Microbiological corrosion of ASTM SA105 carbon steel pipe for industrial fire water usage

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Abstract The large number of metallic systems developed for last few decades against both general uniform corrosion and localized corrosion. Among all microbiological induced corrosion (MIC) is attractive, multidisciplinary and complex in nature. Many chemical processing industries utilizes fresh water for fire service to nullify major/minor fire. One such fire water service line pipe attacked by micro-organisms leads to leakage which is industrially important from safety point of view. Also large numbers of leakage reported in similar fire water service of nearby food processing plant, paper & pulp plant, steel plant, electricity board etc...In present investigation one such industrial fire water service line failure analysis of carbon steel line pipe was analyzed to determine the cause of failure. The water sample subjected to various chemical and bacterial analyses. Turbidity, pH, calcium hardness, free chlorine, oxidation reduction potential, fungi, yeasts, sulphide reducing bacteria (SRB) and total bacteria (TB) were measured on water sample analysis. The corrosion rate was measured on steel samples and corrosion coupon measurements were installed in fire water for validating non flow assisted localized corrosion. The sulphide reducing bacteria (SRB) presents in fire water causes a localized micro biological corrosion attack of line pipe.

1. Introduction
The carbon steel has an optimum corrosion resistance for many fluid services including hydrocarbon. The microbiological influenced corrosion of carbon steel was complex and interdisciplinary in nature. In many number of industrial aqueous environments like crude oil and water, microbes metabolizes results in microbiological induced corrosion [1] [2]. There is no proactive inspection methodology for localized corrosion other than detailed corrosion prevention program of fire water pipelines [3] [4] [5]. The chemical processing industries utilizes carbon steel pipe for fresh or recycled water services. The
fire water service line pipe of chemical process industries carries fresh or recycled water in stagnant full load condition to nullify the severity of fire(s) during mishap, leakages or any other uncontrolled processing chemical reactions. In the present study one such frequent leakage of fire water network service of processing industry was investigated. Root cause and failure analysis of these case studies were performed in this investigation to improve the understanding related to process condition and failures [2] [10] [11] [12].

2. Materials and Methods

The material of construction for fire water service line pipe is ASTM SA105 carbon steel were produced by forging process and supplied in annealed condition. The operating pressure of fire water pipe was specified between 5kg/sq.cm to 7 kg/sq.cm depends on type of fire causes. The temperature of fire water was maintained between 25 deg C to 30 deg C with PH ranges from 6.5 to 9. The chemical composition of SA105 Grade B is shown in table1. The tensile strength, yield strength and elongation was specified as 480 MPa, 250 MPa and 30% respectively [1] [10] [11].

![Table 1. Chemical composition of ASTM SA105 Grade B pipe.](image)

| Elements       | Composition% |
|----------------|--------------|
| Carbon         | 0.35 max     |
| Manganese      | 0.6-1.05     |
| Phosphorous    | 0.035        |
| Sulphur        | 0.040        |
| Silicon        | 0.10-0.35    |
| Copper         | 0.40 max     |
| Nickel         | 0.40 max     |
| Chromium       | 0.30 max     |
| Molybdenum     | 0.12 max     |
| Vanadium       | 0.08 max     |

3. Theory

The thermodynamic free energy equation of corrosion of line pipe was evaluated [1] and shown below

\[
\log_{e} K_{eq} = \frac{nFE_{0}}{RT}
\]

(1)

Where:

- \( K_{eq} \) is equilibrium constant, \( n \) is number of electrons per atom of iron species
- \( R \) is gas constant = 1.987 cal/K.mol
- \( T \) is absolute temperature 298 K and
- \( F \) is faraday constant = 23060 cal/volt equivalent

The electromotive force series of ASTM SA105 Grade B line pipe corrosion reaction with standard potential at 25°C is chosen as fire water operating at room temperature [1]

\[
Fe^{2+} + 2e^{-} \rightarrow Fe \quad E^{0} = -0.440 \text{ volts}
\]

(2)

