AA22 – Corrosion Inhibitor Use in the Gland Seal Water System of a Greenfield Alumina Refinery

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Abstract

Gland Seal Water (GSW) systems in alumina refineries are essential for safe operation of gland sealed slurry pumps. Keeping a closed loop system with integrity intact is key to protecting both the pumps themselves, as well as the personnel operating in the vicinity of these pumps. Over the short years of operating the Al Taweelah alumina refinery, there have been observations of premature pinhole failures in the GSW pipework. To mitigate this problem, the potential effects of chemically treated water on the pipework was studied. The research team conducted laboratory tests to identify suitable chemical treatments before implementing a field trial to evaluate the efficacy of the selected corrosion inhibitor. This paper provides a comprehensive evaluation of the results obtained from both the lab tests and field trials, offering insights into the effectiveness of the chemically treated water in preventing GSW pipework failure. The findings have significant implications for improving the safety and efficiency of alumina refineries.

Keywords: Corrosion inhibitor, Corrosion rate, Gland seal water, Mild steel coupon.

1. Introduction

Steel is unstable in contact with oxygen and water and will undergo reactions that result in a variety of iron oxides, hydroxides and oxyhydroxides. The oxides are favoured at high pH and can impart some protection against further corrosion. Refineries and factories consist of a network of connected metal pipework that are easily susceptible to corrosion. To minimize and/ or prevent this from occurring, several techniques can be applied. These can be by installing galvanized pipework, clamping or replacing parts of failed pipework, by adding chemical(s) in the water (corrosion inhibitors), amongst others.

The objective of this study is to demonstrate the efficacy of chemically treated water, which will form part of the evaluation of the treatment selection on the GSW pipework integrity in the near future.

2. Rusting and Mechanism of the Selected Chemical

Rusting is a redox reaction that occurs when iron comes into contact with air and/or water. Iron is oxidized to Fe^{2+} and Fe^{3+} ions, with the oxygen undergoing reduction in the presence of water to form hydroxyl ions, as follows:

$$O_{2(g)} + 2H_2O + 4e^- = 4OH^-_{(aq)} \tag{1}$$

$$Fe_{(s)} = Fe^{2+}_{(aq)} + 2e^- \tag{2}$$

The ferrous ion is unstable in the presence of oxygen and undergoes further oxidation:

$$Fe^{2+} = Fe^{3+} + e^- \tag{3}$$

The ferric ions react with hydroxyl ions to form a loose precipitate of ferric hydroxide, which then undergoes dehydration reactions to produce oxyhydroxides and oxides:

$$Fe^{3+}_{(aq)} + 3OH^-_{(aq)} = Fe(OH)_{3(s)} \tag{4}$$

$$Fe(OH)_{3(s)} = FeO(OH)_{(s)} + H_2O \tag{5}$$

$$2FeO(OH)_{(s)} = Fe_2O_{3(s)}.+ H_2O \tag{6}$$

In an alumina refinery, the oxide layer is quite compact and acts as a partial passive layer (except at very high free caustic concentrations). However, this passivity can be lost in the presence of chloride ions, leading to pitting corrosion. In addition, crevice corrosion at joints and seams, and galvanic corrosion through poor material selection can sometimes result in early failure. The selected chemical works both as an anodic inhibitor (using orthophosphate to form a passive film) and a cathodic inhibitor using zinc.

3. Experiments

3.1 Laboratory Experiments

For the laboratory experiments, an NCM100 Corrosion Monitor 400 - NCM100.88 was used. A corrosion probe attached to this device is inserted in the water samples for measurement and recording of corrosion rates. The tested water samples were taken from the main distribution tank which feeds the GSW (gland seal water) tanks across the refinery. Corrosion rates were measured over a period of a few days at room temperature, using 500 mL water samples in 1 L plastic beakers with a magnetic stirrer, where the chemical was added using 50 mL syringes. This was done on untreated and chemically treated water samples. Different corrosion inhibitor products with varying dosages were tested to select a suitable chemical to be trialed in the field.

