

# **Mohafezan Behboud Ab Co.**

**MBA WATER TREATMENT CHEMICALS**

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**Preface:**

Prophet Mohammad (PBUH): The best blessing is to know something and pass the knowledge down to others.

One of the most significant approaches to enhance the knowledge in corrosion science is to raise the public awareness by professional experts. The fervent motivation to write this periodical is to publish the acquired experience in diverse fields of corrosion science specially water and steam processes.

Clearly, the above-mentioned precious experiences were acquired by local professional experts in different industries who have been generous to share their knowledge with the experts of our company; therefore, we felt the burden of responsibility to publish and publicize such knowledge. It is our strong belief that God has blessed us to take one small action in such great triumph. We strongly hope that the blessing share of experience continues and more and more professional experts in local industries share their valuable knowledge to expand and extend this awareness, and in return, clearly we assure that their contribution will be published and fully recognized under their own names.

One of the most precious experiences of this company is to economize on water consumption in industry and overcome the challenge of corrosion; thus, our experts may have fair co-operation with other industries to carry out research projects in above-mentioned fields.

At the end, we fervently wish those experts-who contributed tirelessly to this periodical to enhance the awareness against corrosion science and problem resolution- to have continuous prosperous achievements in their lives.

## **Section one: Corrosion and scale Control in RO water**

### **Introduction:**

The waters used as cooling in industries mainly include the fresh Waters (Rivers and Wells), sea waters, or waters with rare slats which are mainly produced by Reverse Osmosis Purification devises. The corrosion and sedimentation behavior of these waters may vary. For instance, RO water has less sedimentation specifications, but high corrosion; while this might be the opposite in fresh waters.

The cooling systems such as open circuit cooling is constructed by diverse material and combinations; therefore, the steels mainly used to make such systems include cast iron, carbon steel, copper and its alloys ,Galvanized steel ,stainless steel, and aluminum .

Stainless steel (type 304L) is highly sensitive in Ro waters with Chloride which consequently leads into crevice and pitting corrosion. Major industries such as petrochemical plants in Mahshar utilize RO waters for their open cooling systems. The most effective parameters in corrosion and scale in such waters are the major cores in this essay which are as follows:

- Water pH, and the required hardness to control corrosion and scale in Open Cooling.
- The maximum permissible amount of chloride in circulating water in stainless steel type 304, and 316.
- Scale control by applying langelier index and the related problems in this approach.
- The maximum permissible amount of Chloride and hardness in Raw Water.

It should be noted the technical issues of the essay are provided by technical documents of manufacturing companies (especially petrochemical plants), credible scientific references, and international standards.

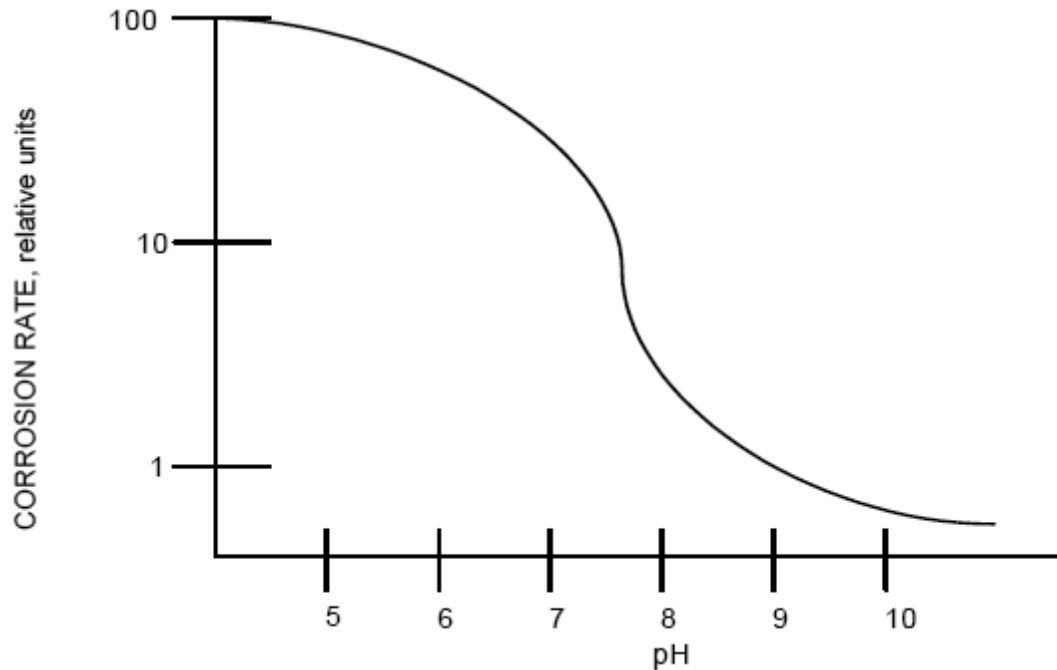
### **1-1-Water pH and the require hardness to control the Corrosion and Scale in Open Cooling**

As it was already mentioned, RO water is mainly used in petrochemical plants in Mahshahar as make up water in cooling tower, drinking water and etc.

As the level of salts in RO water is low, controlling the corrosion of the water without appropriate inhibitors is difficult; therefore, lime used to be utilized in major towers of the mentioned complexes to reduce the water corrosion. In fact, lime increases the amount of water pH and calcium which leads into water corrosion reduction; however, this approach is outdated, as there are some appropriate inhibitors. Some qualified inhibitors in low pH (7-7.5) would have the best efficiency in corrosion and sedimentation.

The graph 1 illustrates the iron corrosion behavior in different pHs. As it is shown, the level iron corrosion decreases in high pHs, therefore, the manufacturing companies increase the pH in circulating water (8-8.5) to maintain the amount of corrosion in standard level; however, in such pH, sedimentation is intensified in such convertors in which the speed of water is low or the temperature of water is high. Besides, the antiscalant materials would lose their antiscalant characteristics in temperature over 50 °C.

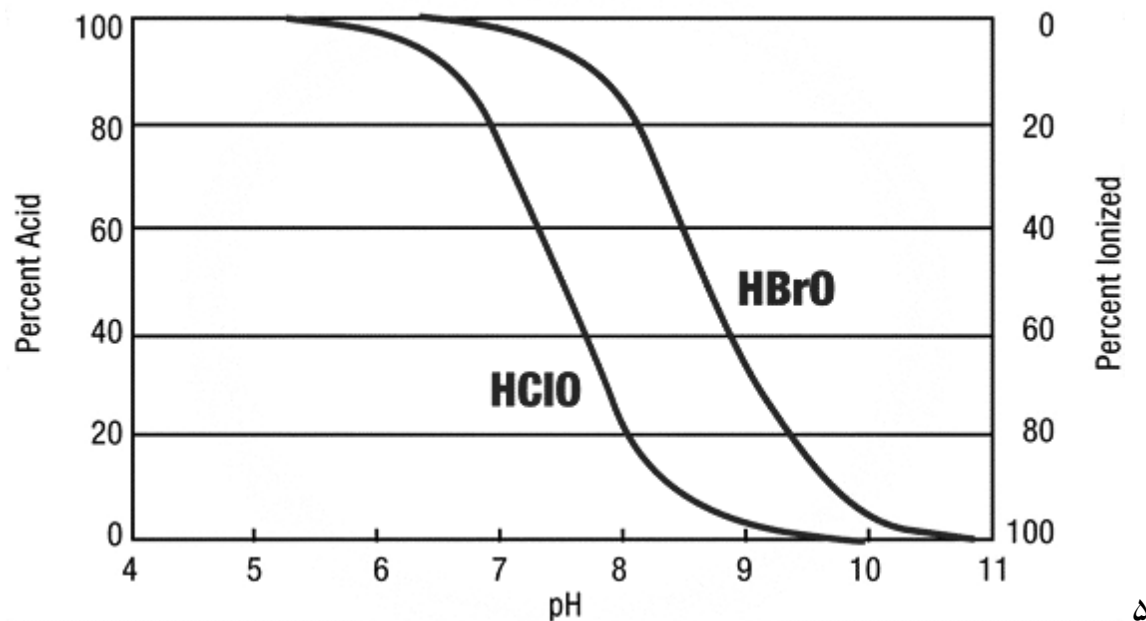
These days, the main criteria for water experts in local industries is the general corrosion level which is measured by coupon placement in cold water flow, but not the sediment-which requires comprehensive revision. Actually, the major problem which causes the unit failure is the sediment that consequently leads into perforation of convertors in system, but not the high level of general corrosion.



