)$$

oxygen electron oxid ion

over all:

$$Fe + \frac{1}{2}O_2 + 2H^+ \rightarrow Fe^{2+} + H_2O \quad \text{……..} \quad (5)$$

Iron oxygen hydrogen ion

This reaction occurs more readily than the direct reaction between iron and protons.

Therefore , corrosion rates are accelerated in the presence of oxygen.

Two types of corrosion can occur with oxygen present.

The first , generalized corrosion on the metal surface, which causes a loss of metal from the entire surface.

The second , oxygen pitting , which causes a highly localized loss of metal that results in catastrophic failure in a short time.

Oxygen pitting begins at weak points in the iron oxide film or at sites where the oxide film is damaged. Instead of growing along the metal surface, the corrosion penetrates into the surface, effectively drilling a hole into (or through) the metal[12].

* CO_2 Corrosion Control by Chemical Treatment

The purpose of chemical treatment is to control corrosion in the condensate system by maintaining a protective coating of iron over the metal surfaces , while supplying sufficient material of an alkaline nature, to neutralize the carbonic acid formed in the condensate system.

The addition of alkaline nature material causes decrease in CO_2 in the steam due to reduction of alkalinity[14].

*** <u>Neutralizing Amine</u>**

It is nitrogen containing compounds which are added to steam system to neutralize dissolved carbon dioxide and increase the pH value of steam condensate so that a protective oxide coating will be able to form. Being quite volatile under boiler steaming conditions , these neutralizing inhibitors simply go off with the steam and then return into solution at the points where the condensation of the steam occurs. In general , the alkaline materials are used where the free carbon dioxide is entering the boiler, and the condensate is virtually oxygen free[13].

<u>Mechanism</u>

Neutralizing amines hydrolyze when added to water and generate the hydroxide ions required for neutralization[12] :

$$R-NH_2 + H_2O \rightarrow R-NH_3^+ + OH^- \quad (6)$$

Neutralizing amine — amine ion — hydrogen ion

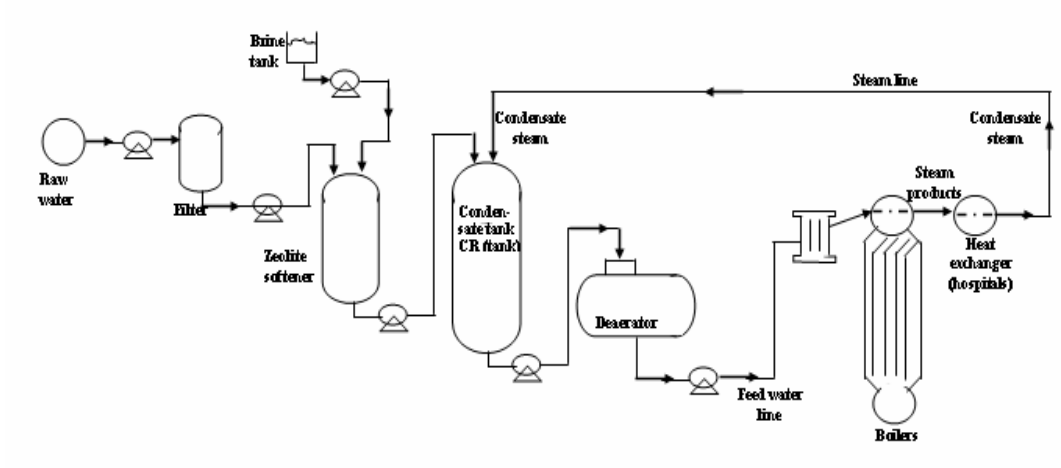
The overall neutralizing reaction can be written as shown [12]

$$R-NH_3^+ + OH^- + H_2CO_3 \rightarrow R-NH_3^+ + HCO_3^- + H_2O \quad (7)$$

Amine ion — hydroxide ion — carbonic acid — ammonium ion — bicarbonate ion — water

By regulating the neutralizing amine feed rate, the condensate pH can be elevated to within a desired range.