3.2 Field Experiments

The duration of the field trial was 5 months, commencing with 150 ppm dose rate based on the laboratory outcome. This had to be lowered after one day as this caused blockages in the discharge pump strainer affecting gland seal water flowrates to the slurry pumps.

The main distribution tank (Process Water tank) feeds the GSW systems and other applications across the refinery. This water is a mixture of generated hot process condensate from the digester units and imported water (average ratio 25:75). To measure the corrosion rates of the untreated water, mild steel coupons were installed on the discharge line of the Process Water tank via a PVC rack on a recirculation line.

The field test of the chemical addition was in the Precipitation facility GSW tank. The chemical was pumped by a solenoid-driven metering pump via a 25.4 mm plastic tube from an Intermediate Bulk Container (IBC) into the top of the GSW tank, near the inlet of the water feedline for proper mixing. The treated water was then pumped off by a GSW pump to the slurry pumps. A 38 mm hose was installed to recirculate the treated water from a drain valve at the discharge of the GSW pump, back to the GSW tank, to allow online corrosion and mild steel coupon measurements via a PVC rack. The NCM device was attached to the corrosion probe for data storage. Figures 1–3 represent a simplified overview of the field setup.

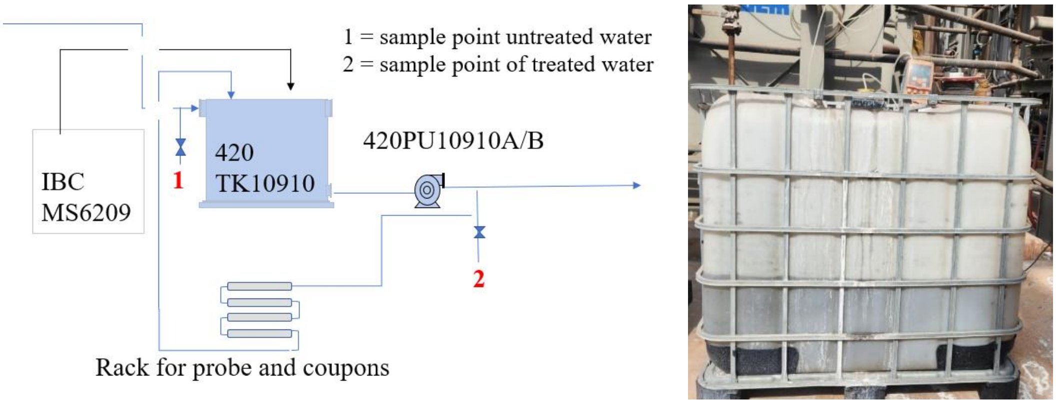


Figure 1. Left: overview of field setup with IBC, Right: IBC with chemical feed pump.

Figure 2. Left: field setup, Right: PVC rack for probe and coupon.

Figure 3. Left: coupon sample location on rack, Right: PVC rack with NCM monitor attached to corrosion probe.

The chemical was diluted to 10 % v/v and the dose rate was 2 L/h, equal to 20–25 ppm for 5 months. The cleaning frequency of the corrosion probe was every 2 weeks to avoid drifting of the readings.

During the field trial, the treated and untreated water (collected in plastic sample bottles of 250 mL) were analyzed on a weekly basis by Al Taweelah alumina refinery and a third-party laboratory. For validation purposes on the results of the external laboratory, Al Taweelah alumina refinery laboratory analyzed random samples using the same analyses method. Field samples were collected at the same time and analyzed by both Al Taweelah alumina refinery and the third-party laboratory.

4. Results and Discussion

In general, the maximum allowable corrosion rate is 0.127 mm/y and is ideally less than 0.076 mm/y. To monitor the performance, different measurement methods were used, and dose rates adjusted where possible and if required. These measurements were done by the online corrosion probe, weekly water analyses, two monthly calculated corrosion rates by third party and by quarterly mild steel coupons by third-party.

4.1 Laboratory Experiment Results for Product Selection

The laboratory tests were measured by using the corrosion probe with varying chemical dose rates. The results are shown in the Figures 4–7 below.