**Figure1-The changes of corrosion rate**

Sediments may cause major problems such as:

- Diverse under scale corrosion such as tuberculation and oxygen in cool water is due to undesirable sediment in system. [2,3]
- The undesirable scale in cool water causes microbial corrosion – which is resulted by SRB bacteria to turn into pitting corrosion. [5,6]
- As it is illustrated in figure 2, the efficiency of chloride gas in pH 8.5 is approximately 10 percent, while, this efficiency in pH 7 is reported to be 80 percent. Therefore, in low pH, the cost of disinfecting material is very low.[7,8]



**Figure2- The efficiency of chloride gas in different**

- Operation in neutral pH not only presents scale deposition, but also cleans the present scale in the system in long term.

Regarding the numerous challenges resulted by deposition, it is concluded that applying inhibitors –which are highly effective in low pH to reduce the general corrosion-is preferred to those which are efficient in high pH.

### **Case study-Number One**

#### **The process to overcome the challenges of deposition in cooling system in HD units in petrochemical Plants**

In some production procession in petrochemical industry, to initiate the primary interaction, heat is required. Therefore, the supersaturated heat is injected into the jacket-in which there is flow of cooling water. Thus the required primary heat is provided.

In steam injection process, the water inside the pipes is not drained, after the steam injection, the inlet and out let valves are closed, therefore, there is a closed cycle of

steam and water in high temperature accelerates and intensifies deposition in mentioned circle.

When the initial reaction is over, the exothermic reaction continues, therefore, the steam injection stops and cooling water is inserted to cool the reactor jacket which consequently leads into some major deposition challenges. The temperature of cooling water increases due to injection of supersaturated steam, therefor, the scale inhibitors might not stop deposition process.

In such units, Revers Osmos(RO) in water is used as circulating water ; however, the little amount of soluble salts in circulating water may form adhesive sediments which are not easily cleaned and removed.

In some petrochemical factories where there are active HD units, the mentioned generators get out of service after a while in order to be cleaned by hydrochloric acid and appropriate inhibitors. Applying appropriate inhibitors which are efficient in low pH eradicate the problem, since in Neutral pH, deposition process decreases at the time of steam injection. Besides, the small amount of scale will be cleaned gradually.

The optimized conditions obtained in the last five years indicate that the mentioned jacket may not require piking. In fact, the inhibitors which are applied in low pH effectively increase the production efficiency. In this regard, the results of corrosion in an open cooling system in Mahshahr will be presented.

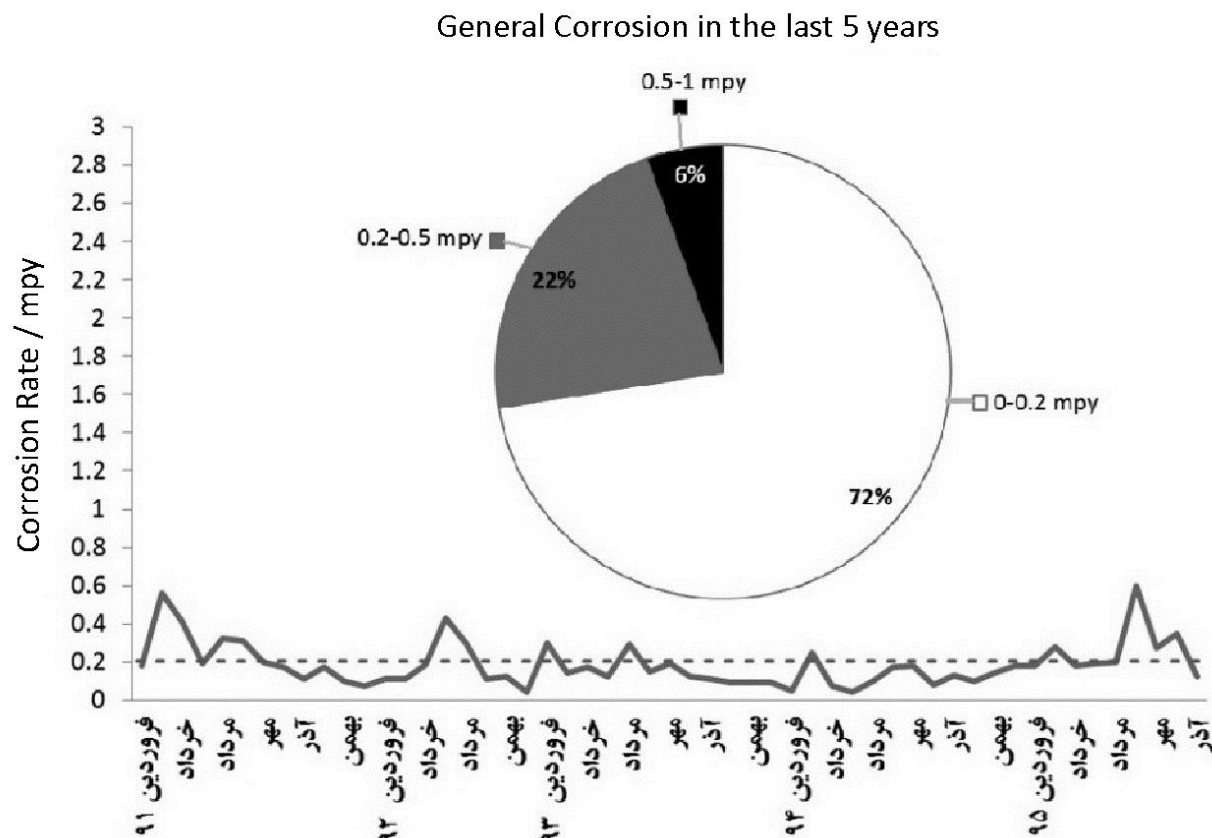
The chemical specification of RO water and circulating water are presented in the table. The results of coupon insertion in the last 5 years suggest that the amount of general corrosion of 72 present of coupons is less that 0.2 mpy; while the maximum is reported to be approximately 0.6 MPY (figure 3)

All parameters presented in table 1 are based on ppm.

Table 1.The specifications of RO in makeup water and circulating water

| Parameter         | pH        | EC       | TH    | M.ALK  | Cl      | T.Fe    | D.Fe  | F.CL2 |
|-------------------|-----------|----------|-------|--------|---------|---------|-------|-------|
| Make up water     | 7,7       | 40-60    | 4-6   | -      | 10-15   | 0.1-0.2 | -     | -     |
| Circulating water | 7,20-7,80 | 800-1200 | 20-40 | 20-100 | 100-400 | 0,4-2   | 0,4-4 | 0,2-1 |





**Figure 3- Alteration in corrosion rate for an open cooling system in the last 5 years (May-2012)**

## 2-1- The maximum permissible amount of chloride in RO water

Stainless steel in aquatic environment is resistant against the corrosion; yet excessive chloride ion (CT) in distilled and RO water causes SCC corrosion in stainless steel 316 L and 304 L. In addition, this type of steel will have crevice and pitting corrosion in the presence of chloride ion.

The maximum permissible amount of chloride ion is announced as 200 ppm by the Nickle Institute in the US. There are some other effective parameters which intensify the crevice corrosion including high concentration of chloride, high

temperature, low pHs, low acceleration, the presence of thin grooves in system, and the presence of biomass. The institute highly recommended 50 ppm of chloride for stainless steel; while in type 316 M the amount is recommended to be 250 ppm. In this regard, Mitsubishi heavy industries announced the maximum amount of chloride ion 50 ppm for Tondgoyan petrochemical company in Mahshar, while the other parameters are the same as the ones in table 3. All parameters presented in table 3 are based on ppm.

