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Full Length Research Paper

Application of chemical injection on cooling treatment technology control of corrosion and fouling in petrochemical plant: Case study of Indorama Plc, Akpajo-Eleme

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Corrosion and fouling has been a major menace to the operation, integrity and life expectancy of process equipment in the production line of refinery and petrochemical equipment. This research focuses on effective cooling water treatment technology by inhibitive and bio-remediative chemical injection to control fouling and minimizes corrosion in process equipment such as boiler, heat exchangers and heaters which form the livewire of a petrochemical plant. The research has been streamlined to consider Indorama Plc, formerly Eleme Petrochemical Plant network as a case study. Models for corrosion rate prediction and treatment level recommendation adopted uses a combination of laboratory, field and experiential data. The models provide tools for evaluating a cooling system under varying conditions to determine the impact of operating parameter changes (for example, acid feed, concentration ratio, pH) upon water corrosivity and corrosion inhibitor requirements. The study reviews the effectiveness and suitability of the existing chemical treatment program in place and measures it with performance indicators such as models, theories and empirical values such as Langelier saturation index (LSI), Ryznar stability index (RSI) to predict the tendency of corrossivity scaling of water, especially cooling water. Relevant data from daily analysis, routine checks, inspection and monitoring over a period of 1 year form the basis of the presented result and deductions. Corrosion coupons and relevant test instrument were employed for the research. Result obtained shows a good inhibitive treatment and consistent bio-activity control from effective chemical dosage given corrosion rate as low as 2 mpy on the average. The cycle of concentration that the cooling tower maintained had consistently been between 4 and 5. Calculated value of LSI and RSI on the average agrees with literature value for good treatment that enhances better performance. LSI and RSI values was obtained respectively to be, -0.1 to +0.1, and 0.4 giving credence to low corrosive and scaling tendencies that breeds fouling.

Key words: Cooling, treatment, control, corrosion, fouling.

INTRODUCTION

The petrochemical plant unit carrying a cooling agent may suffer from internal corrosion, if there is water present in the system. In the cooling treatment unit the corrosivity will vary independence of factors such as the temperature, zinc concentration, ortho-phosphate concentration, calcium hardness ($CaCO_3$), pH, turbidity, total iron, silica, cycles of concentration (based on silica) and Langeller saturation index, aerobic bacteria counts, bioscan counts, flow conditions, use of inhibiting chemicals etc. The corrosion allowance is based on assumption of the corrosivity during the production period. In order to maintain integrity, many cooling treatment plants are subject to intelligent cathodic protection/pig inspection at certain time intervals.

Corrosion monitoring at fixed locations is sometimes used to verify the efficiency of inhibiting chemicals (Singley, 1981; Pisigan and Singley, 1984, 1985; Mc Neill and Edwards, 2002; Imran, 2003).

Corrosion may be defined as the destruction of a material by action of the surrounding environment. Material resistance to corrosion depends on many variables such as materials properties itself, environment characteristics and others.

Various scientists (Pisigan and Singley, 1987; Rossum and Merrill, 1983; Frigeribaum et al., 1988; Ferguson, 1992) have reported that controlling a cooling treatment plant unit from further corrosion by the application of chemical injection operation involves: identification of flow characteristic of cooling and inhibiting fluid, respectively, and determination of the concentration of the physico-chemical parameters of interest.

Research conducted by various groups revealed that when the water phase is dominated by the reservoir water (brine), there is normally no significant variation of the ion concentrations along the pipeline. In wet gas systems the situation is different; the water phase will be dominated by the water condensing from the gas as the temperature drops along the pipeline. This water has no salts dissolved, and the ions accumulating in the water phase have to come from the dissolution of gases (CO_2 and H_2S) and the corrosion process. Dissolution of CO_2 will cause formation of ions like bicarbonate (HCO_3). During corrosion, Fe^{2+} and HCO_3^- ion are released as a result of the electrochemical reaction. For wet gas systems, therefore, it is necessary to adjust the Fe^{2+} and HCO_3^- concentrations along the pipeline due to the corrosion process. This may have a significant impact on the pH profile along the pipeline (Rossum et al., 1990; NNC, 1992; NNPC, 1994; Davernport, 1997; Goody, 2008).