The pourbaix diagram shown in figure1 is used to identify the type of scale film formed on steel surface.
The anaerobic sulphur reducing bacteria containing de-sulfovibrio desulfuricans can be written as,

$$\text{SO}_4^{2-} + 4\text{H}_2 \rightarrow \text{S}^{2-} + 4\text{H}_2\text{O} \quad (3)$$

The aerobic sulphur oxidizing bacteria containing thiobacillus thiosulfates and thiobaccillus thiooxidases can be written as,

$$2\text{S} + 3\text{O}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{H}_2\text{SO}_4 \quad (4)$$

The sulphuric acid formation is localized in aerobic sulphur oxidizing bacterial reactions [3] [4] [5] [6] [7] [9].

### 4. Experimental procedure

The fire water samples were collected for chemical and bacterial constituent’s analysis. The pH of fire water samples were measured using DBK digital pH meter with accuracy of 0.01 pH. The turbidity and orthophosphate of fire water samples were measured using HACH calorimeter DR900 model. Upon addition of 0.25 ml molybdovanadate reagent (ammonium molybdate and sulphuric acid) to 10 ml fire water sample, the orthophosphate constituents in fire water were measured [12]. The oxidation reduction potential was measured using EZODO make of ORP5041 model oxidation reduction potential meter. Free residual chlorine was measured by mixing 1:10 of chlorine testing reagent TESTCHLOR to fire water sample and interprets according to table2. The calcium hardness of fire water sample was measured by titration technique. Beaker solution contains addition of x ml fire water sample, 4 ml sodium hydroxide (NaOH) and one drop Patton & reeders reagent ($C_{34}H_{14}N_2O_7S_3H_3O_5$). Pipette solution was prepared with 0.01M molar strength by addition of 3.7224gm EDTA (ethylenedinitrilotetraacetic acid disodium salt) to 1000 ml distilled water [12]. Titration was conducted using burette and pipette till solution colour changes from pink to blue and final calcium hardness was calculated using equation5 [8].

$$\text{Calcium hardness} = (\text{Initial reading} - \text{Final reading}) \times 1000\text{ml} / x \text{ml of water sample} \quad (5)$$
SA105 Grade B carbon steel specimens of size 2 x 4 cm were used for gravimetric measurements. The specimens were polished, degreased with trichloro ethylene, weighed and exposed in the fire water sample. After an exposure for seven days, the specimen was removed from fire water, washed with water and the corrosion products were cleaned with Clarke’s solution. The specimen was dried, finally weighed and the weight loss was noted. The corrosion rates (milli metre per year) were calculated using the equation [6] [1] [8] [9] [10] [11].

\[
\text{Corrosion rate} = \frac{87.6W}{ATD} \text{ (mmpy)}
\]

(6)

where,

- \( W \) = Weight loss (in mg)
- \( A \) = Area of the specimen (in cm²)
- \( T \) = Time (in hrs)
- \( D \) = Density of the carbon steel (7.86 g/cc)

One set of fire water samples were serially collected at six different locations, diluted and bacterial colonies like sulphate reducing bacteria (anaerobic bacteria) were enumerated by pour plate technique. The nutrient agar used for sulphur reducing bacterial growth nutrient medium [8]. Carbon steel equivalent C1020 grade carbon steel of 7.5 cm in length 1.5 cm in width and 0.25 cm in thick corrosion coupon was prepared and installed in line pipe under fire water service for measuring actual corrosion rate. Another set of fire water samples were collected from another location of fire water pipeline near to frequent failure reported area and mixed with neutralizing compounds (desulfotomaculum and desulfobacter) to nullify the effect of corrosion inhibitor in fire water sample. Thereafter bactaslyde were mixed with fire water sample to make solution and ensured air was completely evacuated in the tube. After mixed, the solution under incubate time starts and blackening of mixed solution begin from the bottom of tube. Thereafter sulphur reducing bacteria were estimated according to table 5 [12]. The corrosion product scale film formed on inner side of steel pipe was scratched by using polymeric wire brush and its chemical composition was analysed by digestion technique.