**Table 2- The maximum permissible amount of chloride for stainless steel in different conditions (Nickle Institute)[8]**

| <b>Chloride Level (ppm)</b> | <b>Stainless Steel Grade</b>                          |
|-----------------------------|---|
| <200                        | 304,316L  |
| 1000-200                    | 316L, duplex alloy 2205                               |
| 3600-1000                   | duplex alloy 2205<br>6% Mo superaustnic, super duplex |
| >3600                       | 6% Mo superaustnic, super duplex                      |
| 26000- 15000(sea water )    | 6% Mo superaustnic, super duplex                      |

**Table 3- The water quality extracted from the instruction made by Mitsubishi heavy industries[9]**

| <b>PH</b>                    | <b>TH</b> | <b>Chloride</b> | <b>Sulphate</b> | <b>Iron</b> | <b>Silica</b> | <b>TDS</b>                |
|------------------------------|-----------|-----------------|-----------------|-------------|---------------|---------------------------|
| <9(as<br>CaCO <sub>3</sub> ) | <30       | <50             | <50             | Traces      | <1.2          | <250 (CaCo <sub>3</sub> ) |

In some mentioned references, it is said that the amount of chloride ion in distilled water may increase up to 1000 ppm; however, when there is biomass on the surface of pipes and generators, this amount shall not exceed more than 200 ppm. The reason of such discrepancy might be the presence of biomass or scale on the surface which consequently lead into the increase in the local density of chloride ion. The mechanism of such corrosion is similar to crevice corrosion. It should be noted that, in crevice corrosion as the chloride ions penetrate in to the crevices, and the density increases considerably.[11]

Notes: For required further information, about the mentioned cases, the content of reference number 10 is identically provided in table 4. In addition, in table 5, which is extracted from the Nickle institute, the maximum permissible amount of chloride ion is precisely according to table 5.[12]

Table 4-The permissible amount of Chloride for 304 and 346 steels[10]

|                               |   |
|-------------------------------|---|
| <b>Stainless Steel 316-SS</b> | <b>Similar to 304-ss with higher chlorldie tolerances.</b><br><b>Tolerates chloride levels of 5000 mg/l when deposit –forming conditions exit.</b><br><b>Tolerates chloride levels up to 30000 mg/l on clean surfaces.</b>  |
| <b>Stainless Steel 304-SS</b> | <b>Susceptible to corrosion from chlorides when deposit – forming conditions exist.</b><br><b>Biomass deposits can cause rapid pitting.</b><br><b>Corrodes at chloride levels of 200 mg/l when deposit-forming conditions exit.</b><br><b>Tolerates chlorides levels of 1000 mg/l on clean surfaces</b> |

Table 5- chloride level for water in environment temperature[12]

| <b>Chloride Level (ppm, mg/L)</b> | <b>Suitable grades</b>                                     |
|-----------------------------------|--|
| <200                              | <b>1.4301 (304), 1.4307 (304L), 1.4404 (316 L)</b>         |
| 200-1000                          | <b>1.4404 (316L), 1.4462 (2205)</b>                        |
| 1000-3600                         | <b>1.4462 (2205), 6% Mo Super austenitic, Super duplex</b> |
| >3600 and sea water               | <b>6% Mo Super austenitic, Super duplex</b>                |

### **3-1- Controlling the scale by Langeliers index and the problems in this method**

Unfortunately, for decades, corrosion experts have believed that considering Langeliers and Ryznar index in mild deposition in the system would reduce corrosion challenges. In this regard, the instructions recommended controlling the Langeliers index for water depositions, but not the corrosion.[13]

The instructions provided by Mitsubishi heavy industries recommended 0.77 as the mentioned index for the quality of circulating water.

Table 6- Ryznar and Langelier index presented by Mitsubishi heavy Industries (Tondgooyan Petrochemical Company)[9]

|            |       |
|------------|-------|
| <b>LSI</b> | +0/77 |
| <b>RSI</b> | 6/59  |

As it was already mentioned, if the water is corrosive -which means the pH is controlled in 7 – 7.5 –deposition process is minimized. The absence of scale in cooling circle not only makes phenomena of under scale, microbial, and tuberculation corrosion impossible, but also it removes the present scale in thermal convertors and cooling circles in long time.

In regard with the increase in above – mentioned cases, the Longelier index would be better kept negative, as with increase of water salts, the possibility of deposition is minimized. Based on the previous experience, it is highly recommended to follow the following table for cooling water with diverse hardness.

One of the major problems in Langelier index is the calculation. In the table, the maximum amount of water TDS and also the calcium hardness is 1000 mg/lit; while in many countries, the real amount is much higher.[14]

**Table 7- Langelier index based on hardness alteration**

| <b>Total hardness amount</b> | <b>Langelier index</b> |
|------------------------------|------------------------|
| <b>500-1500</b>              | <b>(-0.5)– 0</b>       |
| <b>1500-2500</b>             | <b>(-0.5) – (-0.8)</b> |
| <b>2500-4000</b>             | <b>(-0.8) – (-1.2)</b> |

It is noted that, the author may not recommend to dismiss the index; however, it is highly recommended to apply the index to measure the water corrosion, but not to control the scale.

#### **4-1- The maximum permissible amount of chloride and hardness in raw water**

As you may know, there is a possibility to economize on water consumption in open cooling systems by reducing the blow down and increasing the condensed cycle of concentration. The increase of condensed cycle of concentration would enhance the amount of salt precipitates and corrosive salts such as chloride and sulphate.

The increase of water hardness which includes Calcium salt and Magnesium salt would intensify deposition. There are some restrictions presented in technical books or recommended by corrosion inhibitor manufacturer. For instance, the maximum amount of Chloride is approximately 500 ppm and the total amount of Chloride and Sulphate in major references is announced less than 2500. [15]

Mean while, there are some restrictions in regard with the amount of water hardness – which might vary depending on the different manufacturing companies; however, rarely the total amount of hardness is announced up to 2500 ppm. Interestingly, Kurita Handbook of water treatment (Japan)[16] presented water with 700 ppm of hardness as water with high amount of salts. According to the standards of drinking water presented in Europe, the water which contains more than 250 ppm of Chloride is defined as water with high amount of Chloride.[17]

Clearly, in some European countries, Japan and even in America, the amount of salts considerably low owns to high rate of rainfall. The quality standard of treated waste water in Iran to discharge in the environment is announced 100 ppm for Calcium and Magnesium each and 600 ppm and 400 ppm for Chloride and Sulphate respectively [18]; while the electrical conductivity and the amount of TH and CI in the water of Kerman, Yazd and the regions in edge of the deserts in Iran are more than 2500 ppm, 800 ppm and 1000 ppm respectively.