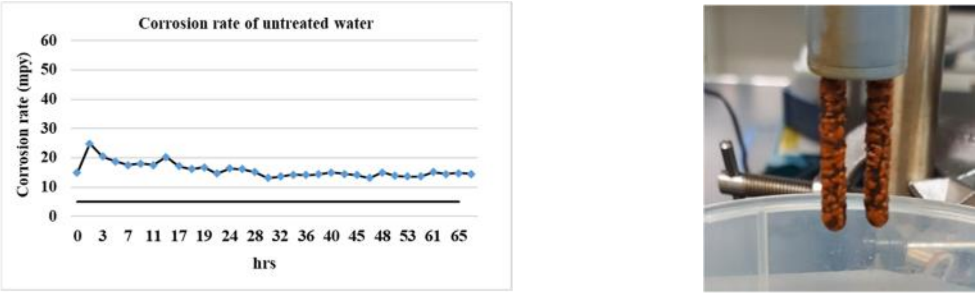


Figure 4. Untreated water over time interval.
Left: corrosion rate, Right: probe with deposit.

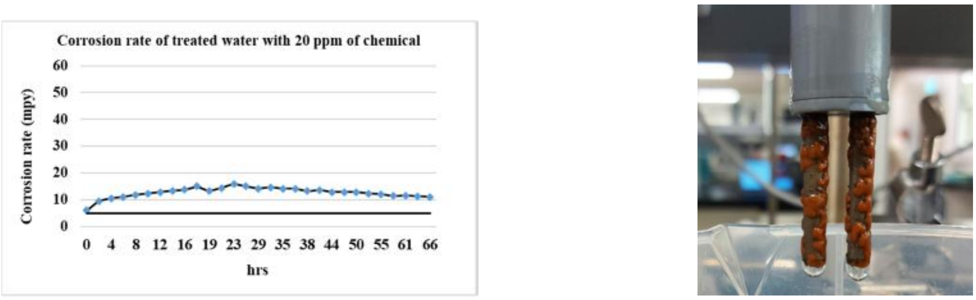


Figure 5. Treated water with chemical dose of 20 ppm over time interval.
Left: corrosion rate, Right: probe with deposit.

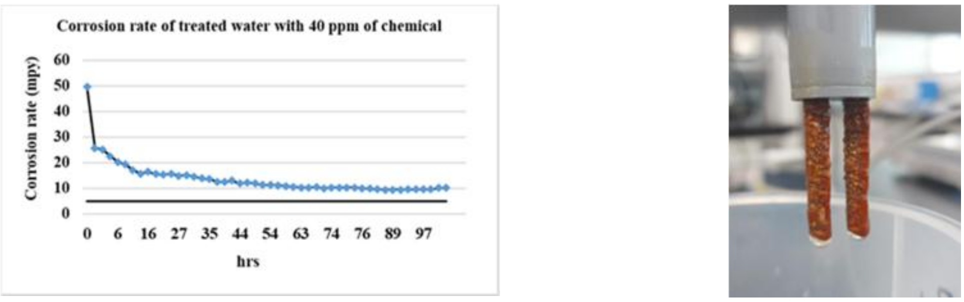


Figure 6. Treated water with chemical dose of 40 ppm over time interval. Left: corrosion rate, Right: probe with deposit.

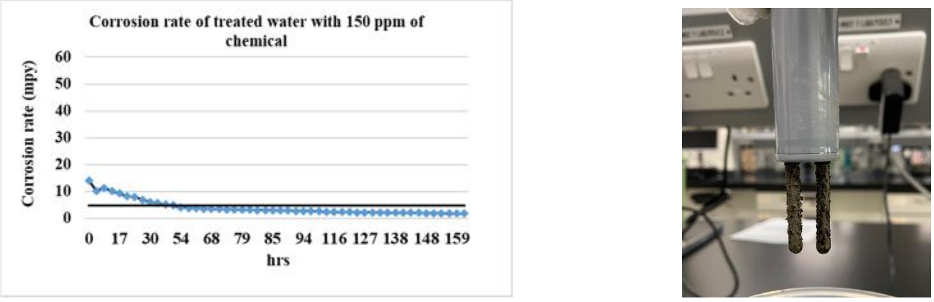


Figure 7. Treated water with chemical dose of 150 ppm over time interval. Left: corrosion rate, Right: probe with deposit.