5. Results and Discussion

From equation 1 equilibrium constant calculated as \( K_{eq} = 1.535 \). The \( pH \) of water was measured 7.30 and with available half negative electrode potential of 0.440 volts, thermodynamic parameters were mapped on pourbaix diagram shown in figure 1. The iron Fe2+ scales were confirmed on the carbon steel surface. The turbidity of fire water sample was measured with respect to demineralised water assuming turbidity of demineralised water is 0 NTU (Nephelometric Turbidity Units).

| Colour produced   | Chlorine in ppm |
|-------------------|-----------------|
| White milky       | 0 (no chlorine) |
| Fluorescent       | 0 (no chlorine) |
| Orange            | 0.1 (no chlorine) |
| Light brown       | 0.2 (suit for use) |
| Red               | 0.5 (suit for use) |
| Violet            | 0.6 (not usable) |
| Black             | 0.8 (not usable) |
| Dark Blue         | 1.0 (not usable) |

The oxidation reduction potential was measured as 225-235mv. Free residual chlorine of fire water sample was measured as zero ppm cl and white milky colour observed in solution. From the weight
loss measurements made on carbon steel in fire water samples collected from entire fire service pipeline of different locations, it is observed that the corrosion rate is $5.0995 \times 10^{-2}$ mmpy shown in table 3. The results obtained from bacterial evaluation of the water samples indicate that bacteria such as SRB are responsible for the corrosion of the fire water pipeline from pour plate technique as shown in table 4. The sulphur reducing bacteria per 100 ml measured and presented in table 5 from bactaslyde mixed solution.

**Table 3.** Weight loss of ASTM A105 Grade B.

| Corrosion rate ($10^{-2}$ mmpy) | Mean corrosion rate ($10^{-2}$ mmpy) |
|---------------------------------|--------------------------------------|
| 5.7630                          | 5.0995                               |
| 4.8928                          |                                      |
| 4.6428                          |                                      |

**Table 4.** Sulphur reducing bacteria enumerated using pour plate technique.

| Number of water samples | Sulfur reducing bacteria colony forming unit per ml |
|-------------------------|-----------------------------------------------|
| 1                       | $3.3 \times 10^{-4}$                          |
| 2                       | $4.2 \times 10^{-4}$                          |
| 3                       | $5.8 \times 10^{-4}$                          |
| 4                       | $6.3 \times 10^{-4}$                          |
| 5                       | $2.1 \times 10^{-4}$                          |
| 6                       | $3.9 \times 10^{-4}$                          |

**Table 5.** Sulphur reducing bacteria interpretation table.

| Blackening in hours | Sulphur reducing bacteria per 100 ml |
|---------------------|--------------------------------------|
| 24                  | 100000                               |
| 48                  | 10000                               |
| 72                  | 1000                               |
| 96                  | 100                               |
| 120                 | 10                                |
| 144                 | <10                                |

The fungi and yeast will grow in bactaslyde either as pure yeast colonies or pure fungi colonies or fungi-yeast mixed colonies with yeast appears in white colour and fungal in either of white, green and brown colour of the solution. Neither fungi nor yeast were estimated from mixed solution, as any traces of white, green, brown colour was not observed in the bactaslyde mixed solution after 144
hours. The turbidity and orthophosphate of fire water sample was measured as 50 NTU and 0 ppm PO₄ respectively. The calcium hardness was measured using titration technique and using equation5, calcium hardness calculated as 74 ppm CaCO₃. The total bacteria count limit and sulphur reducing bacteria limit was measured 100000 counts/ml and 100 counts/100 ml, respectively for SA105 Grade B material. The corrosion coupon installed in line pipe under fire water service and the corresponding corrosion rate calculations were plotted in Figure 2. The corrosion coupon installed for period of one month and corrosion rate were calculated for one coupon, each month. The straight light line in figure 2 indicates corrosion rate limit of installed coupons, and corrosion rate is observed to be under control for the fire water service. After mixing of bactaslyde with water samples and solution was incubated minimum of 144 hours, the sulphide reducing bacteria count per 100 ml from sample water was interpreted and also plotted in figure 3. The straight light line in figure 3 indicates sulphide bacteria count limit. From figure 3 the sulphide reducing bacteria count per 100 ml is observed to be in the abnormal domain. The water analysis also reveals the presence of sulphide reducing bacteria in fire water network, which is considered to be one of the prime reasons for material degradation. The total bacteria count per ml from sample water is plotted in figure 4 and the straight light line in figure 4 indicates total bacteria count limit. From figure 4 it is observed that the total bacteria counts per ml are under control.