The electrical conductivity of some wells around Qom is approximately 4500  $\mu\text{S}/\text{cm}$ . [19]

According to the sever water shortages in different areas in Iran, particularly in edge of the desert, such water first pass RO and then the treated water enters the cooling towers, a long amount of water is wasted as 30 to 35 percent of the water is

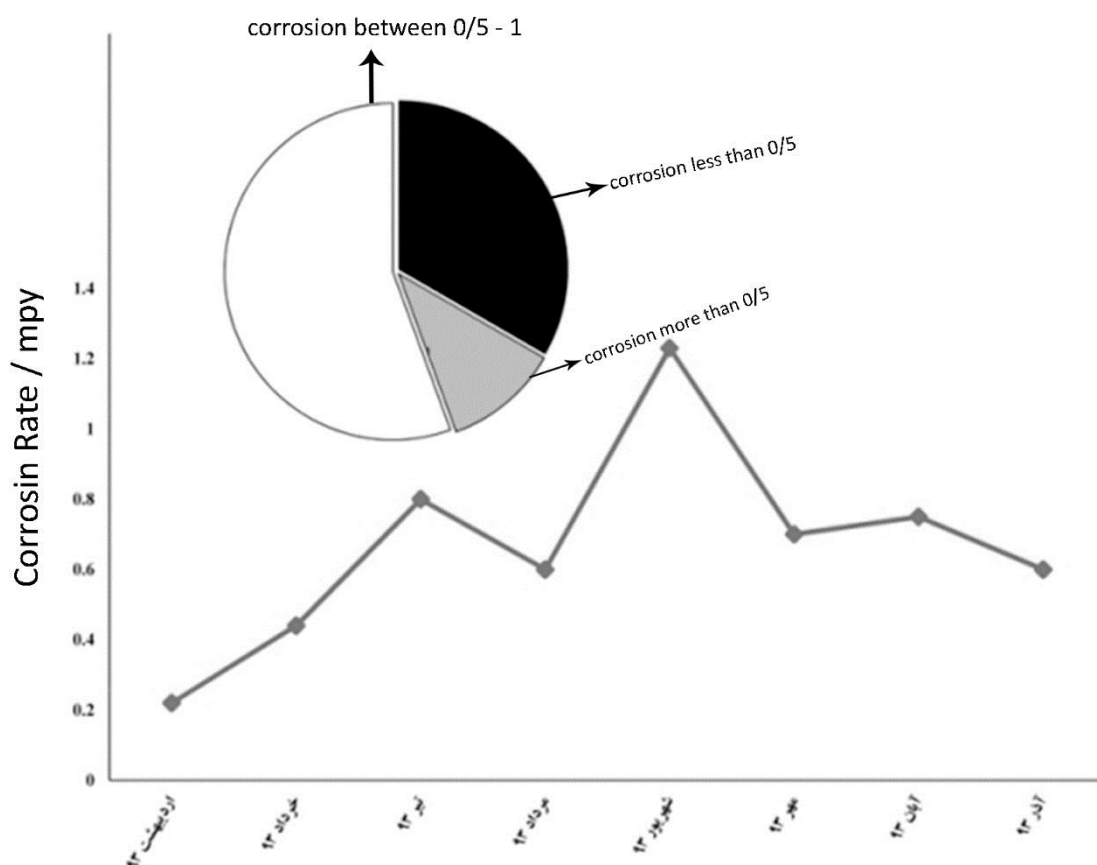
rejected. Therefore, material manufacturing companies should produce such inhibitors with efficient functions in such hard situation.

### **Case study-Number.2**

A rubber manufacturing Company in Kerman applies the rejected RO water with the electrical conductivity of 2500  $\mu\text{s}/\text{cm}$ . ultimately, the electrical conductivity rises up to 8000  $\mu\text{s}/\text{cm}$ . In addition, the electrical conductivity of circulating water in a plant near Kerman is approximately 900-1000  $\mu\text{s}/\text{cm}$  whose hardness, Chloride and Sulphate are considerably high. Their general corrosion rates are obtained less than 2 mpy. The corrosion results of rubber manufacturing company are presented as below.

As it is illustrated in the figure, the changes in corrosion rate of this rubber manufacturing company for 8 months are presented. The average corrosion rate of copper is less than 0.1 mpy.

Fortunately, the results obtained by the inhibitors of this Company is very promising and we are grateful to provide such services by our dedicated and tireless colleagues for local industries in Iran. We fervently wish to reach the deserved position to export the industries to the world.



**Figure 4- the variations of corrosion rate of rubber factory in 8 months**

The average of chemical parameters for circulating water is based on the following table. All parameters are based on ppm.

**Table8- The average of Chemical parameters for circulating water in rubber manufacturing company**

|  | PH         | EC          | TH         | CI           | N.ALK       |
|--|------------|-------------|------------|--------------|-------------|
| <b>The average parameters of circulating water</b> | <b>7/8</b> | <b>2450</b> | <b>493</b> | <b>825/4</b> | <b>79/7</b> |

## **Section two: Chemical considerations to apply human and industrial waste water**

### **Introduction**

Applying the treated waste water is one of the effective approaches to economize on industrial water consumption especially, the waters required for cooling towers and steam boilers. In fact, due to severe water shortages in Iran, some industries such as Shahid Mofateh thermal power plant and Isfahan oil Refinery Company use waste water in their industries.

Using such waste water might not impose any hygienic risk, besides, they are economically justified as the chemical quality of such waters is different from fresh water, thus, an specific considerations are required to apply them. For instance, mainly the amount of Ammonium and BOD of such waters is higher than fresh water.

This section deals with the effects of impurities – present treated waste water – on metals in cooling towers.



| <b>Consideration of cooling system components</b> |  |  |
|---|--|--|
| Material  | Water quality effects  | Required considerations  |
| Wood  | Wood decay   | High amount of Chlorine  |
| Mild steel  | Prone to corrosion deposition resulted by high rate of total dissolved solids, total suspended solids, biomass and heavy metals  | Minimize this phenomenon by chemical sanitation of water   |
| Galvanized Iron                                   | The corrosion resulted by high concentration of prone total dissolved solids and pH lower than 7.5 or higher than 8.5[4]   | Reduce the cycle of Concentration pH adjustment and apply chemical sanitation  |
| Stain less steel 304-304 L                        | Prone to corrosion resulted by the present of Chloride when the situation is optimized for deposition biomass deposit may accelerate pitting corrosion. When the situation is optimized for depositions the present of Chloride with the concentration of 200 mg/l may cause corrosion. The tolerable concentration of Chloride for clean surface is 1000 mg/l | To clean the system by applying antiseptic material. In addition, the present of high concentrated Nitrate reduces the corrosion of stainless steel  |
| Stain less steel 316-316 L                        | Such as stainless 304 with high Chloride tolerance   | Similar to stainless steel 304   |
| Copper alloys                                     | Porn to corrosion resulted by ammonia and high concentration over 0.5 mg/l causes crevice corrosion based on $\text{NH}_3$ . It is also effective in biomass formation which cause copper alloy corrosion.   | Water improvement might minimize such problems. The corrosion inhibitors of cooper such as TTA and BZT might reduce crevice corrosion[20]; however, copper Nickle alloys (10/90 and 70/30) are more resistant against pitting corrosion. |

**Notes:** the present of sludge mass on the Surface of stainless steel increase the Chloride under the mass. Their mechanism is similar to the increase of Chloride in Crevice corrosion. In such conditions the ions of Chloride penetrate into the Crevice and increase many times more than the amount of Chloride outside of crevice.

| <b>The effects of water quality index on cooling systems</b>        |  |
|---|--|
| Water quality index   | The effects of index on cooling systems  |
| Water hardness  | It helps deposition Calcium salts contain reverse solubility which means the increase in water temperature leads into more deposition of the salts.  |
| Alkalinity  | Alkalinity is an important factor in Calcium Carbonate deposition  |
| Silica  | They many Cause Sedimentary deposit which are not easily removed. Based on $\text{SiO}_2$ , the maximum amount of concentration of Silica is as 150 ppm. Meanwhile, if the silica concentration and the amount of Magnesium are high, the Sediment of Magnesium Silicate might be deposited. Then pretreatment with side filtration are highly required.   |
| Total suspended solids including Mud, Gravel Clay and plant species | Mainly they enter into the system with makeup water and air which intensify deposition and corrosion .Total suspended Solids are controlled by pre treatment and filtration process.   |
| Ammonia   | It causes the growth and proliferation of bio films in steam generators and cooling towers .It is so Corrosive for copper alloys with the concentration of 2 ppm. When it is combined with Chlorine, it turns into Chloramine which Neutralize the anti-infectious effects of Chlorine and some other non-oxidizing biocides such as Glutaraldehyde. In the present of Ammonia, Amin Biocides are recommended. |
| Phosphate   | The concentration should be minimized and the pH of the environment should be controlled between 7 to 7.5, and as Phosphate is an anodic inhibitor, therefore, it reduces corrosion. The combination of Phosphate in concentration over 20 ppm with Calcium in concentration over 1000 ppm might intensify Calcium Phosphate deposition. In addition, it is nutrient for bacteria and helps them to grow.      |
| Chloride  | Has already been explained   |