Figure 8 and table 1 below show an estimate of the results which are derived from the laboratory tests and is expressed as corrosion rate reduction.

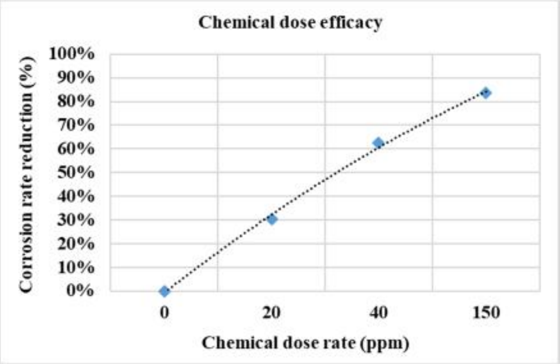


Figure 8. Corrosion rate reduction with different dose rate.

Table 1. Corrosion rates with different dose rates with the same test product.

Sample	Dose rate (ppm)	Corrosion rate (mm/y)-start	Corrosion rate (mm/y)-end	Reduction in corrosion rate (%)	Test duration (days)
Process water untreated	0	0.402	0.402	0	3
Process water treated	20	0.404	0.282	30	3
Process water treated	40	0.653	0.244	63	4
Process water treated	150	0.290	0.058	84	6

4.2 Metallurgical Analysis

A piece of a failed gland seal water pipe was sent to a third-party laboratory for failure analysis. It was reported that across the internal surface of the pipe, hollow lumps of localized corrosion products and deposits (so called as tubercles) were observed, as presented in Figure 9; this seemed to be similar to the formed deposit on the surface of the probe during the laboratory experiments (Figures 4–6).

One study and analyses of V.A. Chukhin and A.P. Andrianov [1] states:

“Several possible ways for the nucleation and growth of tubercles are considered: local accumulation of corrosion products and the formation of a hemispherical membrane when the solubility limit of iron oxides is exceeded, the effect of redox processes on corrosion products under oxygen deficiency, and the participation of a template formed by hydrogen bubbles in the formation of tubular structures that subsequently form tubercles.”

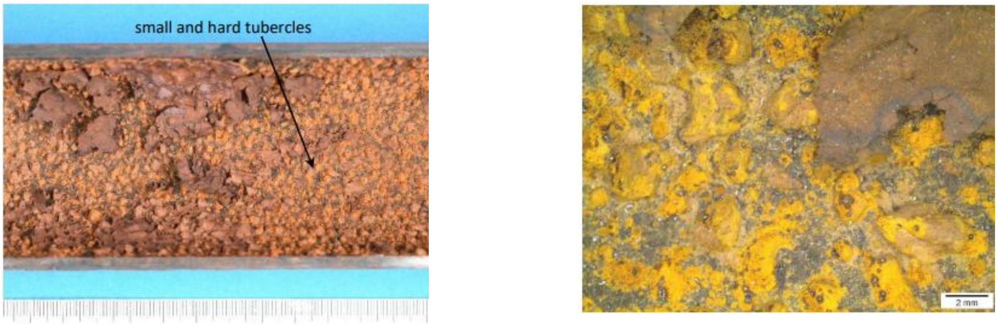
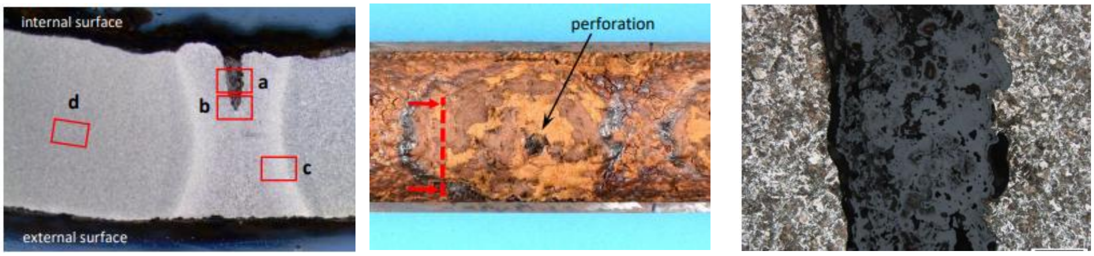