When the chemical is injected into the cooling treatment plant unit, it acts as an inhibitor in the process plant, hereby changing the chemical composition of the cooling water by reducing corrosion rate. The injection of chemical is useful in inhibiting the functional parameters that facilitate the rapid rate of corrosion of cooling treatment plant unit (Cullen, 2002; Flakeysar et al., 1997; Montgomery, 1985; Davis, 1993).

MATERIALS AND METHODS

Research Instrument

This comprises field test instruments and instruments used in the laboratory for analysis.

Field test instruments

This includes, chemical dosing tank network, dosing pumps, infra red, fluke thermometer, coupons, bio-film box, data monitoring panel and colourimeter DR/890.

Laboratory test instruments

This includes, reagents pillows, chemical reagent, conical flasks, beakers, burettes, pH meters, indicators, buffer solutions, refrigerator, oven, weighing machine, sample bottles/cans, spectrophotometer DR/2400, spectrophotometer DR/890 and sample cells.

Research method and procedures

Field tests

Basically this is categorized into daily routine tests, based on daily inspection and monitoring. On the other hand, special attention was given to observable changes and noticeable side effect as direct fallout from field operations and material handling.

Cooling tower operation data

This includes, system designation - unit 23, number of systems – 1 × 10 cell tower, system volume – 1100 m^3, total NEL + blow down – 100 m^3, Make up rate – 508 m^3/h, max. cycle of concentration (COC) – 6, Operating duration – 24 h/day/365 day/yr, recirculation rate total – 27,000 m^3/h, system evaporation rate – 408 m^3/h, supply temperature – 32°C and return temperature – 44°C. The above data forms the basis of the operation of the cooling tower process.

Cooling tower treatment

Corrosion is an electrochemical process by which metal returns to its natural state. For example mild steel will oxidise to form $Fe(OH)_2$. On further exposure to the environment it is further attacked by water and oxygen forming iron (III) oxide, Fe^{3+} which precipitate out of the water as reddish brown colour that causes rust, deterioration, loss of metal properties, fouling of water, deposition and eventual corrosion. Corrosion effect, as a result of inadequate treatment manifest on a short or long term on galvanic metals due to factors such as: corrosive environment, pitting causing perforation on metals, localization, intergranulation along grain boundaries of metal or alloy, erosion, crevice formation, cavitations and stress corrosion cracking accelerated by internal or external stress or a form of impingement attack from turbulent flow regime around bends or inlet into a unit.

Deposition: The constituent of deposits formed on the internal heat surface of a process unit for example, boiler, heat exchanger, as a result of inefficient chemical treatment programme generally comes from water. More of the constituent belongs to one or more of the following groups: iron, oxides, silica, silicates, metallic copper, carbonate, phosphates, calcium and magnesium salts, etc. Poor flow regime- low velocities, can also allow carryover and build up of these substances by settling to form scales, under deposit corrosion, causing clogging of tubes in heat exchangers thus reducing the rate of heat transfer which if not controlled could lead to possible failure of the equipment.

Cooling water corrosion treatment chemicals

GE treatment facilities control corrosion and deposition by a continuous dose of 70 to 90 L of Dianodic DN2108 daily and 10 to 20 L of Flogard MS6208 daily. These are patented chemicals from GE Infrastructures – Water and Process Technologies. The Dianodic DN108 supplies the phosphate active treatment regime formation while the Flogard MS6208, provide the zinc phosphate active treatment regime formation. This was found adequate so the concentration of each chemical can be controlled separately**.** Dianodic DN2108 is a dispersant blend.