| <b>The effects of water quality index on cooling systems</b> |  |
|--|--|
| Iron   | The combination of Iron and Phosphate might form Iron Phosphate and their salts in system; therefore, appropriate inhibitors should be applied.  |
| Biochemical Oxygen Demand (BOD)                              | It illustrates the organic material present in water, therefore, Oxidative biocides are required   |
| Nitrates and Nitrites  | Nitrate in 300 ppm might control the corrosion of mild steel. It is also effective to minimize steel fraction and pitting corrosion. Nitrates have no roles either in destruction of copper alloys or protect them against corrosion.  |
| Zinc   | It might help Phosphate and Nitrates to minimize the rate of corrosion in mild steel and they might stop pitting corrosion. The present of this material with the concentration of 0.5 mg/l in cooling water is effective; however, it may cause deposition in concentration over 3 mg/l |
| Organic material   | As Nutrients, this might cause the growth of Micro- organisms  |
| Fluoride   | In concentration over 10 ppm, it combines with Calcium which causes deposition   |
| Heavy metals (Cu, Ni and Pb)                                 | The deposition of Nickle, Copper and lead on the Surface of steel causes Galvanic Corrosion in thermal generators, when the Copper corrosion is high, the Copper is dispatched from the surface and located on the surface of Iron which causes Galvanic corrosion.                      |

**NOTE:** Copper is mainly applied as a stabilizer in isothiazolinone biocide. As the amount of copper is not usually mentioned in the material safety data sheet (MSDS), therefore, the chemical analysis of this biocide needs to be provided. Such data might be provided by the seller. Additives which contain copper must not be used.

### Case study – Number 3

#### Cooling tower in Esfahan Mobarakeh steel company – unit CT 16

Waste water is mainly used for industrial consumption in Esfahan Mobarakeh steel company. The general corrosion rates of steel for the cooling tower of unit 16 in the plant within 15 months (April – 2015 to Aug – 2016) are presented in curve graph No. 5. As it is illustrated, the general corrosion rate in the given period is less than 1 mpy, and the average amount of copper corrosion is 0.2 mpy.

##### Note 1:

During 4 months in the summer of 2015, the average water conductivity was maintained up to 9500  $\mu\text{S}/\text{cm}$  to sever water shortage.

It should be noted that with the decrease of blow down comparing to previous year , the complex managed to economize on water consumption as much as 1.500.000  $\text{M}^3$  in this cooling.

##### Note 2:

The water conductivity in cooling of panel units increased up to 13000  $\mu\text{S}/\text{cm}$  during the summer time; fortunately, the Iron corrosion amount was measured as much as 1-2 mpy.

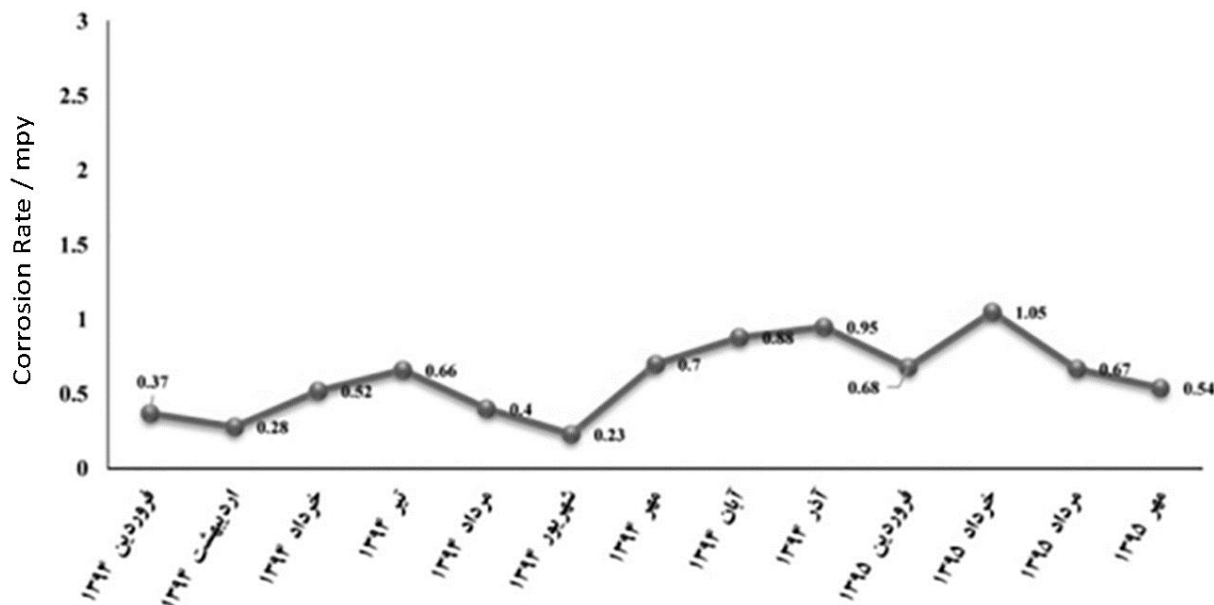


Figure5- changes in corrosion rate of cooling towers in Esfahan Mobarakeh steel company – unit CT 16 (Apr – 2015 to Oct – 2016)

## **Case study – Number 4**

### **Use ground water as an alternative for running water**

In one of the local industries in Iran, running water was consumed in cooling towers due to the low quality of ground water and high rate of deposition in condensers; while ground water might be utilized with appropriate inhibitors in cooling towers, then the blow down water – whose salts have increase – passes through the Ro machine. The produced treated water is applied to produce distilled water for boilers. Then, the surplus of this water might be utilized in cooling water system.

Currently 20.000 M<sup>3</sup> of running water is utilized for cooling tower system in the maintenance and operation units of a pilgrimage holy place in summer time; while ground water with appropriate inhibitors might be used instead. According to one of the experts, using ground water in that place would reduce the level of ground water in the region. Since the level of ground water is high in the region which might have direct impact on the destruction of historical monuments.

Therefore, ground water treatment might save municipal water as drinking water for residents instead.

### Section 3: Measurement of corrosion rate by Weight Loss method

#### Introduction

One of the oldest methods to measure the corrosion rate in water and oil industry is weight loss method. This method measures the corrosion and also the amount of scale by observing the structure and weight loss of the inserted coupons. In addition, this method also assesses pitting corrosion as well.

In the methods, coupons are made of special alloys with specific weight. As it is illustrated in figure 6, those coupons are installed in corrosion Rock. It is noted that, all mentioned issues are driven from standard NO. ASTM D 2688-94. Besides, for any further information, please refer to the reference. NO.21