Many amines are used for condensate acid neutralization and pH elevation . The ability of any amine to protect a system effectively depends on the neutralizing capacity, recycle ratio and recovery ration , basicity , distribution ratio and thermal stability of the particular amine.



fig(1)

Laboratory Measurements and Test Runs

It included the following steps :

Step –1- laboratory Measurements :
(before Hexamine addition)

Many samples took every 2 days from condensate tank (the total test period is 60 days) , and calculating their following characteristic are included :

- (a) pH values : Determined using electric pH meter model (595 – pH) in which its specification are :
  1.standard measuring range : 0 – 14 pH
  2.Indicator : digital , Liquid crystal (LCD) , $3\frac{1}{2}$ digit , h = $\frac{1}{2}$ ``
  3.Current output 4-20 mA Dc on load < 700 ohm

- (B) M- alkalinity : Commonly expressed as mg / L (ppm) of $CaCO_3$, it was defined as the capacity to neutralize an acid , it can be measured by titration of a sample with a strong acid as follows [15]:
  * pour 50 ml of the sample measured in the cylinder into the flask , add 4-5 drops of methyl – orange
  * If the solution turns yellow , titrate with sulfuric acid until the colour changes into red – orange.
  * Record the volume of acid consumed (V), M- alkalinity in ppm of $CaCO_3$ = V x 20

- (C) Corrosion Rate :
  It was determined using corrosion coupon (small bar manufactured from the same metal of the tested system) . This coupon is placed in a suitable place in condensate system and measuring the weight loss in milligram of coupon every 20 days (total test period is 60 days using sensitive balance.Then determined the corrosion rate using the following eq. :

$$MPY = \frac{areafactor \quad xwt\ .loss\ (mg)}{Days \quad \exp\ osed} \qquad (8)$$

where :-

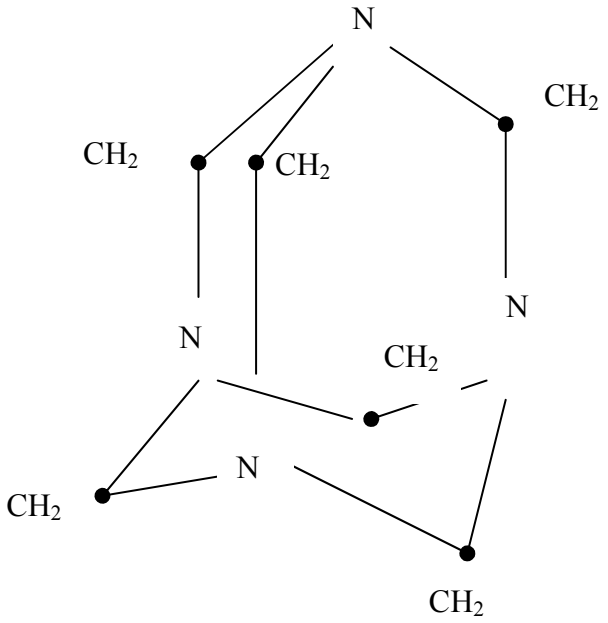
Area factor is constant fixed on coupon = 0.83

1 MPY = 0.040 mm/y

Step –2- Hexamine preparation :

Hexamine is a product of reaction of 6 moles formaldehyde and 4 moles ammonia , it is a white crystalline powder, have the following properties :

* slight amine odor
* sp –gr- 1.27 at 25^{o}C
* soluble very well in water at 120^{o}C
* Molecular wt. = 140.19



* formula $(CH_2)_6 N_4$

* It was used because of its low cost and its availability in Iraq.

Hexamine in this research is used as Aquous solution with two concentrations 10% and 14% and measured the pH value these two concentrations as follows

pH of 10% Aq. Solution of hexamine = 8.5 – 9.5

pH of 14% Aq. Solution of hexamine = 11.2 – 12.5

Step –3- Test runs by hexamine injection:

This step include dosing two known concentrations of hexamine (10% , 14%) very carefully and at different flow rates (ppm) using suitable dosing pump, these flow rates are o.5 , 1 , 2 , 3 , 4 , 5 ppm respectively.