Cooling water micro-biological treatment

Cooling tower can provide an environment suitable for growth of bacteria, fungi, yeast, and algae. These microbes cause fouling, corrosion, formation of gases, wood attack and can protect one another from biocide attacks. Recently, of great concern is a bacterium namely *legionella pneumophila*, which causes 'Legionnaires disease' in human. The metabolic activity of these micro-organism can either directly or indirectly cause deterioration of metal by corrosion process. This activity can**:** cause a corrosion environment, create electrolytic concentration cells on metal surface, alter the resistance of surface film and can influence the rate of anodic or cathodic reaction, alter the environmental composition. Disinfection to arrest or reduce to the barest minimum the invasion and activities of these microbes is therefore imperative. Disinfection is a process of removing bacteria, algae, and other micro-organism from water either by one or a combination of the following method: chemical injection for example, chlorine gas, calcium hypochlorite (HTH), sodium hypochlorite etc, ozonation, ultraviolet light, boiling and microfilteration. A GE operation employs chemical injection method to combat the activities of microbes in cooling water treatment.

Micro-biological treatment chemical: GE controls the activities of primary biocides through a timely shot dose of oxidising and non-oxidising biocide chemicals.

Oxidising biocides: 135 kg calcium hypochlorite daily dose supplies the cooling system calcium, and needed 110 kg of Spectrus OX909 and liquid bromine dosed alternately on weekly basis. The above chemicals uses halogen release agent, to meet the microbiological treatment the system requires.

Non-oxidising biocides: 800 kg of Spectrus NX1101 is dosed fortnightly and 800 kg of spectrus NX1164 dosed alternately fortnightly. A secondary treatment employed the use of non-oxidising biocides dosed fortnightly in an alternate manner to cover the month thereby complementing the dose of oxidising biocide to combat the activities of microbes in the system. This is so done to avoid the micro-organism developing a resistance to a specific chemical dose. The chemical dosed has been found effective to destroy the cyst of the microbes, and washing them off the cell walls of the tower where they are entrapped in the strainer for scooping off the water system. Bio-Dispersant: 100 kg of spectrus BD1500 dosed once in the week on Saturday and another chemical dosed is spectrus BD1500, a bio-enhancer, surface active agent and bio-dispersant that provides a good interface for the effectiveness of calcium hypochlorite, spectrus OX909 (Liquid bromine) and enhances the effectiveness of other biocide treatment chemical dosed by keeping the suspension in the water until blow down is considered necessary.

Field test/Monitoring

Monitoring: This involves daily assessment of the client facility; the tower assembly, the cells (1 × 10), flow in the cells, cooling water outlook and quality. Also included in daily monitoring of GE treatment facilities; the panel assembly, taking of field readings/parameters on TDS, pH, corrator, wet bulb, tower supply and return temperature from control room. On daily basis, sampling is done from cooling water return line sampling point for laboratory analysis to ascertain if the major control parameters are within control limit established.

Field activity: On daily basis, we carry out residual free chlorine test to ascertain if there is sufficient disinfection/micro-biological treatment for the cooling process water. Treatment target before now had been between 0.3 to 0.6 mg/L, temperatures of the cells, that makes up the tower is taken respectively and reported on daily basis, approach temperature is also monitored for the cells with reference to the supply temperature.

Coupon installation and analysis

Coupon analysis was also undertaken by exposing prototype sample coupon of distinct material as available in the plant make up such as mild steel, admiralty brass and copper into the return line of the cooling water. The coupons which may be treated or untreated are a replica of process unit material as the heat exchangers, furnaces, boilers, column etc where cooling water passes. These coupons are exposed differently for 30 and 90 days respectively in the cooling water test rack. A corrater dipped in the water in one of the compartment measures the rate of corrosion while the sample coupons on removal are sent outside the country for analysis for onward result to the client. The outlook on removal depicts and reveals what is happening in the entire system with the same process unit material as available in the plant. Result of previous exposures shows values averaging 1 mpy/year.

Emergency operation

Outside the daily routine operation we are always at the beckon and call of our client to attend to emergency situation that may arise in the plant regarding our operation that requires our attention. Some of these in recent past include: sampling of opened exchangers, analysing sample and reporting observation, troubleshooting for source of leakages into cooling tower, rouble-shooting serious deviation of certain parameters from normal to arrest the situation and bring it under control for example, silica increase in furnaces or boiler feed water, need for passivation of a single exchanger and passivation from the cooling water source. The above are some of the major challenges encountered in the cooling water monitoring, few of which will be discussed in detail later.