Figure 9. General view of internal surface of pipe.
Left: General view, Right: Close- up view

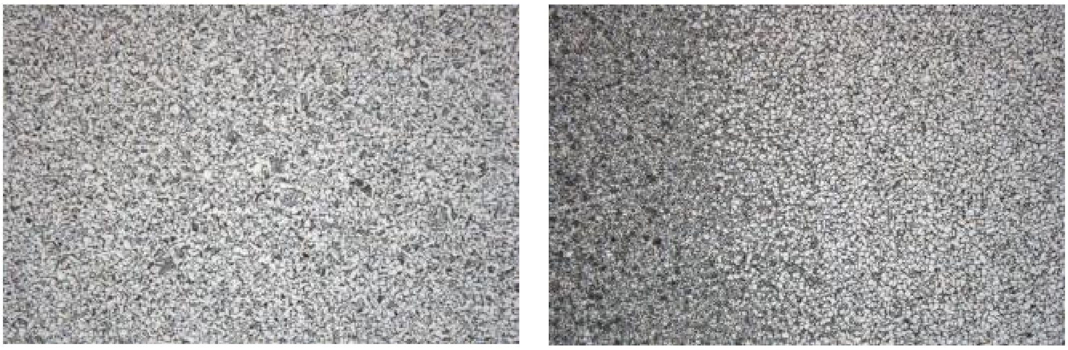
It was also concluded based on the pipework sample analysis, that the failures were found around the welding joints, as shown in Figure 10. Comparing the microstructures of the weld heat affected zone and the weld to the base metal, it can be observed that these differed, caused by a metallurgical change in the carbon steel, as shown in Figure 11.



b)

a) c)

Figure 10. Pipe section. Stereoscope of weld seam (a), Location where metallography was conducted (b), At middle perforation (boxed area "a"), 200x magnification (c).



b)

a)

Figure 11. Microstructure of gland seal water pipe. Base metal (a), Across heat affected zone (boxed area "c"), 200x magnification (b)

Jannifar [2] gave a review of the effect of weld joints:

"Welding is the process of metal attachment by dilution through heating. Due to the heat of the metal around the weld will undergo thermal cycles that cause metallurgical changes in microstructure, which will affect corrosion rate and the mechanical properties such as hardness. Weld joints are one of the critical parts of a structure. The weld joints that get excessive friction will be worn fast and corrosion rate higher than the base metal."

4.3 Water Quality and Analyses

The product functions with phosphate as anodic inhibitor and zinc as cathodic inhibitor, the treated water was therefore measured and monitored on these elements and are presented in Figure 12 and 13. Phosphate level increased from average 5 to average 14 ppm with recommended limits between 20–30 ppm and Zinc level increased from 0 to average 3 ppm with recommended limits between 2–5 ppm.

Impurities in the water samples were measured using the Perkin Elmer Optima 8300 Inductively Coupled Plasma Optical Emission Spectrometer (ICP- OES) by ATA laboratory. The third-party laboratory used the ascorbic method and zincon to analyze resp. the phosphate and zinc levels in the water samples.

Untreated and treated water were also analyzed on PH, TSS (total suspended solids), Conductivity, Fe_2O_3, SiO_2, CaO, P_2O_4, ZnO, calcium, hardness, and alkalinity to determine the Langelier Saturation Index. Alkalinity and hardness were measured by manual titration using a phenolphthalein and a bromcresol green- methyl indicator.