The feed water line was chosen as injection point of hexamine as shown in the following flowchart

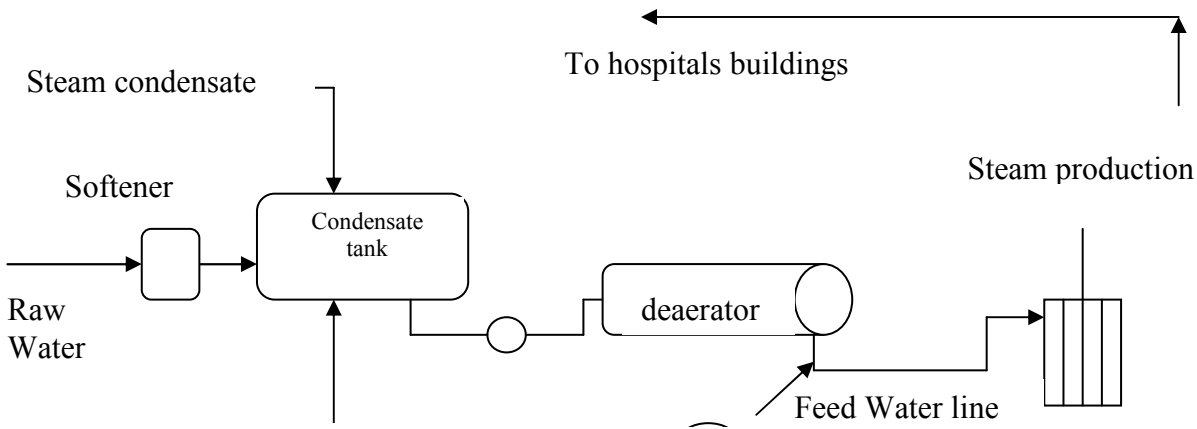


Fig (2)

Step –4- Laboratory measurements (after hexamine injection)

The same measurements were repeated as in step-1- for the two concentrations (10% , 14%) at different flow rates (0.5 , 1 , 2 , 3 , 4 , 5 ppm) to determine the optimum concentration and flow rate of hexamine in which the values of pH and M-Alk. Were in desired range , therefore calculate the corrosion rate at the optimum range of pH and M- Alk (using coupon method) comparison is made between corrosion rate then before and after hexamine addition.

Results and Discussion

Table(1) shows the chemical analysis of water samples taken from condensate system as shown in Fig (2) .While Table –2- shows the results of corrosion rate these results are before hexamine injection.

Table –1-

Sample	PH	M- Alkalinity
1	5.2	320
2	5.18	325
3	5.09	333
4	5.01	351
5	4.98	362
6	4.85	370
7	4.73	375
8	4.68	379
9	4.59	384
10	4.53	389
11	4.49	393
12	4.39	399
13	4.31	408
14	4.28	415
15	4.22	422
16	4.18	437
17	4.09	442
18	3.85	446
19	3.62	452

20	3.51	458
21	3.33	463
22	3.18	467
23	3.09	473
24	2.98	481
25	2.83	486
26	2.73	492
27	2.60	497
28	2.42	504
29	2.32	510
30	2.2	513

Table –2-

Day exposed	Wt-loss (mg)	MPY
20	125.345	5.2
40	296.349	6.15
60	490.961	6.8

MPY is calculated using Eq. (8) as follows

for wt. Loss = 125.345 mg $\rightarrow$ MPY = $\frac{0.83\ x125\ .345}{20} = 5.2$

The other values of MPY calculated in the same manner .

* Effect of Low pH and Insufficient M

The results in Table –1- refer to low pH values of condensate and in sufficient alkalinity , these parameters result in a corrosive acidic attack as shown in the chemical equation (9) . Condensate pH is very important factor as the stability of the passivating iron oxide layer is critically dependent on it.Carbon dioxide (CO_2) is the primary cause of decrease in condensate pH. CO_2 enters the system with air leaking in to the condensate system or from decomposition of feed water alkalinity . Decrease in pH causes dissolution of the oxide layer and increased corrosion (table 2 and Fig 3).

As the steam is condensate , CO_2 dissolves in water and depresses the pH by increasing the hydrogen ion concentration as shown below:

$CO_2 + H_2O \rightarrow H_2CO_3$ …… (9)

$H_2CO_3 \rightarrow H^+ + HCO_3^-$ ……. (10)

$HCO_3^- \rightarrow H^+ + CO_3^{2-}$ …… (11)

All these factors depresses pH values as shown in results of Table 1 , it is found that carbonic acid promotes the iron corrosion by supplying a reactant H^+ . The overall reaction is :

$2H^+ + 2HCO_3^- + Fe \rightarrow Fe(HCO_3)_2 + H_2$ …… (12)

Equation (12) explain the increasing of MPY with time.