Passivation

Passivation is a pre-treatment programme applied to the cooling water system in order to ensure all new and/or recently cleaned carbon steel surfaces receive the best possible protection from corrosion. Pre-treatment promotes the rapid formation of a uniform passive film that stifles the corrosion reaction. Once the film has been established, it can be maintained through continuous, low treatment levels to deter the accumulation of corrosion products. Pre-treatment of equipment in cooling water systems is recommended following initial installation, chemical cleaning, and prior to start-up after turnaround or inspection. Pre-treatment, followed by ongoing treatment programs, minimizes corrosion for improved heat transfer, longer service life, and reduced plant maintenance. It is expected that the treatment will be applied twice in the first year of operation as below: Application could be general and central from the cooling tower sump, with circulation done via the tower to the entire equipment network in the plant. It is necessary to drain the tower sump, clean the basin out and refill the system. The system will then be put in partial operation (that is, not all plant on line). It is proposed to carry out the Pre-clean and Passivation process after the tower is initially re-filled and the treatment will also be applied once any new heat exchangers are

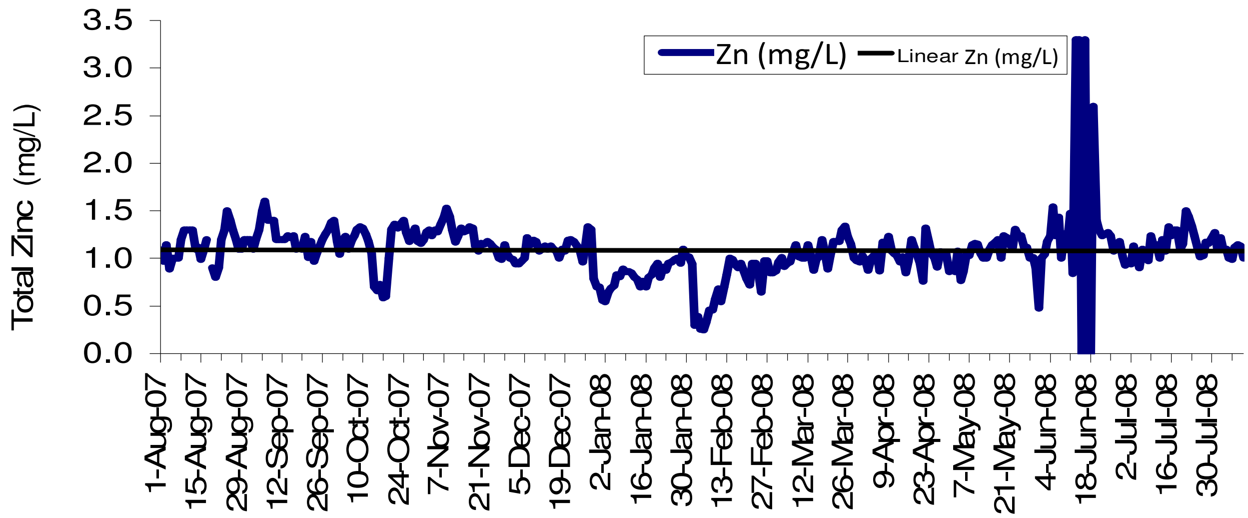

Figure 1. Zinc concentration versus time.

brought into service or when plant not previously pre-treated is brought online.

Treatment programme: The specific products recommended for the Pre-clean/Passivation treatment programme are: GE Betz Dianodic DN2300: a surfactant dispersant containing GE Betz HPS co-polymer, GE Betz Dianodic DN2200: a dispersant blend containing ortho-phosphate, poly phosphate, HEDP and TTA. In the last one year, the general passivation below is the passivation process undertaken- single unit passivation of exchanger 1-E-301A at Polyethylene with dianodic DN2108 in March '08 due to unavailability of DN2300 and DN2200. Recirculation period was 12 h, and general passivation from cooling water sump with Nalco Chemical equivalent of GE Betz chemical. Due to delay in clearing and delivery of GE Betz passivation the chemicals and single unit passivation of exchanger 1-E-301B at polyethylene with DN2300 in September 5th/6th 2008 circulated for 24 h.