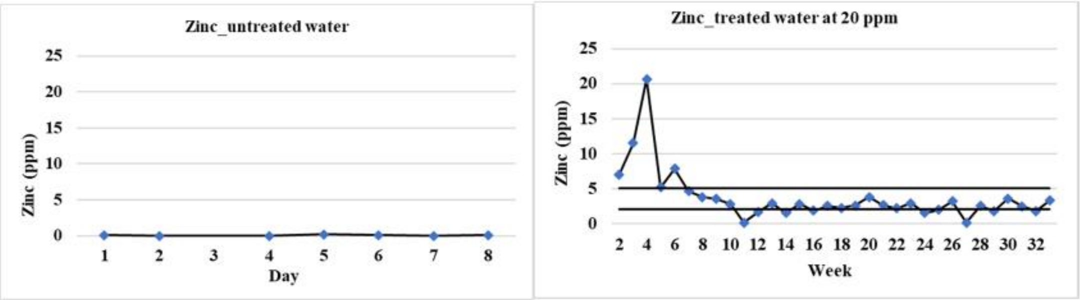


Figure 12. Zinc levels. Left: untreated water, Right: treated water.

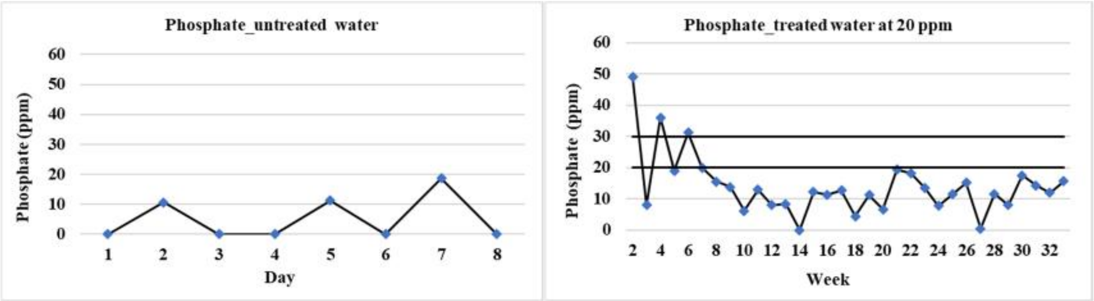


Figure 13. Phosphate levels. Left: untreated water, Right: treated water

4.3.1 Langelier Saturation Index (LSI)

Figure 14 shows the Langelier Saturation Index (LSI) which was calculated to indicate potential scale formation and/ or corrosivity. The LSI indicates the saturation of water with calcium carbonate which is naturally present in water. The other required analyzed indicators to calculate the LSI were calcium hardness, total alkalinity, total dissolved solids (TDS), pH, and temperature (Figures 15 and 16) show whereby:

The calcium hardness indicates the amount of calcium ions in the water, the total alkalinity measures the water ability to neutralize acids, the total dissolved solids (TDS) are solids which are not able to be filtered.

According to the Langelier Saturation Index, the ideal range should be between -0.5 and 0.5 for resp. slight corrosivity and scale formation. The field trial results appear to be in the positive range, indicating non- corrosivity and potential scale formation but still not serious.

Looking at the factors for the LSI calculation, the calcium hardness showed an increase without minor changes in the water quality. This increase can be discarded as this was the cause of an incorrect analysis' method. An increase in the total suspended solids was also measured but was also visible in the water sample and thus not related to an analytic error. Both the calcium hardness and total suspended solids returned to normal ranges.

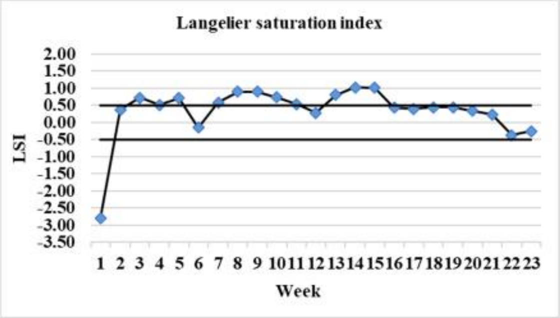


Figure 14. Calculated LSI of treated water.