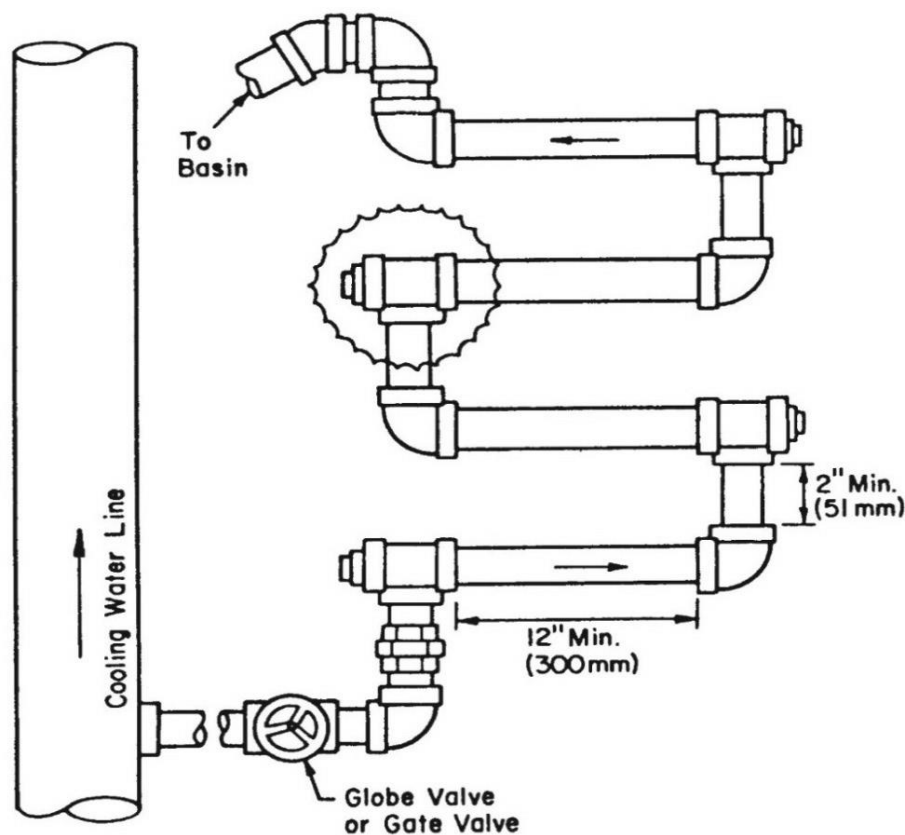


Figure 6-the schematic figure of Corrosion Rock

### 3-1- Corrosion Rock

The figure No.6 illustrates a corrosion Rock which holds corrosion coupons. As it is clearly shown in the picture, Rock pipes are located at least 51 mm away from each other and the length of the pipes is 300 mm. To minimize the effect of current due to the open space around coupon, the pipe size should at least be considered 0.6in. The steel samples need to have almost the same chemical combinations to the ones of applied alloys in the system. If such balance is not considered, then cooled – Rolled steel or steel with low carbon are required. (The amount of carbon should be based on SAE 1020-1005 standard)

If diverse alloys are applied in system, the coupons of the alloys are used in corrosion Rock to assess the corrosion rate. Sometimes, the alloys of copper, brass, and stainless steel, aluminum are use in the system. First, the makeup water passes through Aluminum coupons and then it goes through the coupons of steel, copper, and the alloys and finally it crosses through stainless steel. The size of the applied coupons should be approximately  $13 \times 76$  mm (if they are made of mild steel) with the thickness of 1.6; while, if they are made of hard steel, they should be approximately  $13 \times 76$  mm with thickness of 3mm. In general, the level of coupons should not exceed more than 2580mm, which indicates the fact that the level of coupon in the proximity of the current should always be more than the thickness of the edges.

To minimize the errors in result, the distance of coupons with different materials should at least be 76 mm. The alteration in water current inside the rock may affect the corrosion calculation. When the coupons are withdrawn, the visual observation about the present of pit, type and amount of scale and the present of biomass might contribute remarkably to inspect the problems.

The bracket to hold the coupons should be made of Bakelite. It is selected with a plastic bar which is approximately 150 mm long and 13 mm (0.5 in) thick. This bar is the holder of coupon bracket. To hold the bracket, special bolts and coupon are used to prevent the crevice corrosion in the space between the bolts and coupons which might affect the result accuracy. (Figure 7)



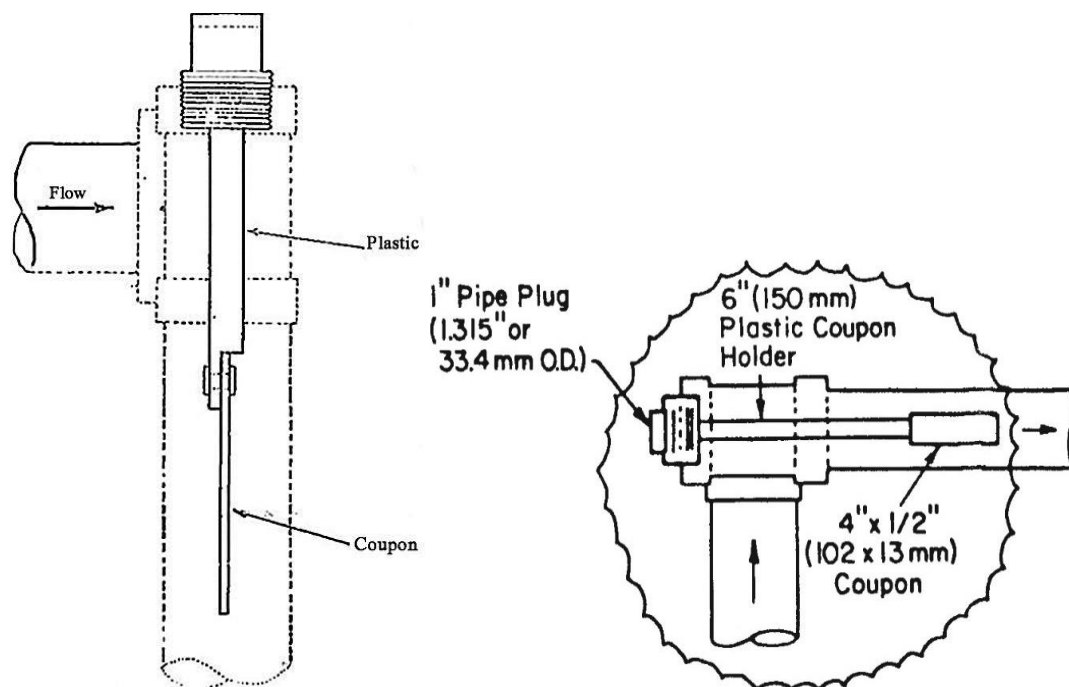


Figure 7. The location of Coupons in the Rock

As it is displayed in figure 7, the coupon holder should be positioned in the Rock pipe appropriately which prevent the turbulence of current in pipe tee; on the other hand, it should keep the suitable distance from pipe wall to facilitate the current of water. The above mentioned consideration leads into result accuracy.

### 3-2- Testing method

First, coupons are required to be weighed with the accuracy of 0.1 milligram, then the followings need to be considered.

- It would better to use coupons manufactured by credible producers.
- Prior to weighing, coupons are required to be kept in desiccators – as the exposure to air might causes inaccuracy.
- Standard coupons are mainly kept in an appropriate paper cover, on which the weight is written.

- First, coupons need to be appropriately installed on a holder with suitable washers and bolts.
- It is recommended to install a flow meter on corrosion Rock, so that the testing is carried out with constant flow.
- Note: It is recommended to set the water flow approximately to 0.6 - 1.8 meter in a second. However, in case the scale assessment in system is highly important, lower speed of flow is recommended. (approximately 0.5 to 0.7 meters in a second)

It is noted that, in order to obtain reliable result, at least two samples in two separate locations are required.

It is recommended to withdraw the coupon out of the loop after a while (4 to 7 days) to measure the corrosion rate, then after a long time ( 30 to 60 days) other coupons are required to be withdrawn to compare the results.

### **3-3- Cleaning coupons after testing**

When coupons are withdrawn out of the Rock and dried, they need to be weighed in desiccators and then they need appropriate cleansing. There are diverse ways to clean coupons depending on coupons material.

#### **❖ Physical method to clean coupons**

When the coupon is withdrawn, first clean it with a plastic knife, and then saturate it in Trichloroethylene for a while, henceforth, brush off the dirt with a plastic brush and finally put the sample in acid containing an appropriate inhibitors.

#### **A) Carbon steel corrosion coupons**

Immerse the sample for 30 seconds in hydrochloric acid which contains 1 to 2.8 percent of appropriate inhibitors. After cleaning, wash the Acid coupons with distilled water and then rub it with little amount of Trisodium Phosphate and silica scale. Finally, wipe out the sample with tissue and dryer.

#### **B) copper coupons and its alloys**

similar to above – mentioned method, first clean the coupon with a plastic knife, then saturate it in Trichloroethylene for a while, henceforth put it in hydrochloric acid which contains appropriate inhibitors (inhibitor plus 1 to 2.8 percent of hydrochloric acid) for 30 seconds.