Note: Necessary calculation was carried out with available data to ascertain the chemical requirement for the treatment and for general passivation blow-down is not meant to be effected until considered necessary. Test analysis was carried out and phosphate, pH, and Turbidity level were been monitored on daily basis until an acceptable level comfortable to cooling tower standard treatment range was obtained before blow-down was initiated and pre-cleaning is necessary before commencing full treatment for effective passivation.

Laboratory analysis of parameters

In cooling water treatment GE Water and Process Technologies analyses and monitors, consistently on daily basis, up to 14 parameters called 'analytes' to ensure each is in order with the range of design and operational data given to our client. This informs the proactive action taken whenever there is any deviation from normal in any of the parameter from the results of analysis. The analytes are zinc, filtered and unfiltered phosphate, calcium hardness, magnesium hardness, methyl alkalinity, total iron, turbidity, silica, bioscan count, aerobic bacteria count, and free residual chlorine. Also, we check the azole level in the cooling water system from the continuous dose of dianodic chemical when the need arises but not on daily basis. Tolytriazole is a blend constituent chemical in dianodic that function to provide protection for material unit made of copper alloy forming a protective film on the surface to inhibit corrosion. Each of these parameters has positive or negative effect on the treatment program as the case may be.

Routine operations

Chemical stock

Monitors in-house/ laboratory analysis, chemical reagent usage and depletion, reporting same for the purpose of order placement and replenishing, stocks of corrosion control and micro-biological treatment chemical is monitored and reported on daily and monthly basis and monthly report of chemical consumption and stock balance is sent to the client for record purpose and ordering procedure decision when the need arises.

RESULTS AND DISCUSSION

The results were presented in figures. Results include: monitoring and analyzing parameters from cooling water sample, monitoring of control parameters and performance of process equipments with special attention on boiler in olefins unit of the plant, and calculated values of models and performance indices used in predicting the efficiency of treatment program.

Cooling tower monitoring and analysis result

Daily laboratory analysis of cooling water sample and monitoring for an estimated period of 1 year as could be seen in the result of cooling water treatment monitoring of parameters between August, 2007 and July, 2008 for 1 year is shown in Figures 1 to 11 for different parameters.