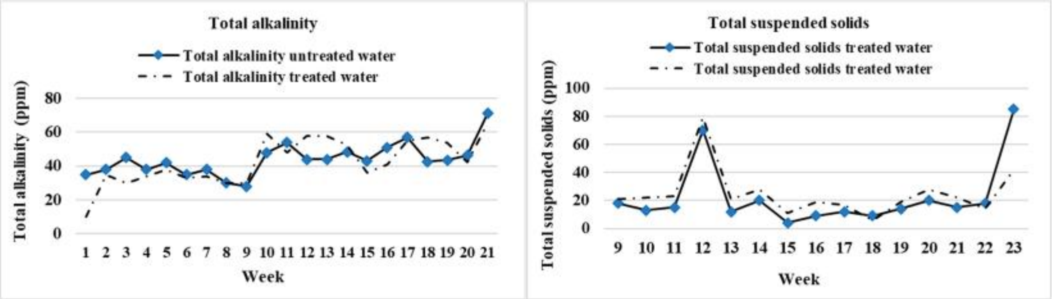


Figure 15. Left: Total alkalinity in untreated and treated water, Right: total suspended solids in untreated and treated water.

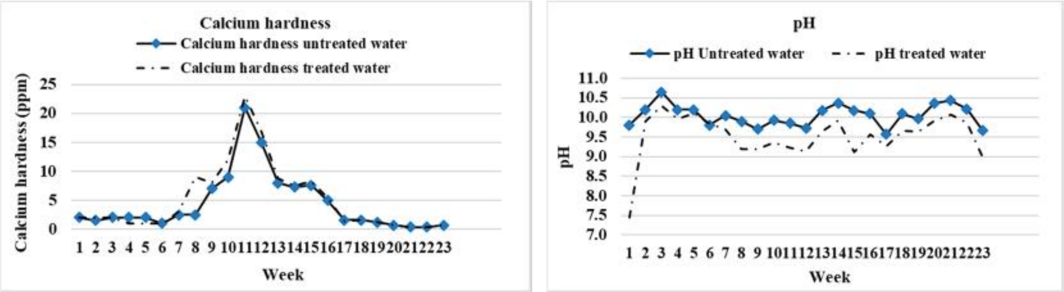


Figure 16. Left: Calcium hardness in untreated and treated water, Right: pH in untreated and treated water.

4.4 Corrosion Probe

The NCM100 Corrosion Monitor 400 - NCM100.88 with the corrosion probe failed prior the end of the trial and its stored data could not be extracted. Corrosion rates were measured between 0.038–0.102 mm/y as shown in Figure 17.

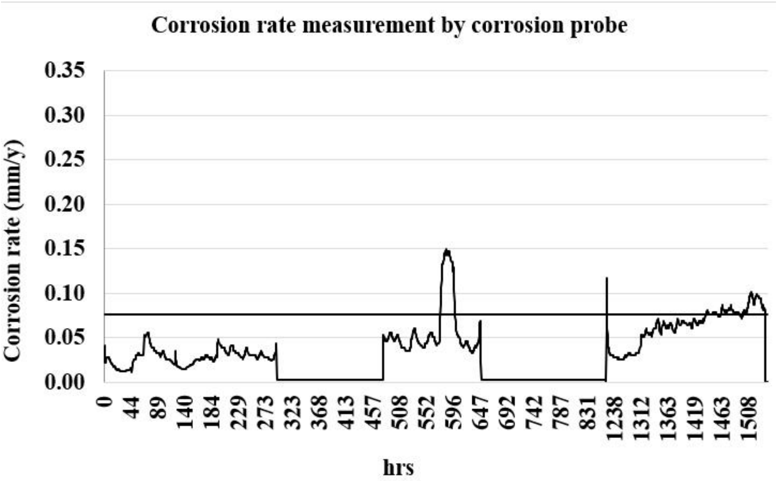


Figure 17. Corrosion rate during field trial.