It should be noted that, concentration of hydrochloric acid should be 1 to 1.8 percent. Afterwards, wash the sample with water and saturate it in isopropyl Alcohol. Next, immerse the coupon in benzene and wipe it out with a cloth and finally put the cleaned coupon in desiccator for one hour.

### **C) Aluminum coupons or its alloys**

Similar to above – mentioned method, first clean the coupon with plastic knife. Then, saturate it in Trichloroethylene, afterwards, put in solution containing Chromic Acid and Phosphoric Acid for 30 minute in room temperature. Next, wash the sample with water, and saturate it in isopropyl Alcohol. Finally, wipe it with tissue and put in desiccators for one hour.

### **Chemical method**

#### **1- Steel samples**

First clean the surface of the samples with soft brush or running water to remove the soft material off the coupons, and then put the sample in a solution made of pretty strong hydrochloric acid and corrosion inhibitor in room temperature for 15 second. Next wash the coupons with the mixture of water and isopropanol – finally wipe it out with a piece of cloth and put it a desiccator.

#### **2- Sample made of Copper**

Washing these types of coupons are similar to above method.

#### **3- Sample made of Aluminum**

First put the coupon into the distilled water containing 3 percent of Chromic acid and 5 percent of Phosphoric acid for 5 minutes in a temperature between 71 – 77 °C. Then similar to method 1, wash, wipe it dry and put it in desiccator for 2 hours.

**Notes:** The above – mentioned method is one of the most common method to wash coupons; However, the important point is to apply the above – mentioned method to clean non–corroded coupons similar to corroded ones. Since the measurement errors in both conditions are similar.

### 3-4- Calculating the rate of pitting corrosion

Corrosion rate in average is calculated as of the amount of penetration based on mpy on the weight loss in milligram.

$$\text{Corrosion rate} = \frac{22.3 w}{dat}$$

W: weight loss in milligrams

d: metal density in g/cm<sup>3</sup>

a: area of sample in cm<sup>2</sup>

t: time of exposure of the metal samples

It should be noted that the penetration rate which is calculated based on the above method is based on the uniform corrosion of the samples.

The densities of different steels are presented in the following table:

**Table 9- specific weights of different steels**

| Type of steel                         | Ad miralty brass | copper | Yellow brass | aluminum | Carbon steel | Lead  |
|---------------------------------------|------------------|--------|--------------|----------|--------------|-------|
| Specific weight (gr/cm <sup>3</sup> ) | 8.17             | 8.9    | 8.02         | 2.70     | 7.85         | 11.34 |

**Table 10- general corrosion standard for different metals in weight loss method**

| Metal                | mpy          | Comment      | Metal                    | mpy          | Comment      |
|----------------------|--------------|--------------|--------------------------|--------------|--------------|
| Mild steel piping    | < 1          | Excellent    | Copper and copper alloys | < 0.1        | Excellent    |
|                      | > 1 to 3     | Good         |                          | > 0.1 to 0.2 | Good         |
|                      | > 3 to 5     | Fair         |                          | > 0.2 to 0.3 | Fair         |
|                      | > 5 to 10    | Poor         |                          | > 0.3 to 0.5 | Poor         |
|                      | > 10         | Unacceptable |                          | > 0.5        | Unacceptable |
| Mild steel Hx tubing | < 0.2        | Excellent    | Galvanized steel         | < 2          | Excellent    |
|                      | > 0.2 to 0.5 | Good         |                          | > 2 to 4     | Good         |
|                      | > 0.5 to 1.0 | Fair         |                          | > 4 to 8     | Fair         |
|                      | > 1.0 to 1.5 | Poor         |                          | > 8 to 10    | Poor         |
|                      | > 1.5        | Unacceptable |                          | > 10         | Unacceptable |
| Stainless steel      | < 0.1        | Acceptable   |                          |              |              |
|                      | > 0.1        | Unacceptable |                          |              |              |

### 3-5- Study of the pitting and localized corrosion

The clean sample should be assessed to check the localized and pitting corrosion. If pitting corrosion is not observed on the coupons, the following arrangements are required:

Phase one: It is when there is no localized corrosion.

Phase two: check the uniform and non-uniform corrosion. The pitting corrosion is calculated based on the ratio of the corroded surface to the total surface of the sample.

Phase three: If there are pits on the surface, the depth should be measured precisely. Besides, the size and the number of pits should be calculated in square inch unit. The shape and type of holes should be precisely determined and reported.

d: The intensity of pitting – as a maximum depth of the hole on mils- should be checked and measured by a filler Gauge or a microscope.

The rate of pitting is calculated based on the following equation:

$$PR = 365 \times \frac{\text{Maximum depth of hole}}{t}$$

PR: Pitting rate based on mpy

t: Time of immersion based on day

Note 1: As the rate of pitting might change depending on the increase in duration of immersion, the result obtained from short duration might not be generalized for a long duration of immersion.

Note 2: The resulted number in any tests shows the maximum rate of pitting in the duration of the test. It also should be noted that pitting might be intensified or stopped in some situations. Therefore, the results should be precisely observed.

### 6-3- Effective elements in weight loss method.

There are diverse effective elements in weight loss method in cooling water which are presented as follows.

Metallurgy: the common coupons applied in corrosion Rock are mainly Carbon steel, Galvanized steel, Stainless steel, Aluminum, copper and the alloys. The kind of alloys is selected based on cooling water system alloys.

Temperature: As the temperature has a direct role in corrosion rate, if there is only one coupon installed on the system, the coupon should be installed at the entry of

reject water from the cooling water tower, as at this point, the water is at the highest degree and the measured corrosion is at the highest rate. In addition, coupons should be installed at points where there is deposition to determine the rate of deposition.

Testing duration: As the time passes, there is a protective layer formed on the coupons which mainly reduces corrosion rate (figure No. 8). Therefore, it is recommended to consider 60 to 90 days for weight loss testing. Certainly, the testing is in 30 days. It is highly recommended to follow one fixed method to determine the function of the inhibitors.

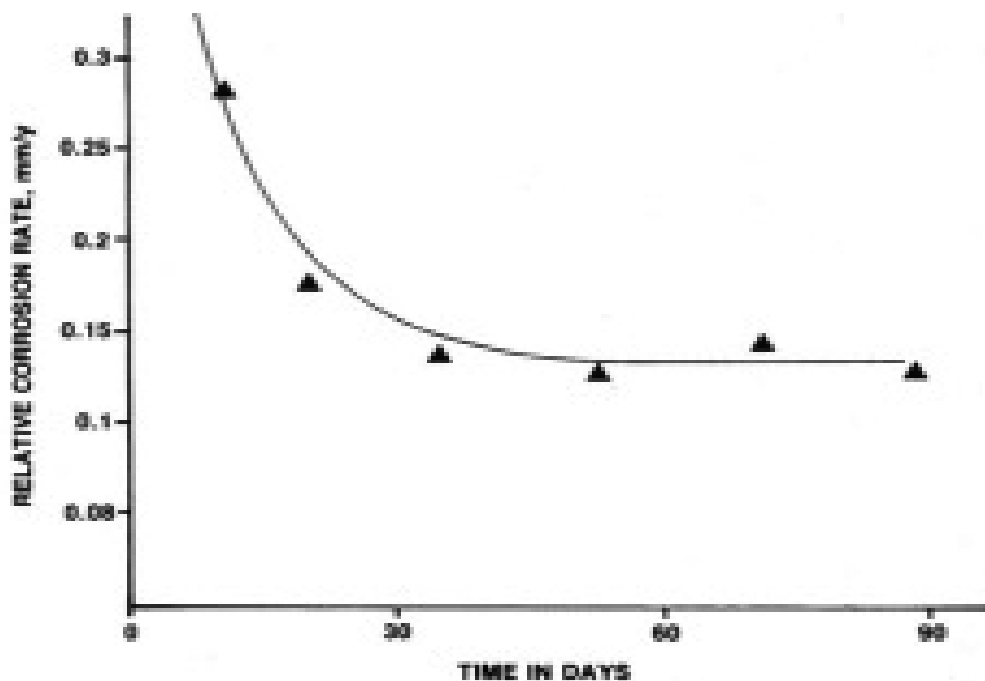


Figure 8- The corrosion rate based on time in days

### 7-3- the advantageous and restrictions of the weight loss method

The major advantage of this method is the low cost and the facile installation. In addition, applying this method contributes greatly to the assessments of different factors such as deposition rate, the amount of sludge formed on coupons resulted

by the function of disinfectants and also the type of corrosion ( pitting, localized, and uniform) Which consequently leads into optimized function of the system. The main problem and disadvantage of this method is ignoring the effects of present shocks in system. It is noted that, covering the coupons with oil does not precisely show the corrosion rate. Unfortunately, recently such issue has been reported several times .