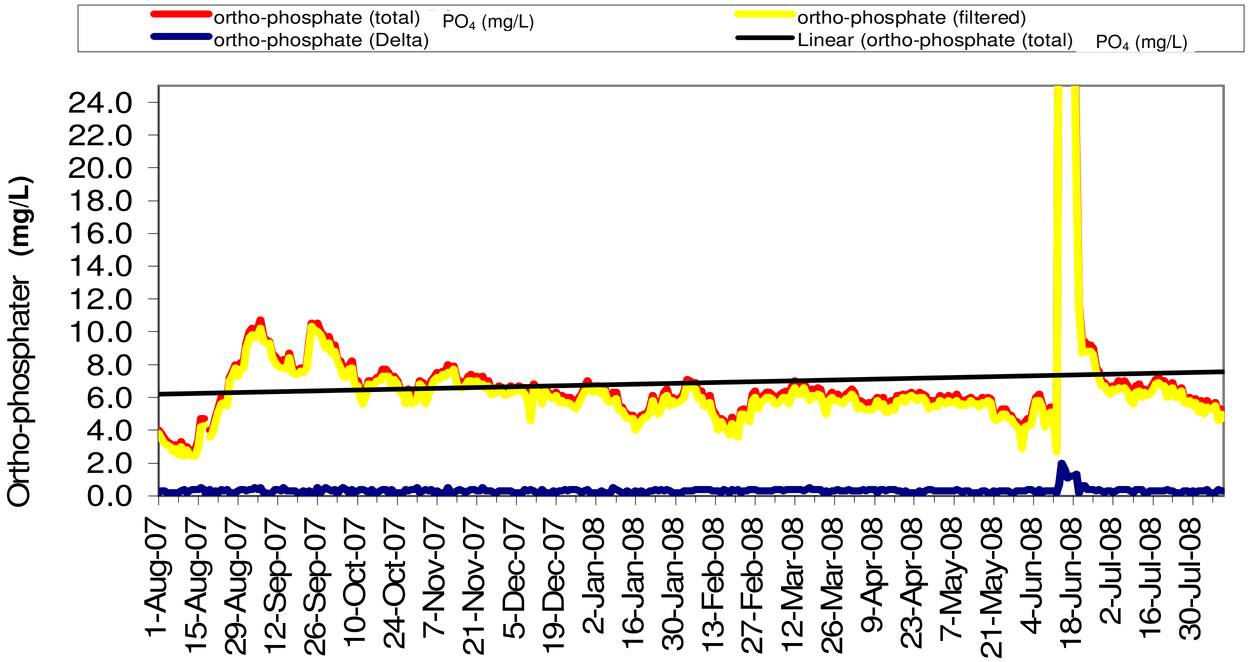

Figure 2. Ortho-phosphate concentration versus time for filtered component.

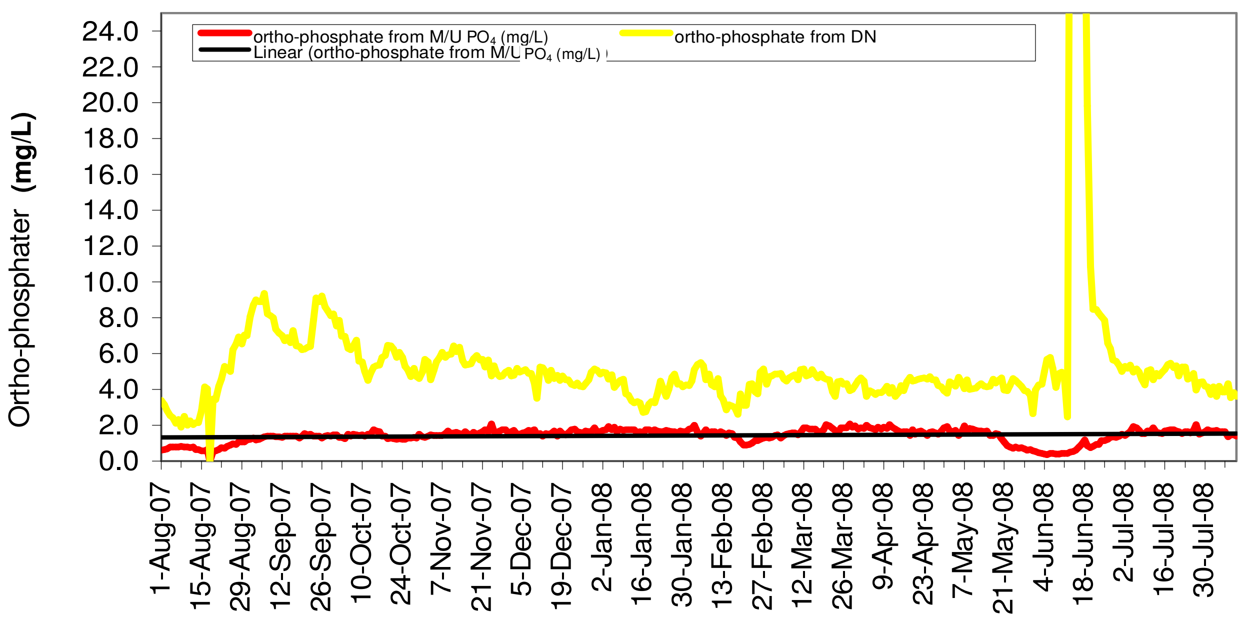

Figure 3. Ortho-phosphate concentration versus time for DN component.