4.5 Calculated Corrosion Rate

Table 2 shows a summary of the modelled calculations were done by using the water analyses to predict corrosion rates; the model which was used was from a third party.

Table 2. Calculated corrosion rates during the field trial by third- party.

Date		Untreated	Treated
November 2022	Corrosion rate (mm/y)	Over Limit (> 0.508)	0.122
January 2023	Corrosion rate (mm/y)	Over Limit (> 0.508)	0.127

4.6 Mild Steel Coupon

The initial mild steel coupon which was inserted in the allocated rack could not be used as it was not a representative measurement due to intermittent (non-continuous) water flow. An additional coupon was installed in the tank in case the water flow would be disrupted again.

The mild steel coupons were analyzed by third- party laboratories on weight loss. Table 3 gives an overview of the measured corrosion rates with the exposure duration, while Figure 18 presents the related physical coupons.

Table 3. Mild steel coupon corrosion rate.

Sample	Corrosion rate (mm/y)	Period of exposure	Location installed coupon
Untreated water	0.049	7 Mar. 2022- 16 Sep. 2022 (154 days)	Main source tank in the discharge line via rack
Treated water	0.021	22 Dec. 2022- 14 Mar. 2023 (82 days)	GSW tank in the discharge line via rack
	0.005	6 Jan. 2023- 14 Mar. 2023 (61 days)	GSW Tank

a) b) c)

Figure 18. Coupons for untreated water (a), treated water (b) and (c).

Of all the different measurements methods on the chemically treated water, the corrosion rates happen to be in different ranges after comparison. The corrosion probe measuring average 0.063 mm/y, by calculations using the average water quality resulting in 0.0127 mm/y and using physical mild steel coupons 0.021 mm/y and 0.005 mm/y. Both the corrosion probe and modelled results are higher than the physical mild steel coupon method. The calculated results showed higher numbers as the model predicts the worst-case scenarios.

Using the mild steel coupon as measurement method is widely accepted in the water industry and reflects a better representation of the actual corrosion rate rather than the other methods since it has been exposed under continuously changing and variable field conditions (i.e., change in water quality such as pH, conductivity, temperature, TSS, mixture of different water quality feeding the source tank, etc.). This measurement method is neither sensitive to drifting of instrumentation or failures (corrosion probe) thus minimizing the errors in measurements.

Another observation is on the different results of the mild steel coupons in the treated water at the two different locations. The corrosion rate from the coupon, installed in the tank reported much lower (0.005 vs 0.021 mm/y). The difference might be in the sample location where the water flow conditions are not similar [3].

4.7 Conclusion

Based on the laboratory result and by using the corrosion probe, it was demonstrated that chemical injection shows a reduction in corrosion rates varying from 30 % to 84 % with increased dose rates. By interpolating this laboratory data and comparing these to actual field results, the corrosion rate reduction in the field was higher by 19 % at the same dose rate of 25 ppm.

Ideally, the corrosion rate limit is set to be less than 0.076 mm/y and a maximum limit of 0.127 mm/y. By using the mild steel coupon results from the source of the GSW system during the field trial, this showed uniform thinning (general corrosion) with a measured corrosion rate of 0.048 mm/y. This is less than 0.076 mm/y and can therefore be concluded that chemical injection is not required. However, referring to the metallurgical analysis report, it was clear that the main cause of failure was pitting corrosion due to welding-induced defects in the metal’s crystal structure, rather than generalized surface corrosion. This source of failure could be reduced by suitably stress-relieving the welds; however, the use of a passivating corrosion inhibitor is also helpful in this situation. Using a corrosion inhibitor at a dose rate of minimum 25–30 ppm should be sufficient, which comes at a relatively low cost compared to other techniques such as galvanized pipework or clamping. It is also recommended to continue monitoring the water streams by using mild steel coupons to gain more data points since the duration of this process happens over longer terms.

However, it should be noted that the chemical cannot be added in the main distribution tank since this water is also used for other applications throughout the refinery which might impact the process negatively.

5. References

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