Effect of Hexamine

Hexamine is a sufficient material of an alkaline nature used to neutralize the carbonic acid formed in the condensate system .Table (3)shows the results of pH and M- Alk values after 10% hexamine was injected with different injection rate (0.5 , 1 , 2 , 3 , 4 , 5 ppm)

Table –3- Hexamine 10% (pH = 8.3 – 9.3)

Injection Rate	PH	M- Alkalinity
0.5 ppm	7.15	300
	7.20	290
	7.22	290
1 ppm	7.31	280
	7.325	275
	7.33	271
2 ppm	7.51	270
	7.53	269
	7.54	265
3 ppm	7.56	260
	7.61	258
	7.68	258
4 ppm	7.81	256
	7.83	250
	7.85	248
5 ppm	7.86	240
	7.88	236
	7.92	234

It was found by most investigations[12,13,14,15,16] that quantity of any neutralizing amine (hexamine in our reaserch) depend on degree of corrosion protection desired for the most critical system components. To provide this protection it must be achieved to complete neutralization.

Complete neutralization is achieved if condensate pH in all portions of the system is above 8.4[13,14,15,16] for this reason we increased the concentration of hexamine to 14% and when measured its pH value it was found 11.2 – 12.4 in which this range provides the increasing pH values of condensate at desired range. Hexamine of concentration 14% is injected continuously at different injection rate (0.5,1,2,3,4,5 ppm) to determine the optimum ppm , table –4- show these results

Table –4-Hexamine 14% (pH = 11.2 – 12.4)

Injection rate	PH	M-Alkalinity

0.5 ppm	8.01 8.04 8.06	190.50 190.20 190.00
1 ppm	8.20 8.22 8.24	179.2 179.05 179.00
2 ppm	8.35 8.38 8.38	142.1 142.05 142
3 ppm	8.47 8.52 8.55	120.22 120 119.2
4 ppm	8.60 8.63 8.75	115 115 112
5 ppm	8.89 9.00 9.03	100 99.5 99.5

Hexamine feed should be controlled very carefully to avoid condensat pH values above 9.00[15,14] because:

1-Alkaline solutions over pH values of 9.00 will have a deleterious effect on metals.

2-High pH can result in another severe problems such as carry over problem.

3-More cost

Due to above reasons the injection rate stopped at 5 ppm and consider hexamine with concentration 14% and injection rate 3-5 ppm the best results (optimum conditions).

Table –5- show the effect of optimum condition on corrosion rate for two cases , first case for concentration 10% and second case 14% .

Table –5-

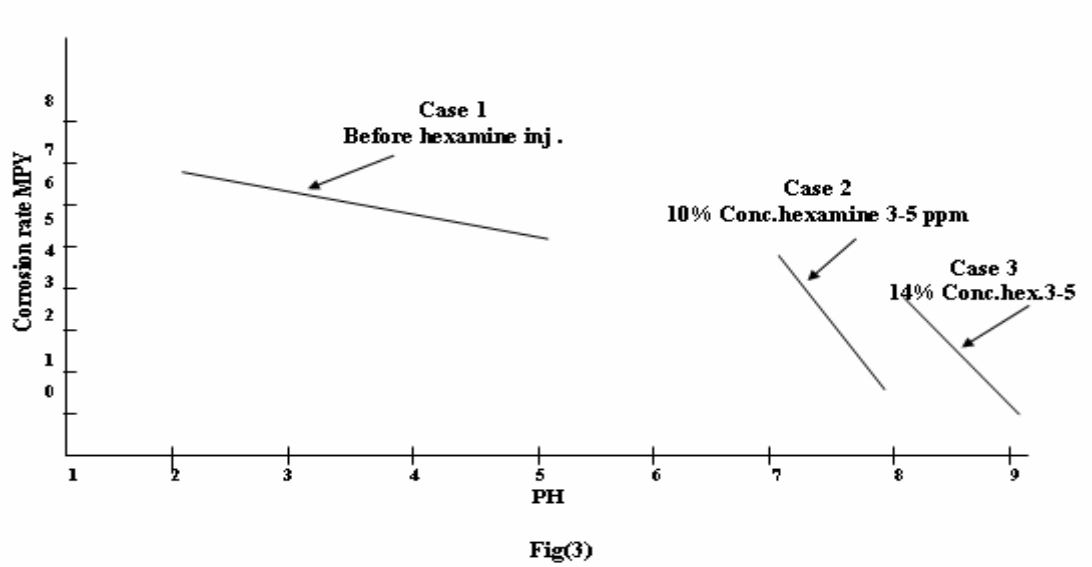
Day exposed	10% hexamine at 3-5 ppm wt – loss (mg)	MPY	14% hexamine at 3-5 ppm wt-loss (mg)	MPY
20	115.964	4.8	90.941	3.77
40	110.481	2.3	85.841	1.78
60	108.941	1.5	75.932	1.05

Fig (3) shows the comparison between three cases, first case before hexamine injection , the second after 10% hexamine injection at 3-5 ppm and the third case after injected 14% hexamine at 3-5 ppm.