Figure 2. Corrosion rate plotted for corrosion coupon in fire water.

The Algae observed vicinity to localized failure however barnacles or other aqueous organisms are not observed, as represented by arrow in figure 5a. The compositional analysis performed by digestion technique details are given below

Iron content (as elemental Fe) = 53.4 wt%
Sulphur content (as elemental sulphur) = 1.1 wt%
Silica content (as SiO2) = 1.3 wt%

Rest is unconvertible materials like mud, sand etc were also found. Anaerobic bacterium formed on internal side of pipe revealed from sulfur reducing bacteria count experimentation. The soil and vegetation contact of line pipe further increases the corrosion rate to localize near damage portion of the component. It can be attributed to the presence of organic products, cellulose and microorganisms present in soil and vegetation.

Table 6. Sulphur reducing bacteria measured from water sample analysis.

| Number of water samples | Sulphur reducing bacteria per 100 ml |
|-------------------------|-------------------------------------|
| 1                       | 100>SRB>1000                       |
| 2                       | 100                                 |
| 3                       | 100                                 |
| 4                       | 1000                                |
| 5                       | 100                                 |

Figure 3. Sulphide reducing bacteria plotted for water sample obtained from fire water.
De-sulfovibrio desulfuricans forming sulphur reducing bacteria count above 100 counts per 100 ml in water sample is suspected to be the prime cause of failure. The desulfuricans anaerobic bacteria form on internal side of pipe, where sulphur tends to accelerates dis-solution of metal due to stagnant water deposits for long time and low fluid flow with or without mere oxygen under dark conditions leads to the growth of micro-organisms, which further promotes the micro-biological induced corrosion in line pipe steel under fire service.
The pour plate technique and corrosion analysis data for last one year also clearly reveals that the presence of sulphide reducing bacteria is root cause of failure.

6. Conclusion

The process parameters of fire water sample like pH, turbidity, orthophosphate, free residual chlorine, oxidation reduction potential and calcium hardness are under control and not influencing corrosion of steel. From weight loss measurements (gravimetric) corrosion rate of carbon steel is found to be very low. The microbiological corrosion was also revealed by composition evaluation of internal corrosion product scale contains 1.1% sulphur which is prime source of anodic reaction. Based upon various chemical and microbiological experimental results it could be concluded that fire water service pipeline failed due to sulphide reducing bacteria. Sulphur reducing bacteria is responsible for microbiological influenced corrosion of fire water service pipeline. The fire water reacts with steel under dark conditions without or with little oxygen promotes sulphur reducing bacterial growth leads microbiological corrosion.

7. Recommendations

Fresh or recycled water could be treated with chlorine, bromine or iodine compounds. Frequent water flushing could avoid water stagnation greatly and reduces micro-organism growth to prevent the failure. Fire water could be treated with ClO2 poly silicate treatment to prevent sewage or foreign particles carry over and further reduce sulphur content in water. Corrosion protection by cathodic protection of carbon steel pipe shall be provided after appropriate external coating. Internal epoxy or polypropylene coatings are used to prevent carbon steel pipe from micro biological corrosion. Soil and vegetation contact with water piping shall be avoided to reduce the corrosion rate near damaged localized area and further retards aerobic bacteria’s growth. The corrosion observed in the fire water pipelines can be controlled by the addition of biocides as well as suitable corrosion inhibitors.

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