### **Case study- number 5**

#### **Deterioration in water wall pipes in a huge thermal power plant**

In a thermal power plant in Iran, there are several cases of deterioration in water wall pipes in a short distance away from the boiler burners. The precise assessment showed the mentioned pipes are under high severe thermal pressure as they are located close to the boiler burners. Besides, the boiler manufacturer enhanced the capacity to produce considerable amount of steam to increase the production capacity of the generator.

When there was a reduction of 15% in generator production, the problem was fixed.

### **Case study- number 6**

#### **The cause of fast rust on steel sheets in open air in a steel manufacturing complex**

The production of a steel manufacturing company started to rust in open area after a while. The observations and assessment showed that there were different types of salt (especially NaCl) contained in cooling water in the last phase to cool down the sheets. Consequently, there was a very thin layer of salt on the sheets; no sooner, they were exposed to humid weather, they would have steel rust. In such condition, prior to being dispatched from the company, the sheets need to be washed with high pressure clean water. It is also recommended to replace the water with qualified water.



## **Case study- number7**

### **Applying RO water in industry, and the method to control corrosion**

In one of the transit industries in Iran, there was water (with high amount of salts) in the radiator (engine cooling) of traction.

The radiator was disassembled and taken to relevant contractors to remove the scale. Per as the above explanation, it was supposed to clean the radiator with cleaning materials without disassembling the coolant before the coolants pipes were completely blocked up (when the car temperature gauge is rising )and filled it with qualified water and appropriate inhibitors.

The water quality used by coolant manufacturing company is as below.

Please be noted that, inhibitors with Nitrite base such as Sodium Nitrite, or the combination of Sodium Nitrite / Borax are not used in closed cooling circles which are made of galvanized pipes. Such inhibitors are not also used in closed areas which are made of Zinc sacrificial anodes.

**Table 11 – The water quality presented by GM locomotives manufacturing company**

| <b>pH</b>      | <b>TH</b>      | <b>Cl</b>          | <b>So4</b>         | <b>Sio2</b>        |
|----------------|----------------|--------------------|--------------------|--------------------|
| <b>6.5 - 8</b> | <b>180 ppm</b> | <b>&lt; 50 ppm</b> | <b>&lt; 50 ppm</b> | <b>&lt; 25 ppm</b> |

The mentioned water should not also contain ammonia and H<sub>2</sub>S.

## **Case study-number 8**

### **Prevent seashells from thermal condenser in sea makeup water**

One of the thermal plants in Iran used Caspian Sea water to cool down the condensers. Sea shells used to make lots of challenges for condenser pipes.

They entered the canal of makeup water and the condensers water box which cause a major blockage in the entrance notes and condenser pipes.

To stop them, bleach was used as a shock once in an hour; in such state 1 ppm and 7 ppm of Chlorine was injected respectively for 5:30 hours and 30 minutes. Such injection did not affect; therefore, constant amount of 2.5 ppm was injected which brought appropriate results.

The injection method in shock state showed that shells keep the mouths closed and the started breathing when the amount of Chlorine was low.

### **Case study -number9**

#### **Erosion corrosion in circulating water of a thermal plant**

Due to inappropriate design in one of the boilers of a thermal plant, high speed circulating water caused major erosion corrosion in the pipe transiting hot water. In such condition, there were particles in the water. The suspension of iron particles in beaker was observed by putting a magnet under the beaker.

It is necessary, to explain the differences of erosion and erosion – corrosion.

Erosion is the mechanical wear of materials under the conditions of repeated contact with fluid containing abrasive solids.

Erosion – corrosion

The simultaneous act of erosion and corrosion in the presence of corrosive fluid . In fact, that is the process in which the moving fluid destroys the surface of a solid and accelerates the corrosion.

Note: if the erosion occurs in water pipes, the iron mechanically is dispatched from the surface; in fact, iron is observed as Fe particles in water; while in erosion – corrosion phenomenon, the act of erosion corrodes iron in which iron is observed as  $\text{Fe}^{2+}$  which then converted in to  $\text{Fe}^{3+}$  .

Actually, in erosion – corrosion, the erosion causes electrochemical reactions which separate the  $\text{Fe}^{2+}$  from the steel surface and makes it enter the solution.

### **Case study number 10**

## **The phenomenon of carryover in drum**

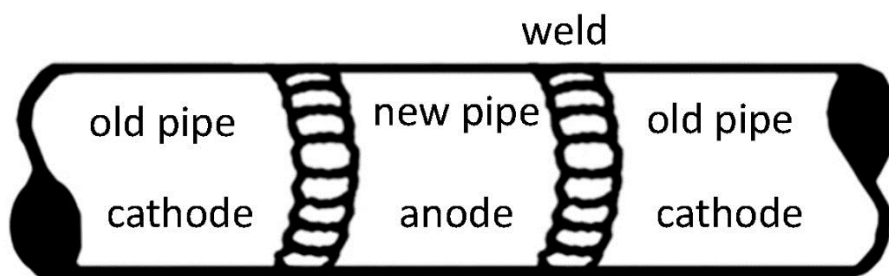
In one of the huge plants in Iran, the phenomenon of carryover occurred. At first, it was assumed that the separator was not designed appropriately; however, further observations showed that applying phosphate with excessive impurities caused vaporized CO<sub>2</sub> in carry over from Boiler drum.

Such challenge was overcome by providing high quality Sodium Phosphates.

## **Case study -number 11**

### **The perforation of old pipes buried under the ground**

In diverse industries, when the old pipes- which are buried under the ground – are perforated (mostly water transit pipes), the perforated part is removed and replaced with new pipe by welding. Generally, the life span of the new pipe is shorter (approximately 3 – 4 years) and it soon faces corrosion. As the old pipes with oxidized surface act as cathode, when they are located next to new pipes with non- oxidized surface; whilst, the new pipes take the role of anode. Such interaction leads into the perforation of new pipes. Therefore, the buried water pipes are recommended to be protected by cathodic protection both before and after the corrosion. Such experiment is explained in the first volume of corrosion control in industry [14]



**Figure 9 – Galvanic corrosion due to the connection of old and new pipe**

## **Case study number 12**

### **High amount of chlorine in water of most cities, and the urgent requirement to reform it**

As you may be informed, Chlorine and its derivatives are used in urban water treatment plants in Iran to disinfect water. The standard amount of Chlorine remained in drinking water are 0.3 – 0.1 ppm. Based on the instruction, a large amount of Chlorine should be neutralized with Sodium bisulfate which is mostly ignored and the amount of Chlorine remained in water is approximately 1 – 0.5 ppm.

This amount of chlorine in drinking water destroys the good bacteria ( *Lactobacillus acidophilus*) which helps in the digestion of food. It should be noted that approximately 2 billion of a good bacteria are excreted daily. The presence of such bacteria accelerates chemical interaction and food digestion.

One of the main reasons of death among gold fish purchased in Iranian New Year – is the high amount of Chlorine in drinking water.

Therefore, to reduce the death toll of gold fish in the first a few days of New Year, keep drinking water in a pot for a few hours and then stir it with a spoon to remove the excessive Chlorine.

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