The curve of case 3 shows the strong effect of hexamine in reducing corrosion rate because of hexamine ability to depress the active of CO_2 , the range of pH values of this case are 8.01 – 9.03 in which this range considered the best range since CO_2 does not exist in this range. The corrosion rate in curve of case 2 is higher than in case 3 , because the concentration 10% is less effectiveness than concentration 14% in reducing CO_2 active , the range of pH values of curve 2 are (7.15 – 7.92) in this range CO_2 is still present.

Curve of case 1 refers to elevation of corrosion rate at pH range (5.2 – 2.2) and insufficient M- Alkalinity because of acidic attack by CO_2 .

All results refer to present quantity of corrosion in condensate system due to presence of free oxygen which causes severe corrosion also.



Fig(3)

Conclusions and Recommendation

1. CO_2 is the primary cause of decrease condensate pH and insufficient alkalinity which cause dissolution of oxide layer and increased corrosion.
2. Hexamine is a sufficient material of an alkaline nature used in this research to neutralize the carbonic acid because of its low cost and availability in Iraq.
3. Good results for pH values and M- Alkalinity are obtained using optimum operating conditions as follows :
   - concentration of hexamine is 14% .
   - pH of hexamine in above conc. Is 11.2 – 12.4 .
   - injection rate 3-5 ppm
4. Hexamine should not be fed to the deaerating equipment because hexamine is volatile in nature and will leave with the deaerated gases if fed to the deaerator for this reason it feed to the feed water line as shown in fig (2) .
5. There is quantity of corrosion in condensate system due to presence of free oxygen which cause severe corrosion for this we recommende to making research using sufficient material (Filming amine) to treat the system from both CO_2 and O_2 Corrosion .

References

1- *"Collins and Henderson Boiler – water Treatment : A General Review ",* Corrosion prev. and cont. , 3 , No. 9 , 37 – 40 (1950) .
2- Skaperdas and Uhlig "*Water treatment for low – pressure Heating Boilers* ", Power , 97 , No.8 , 118 – 9 (1953) Aug.
3- Laird.A Boiler corrosion and its Alleviation by feed water conditioning, Corrosion Prev. and cont., 5 , No. 2 , 35-8 ; No. 3 , 57-62 (1958) .

4- *"Boiler corrosion and water treatment"* . London : Gt. Brit. Admiralty , 1965 . pub. 1947.
5- Calise .V. J. and Duff .J.H. *"Treatment of makeup feed water"* , condensate , and Recycle water for supercritical and Nuclear – Reactor power – plant cycles Trans Am. Soc. Mech. Engrs. 80, 1659 – 75 (1958).
6- Symposium *:" High purity water chemistry of Nuclear power plants"* , proc. NACE 25th conference , 1969.
7- Ammonia Reduces oxygen Attack on Zr Alloys under Reactor Radiation J.A. Lesurf and P.E.C. Bryant , High purity water corrosion of metals NACE, 1967, pp 42-48.
8- *"Bibliography of corrosion inhibitors for high purity water"*. NACE T-3 F Report, 1963.
9- Tash .J.A. and . klein . H.A, Boiler – *"water chemistry operating Experience at the shipping port atomic power station"*.
10- Grabows. "*Present – Day feed water treatment for High – pressure Boilers*" , Eng. And Boiler House Rev. , 74 , 368-71 , 374 (1959).
11- Homig and Richter "*Corrosion*" , 18 , (1962) Jan.
12- Fabio Gigli *." The shape of water publication "*May 18th , 2000 chemic company.
13- Bruce. T. ketrick ; Neutralizing Amine , Guardian Chemical Specialities Corp , York , Penns.
14- Albatross fine chemicals Ltd , *"India Water Treatment"* , India Chemicals , Technical Bulletin 394 htm.
15- Pierce W.C. E.L. ; 4th edition *" Quantitative Analysis "*.
16- http// www. gc 3. Com / tech db/ boilerext . htm.