The plot of zinc concentration versus time shows a great degree of compliance with standard treatment regime of 0.8 to 1.2 mg/L, zinc been a major harmful element to the environment, hence discharge must be minimal to the environment. Although certain deviation from standard value as high as >3.0 occurs and control were often regained on timely manner through effective treatment (Figure 1).

Orthophosphate concentration within the period was effectively managed within the specified control limit of 4 to 6 mg/L, however certain deviations occurs within June 2008 after which control was regained. Offset went as far

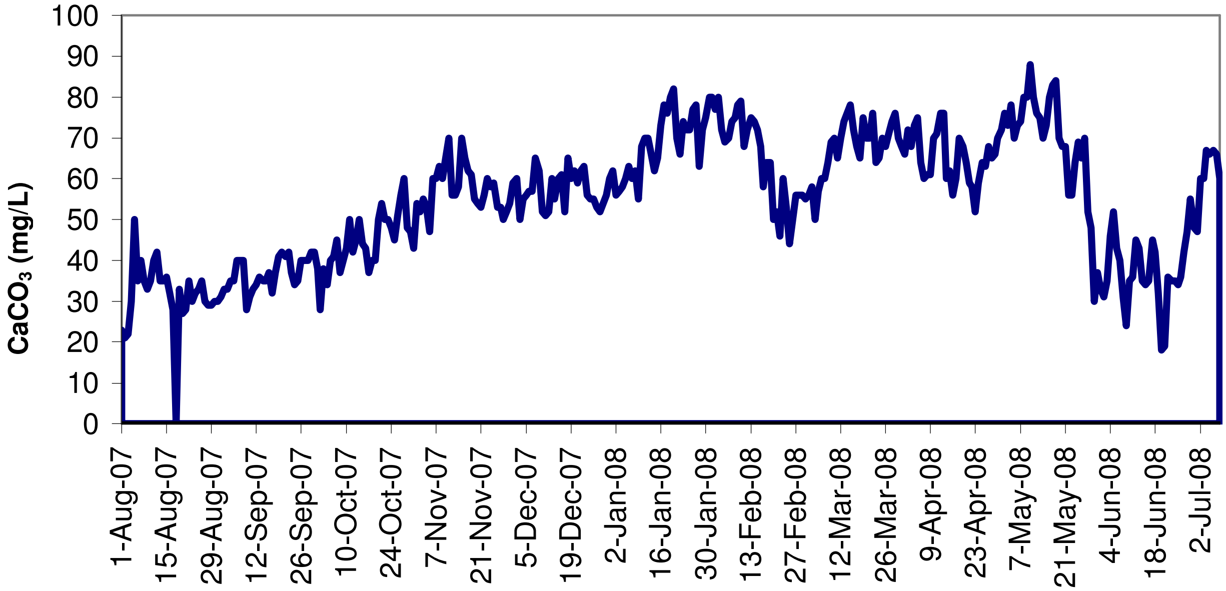

Figure 4. Calcium hardness $CaCO_3$ versus Time.

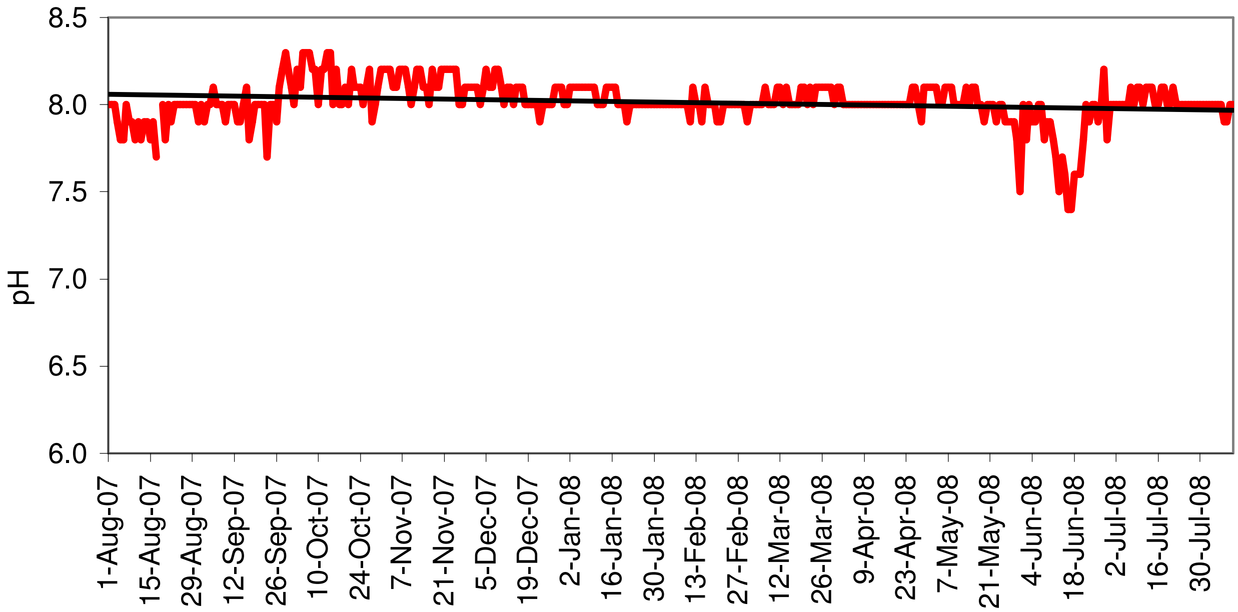

Figure 5. pH versus Time.

as >20 mg/L (Figure 2).

The Figure 3 illustrates the characteristics of the ortho-phosphate concentration upon the influence of time on the DN component as well as the linear ortho-phosphate concentration in the system.

Calcium hardness concentration was excellent during the period of treatment showing the effectiveness of calcium supplement from 135 kg of calcium hypochlorite daily dose, 6 days within the week. Control was kept with the treatment range specified as 40 to 100 mg/L (Figure 4).

The pH concentration plot against time shows alkaline behavior within the given control treatment of 8.0 to 8.5 mg/L, although on few occasion a departure to acidity scale was experienced which is not good for the system. At such period, neutralization is effected by dosing 4 to 5

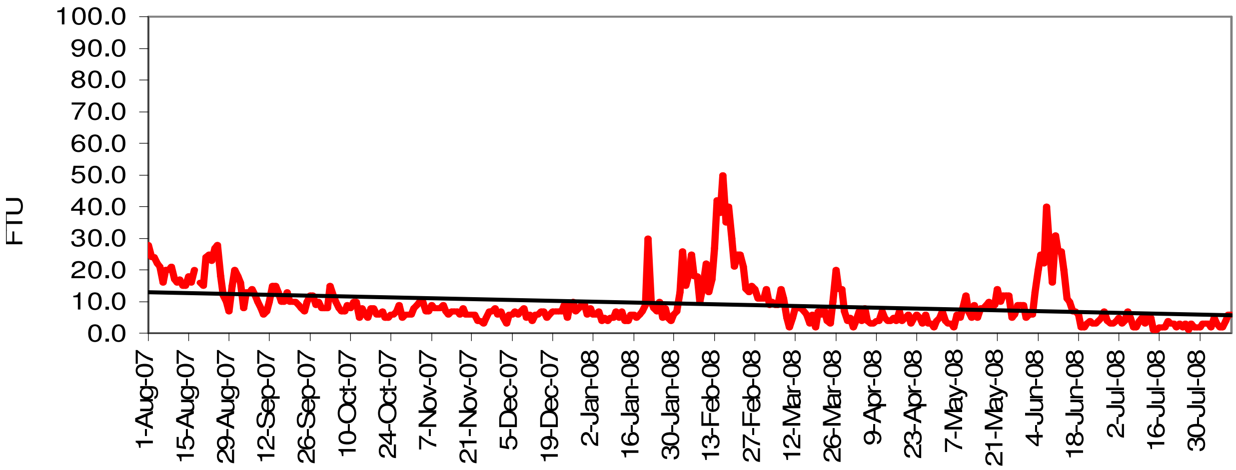

Figure 6. Turbidity versus time.

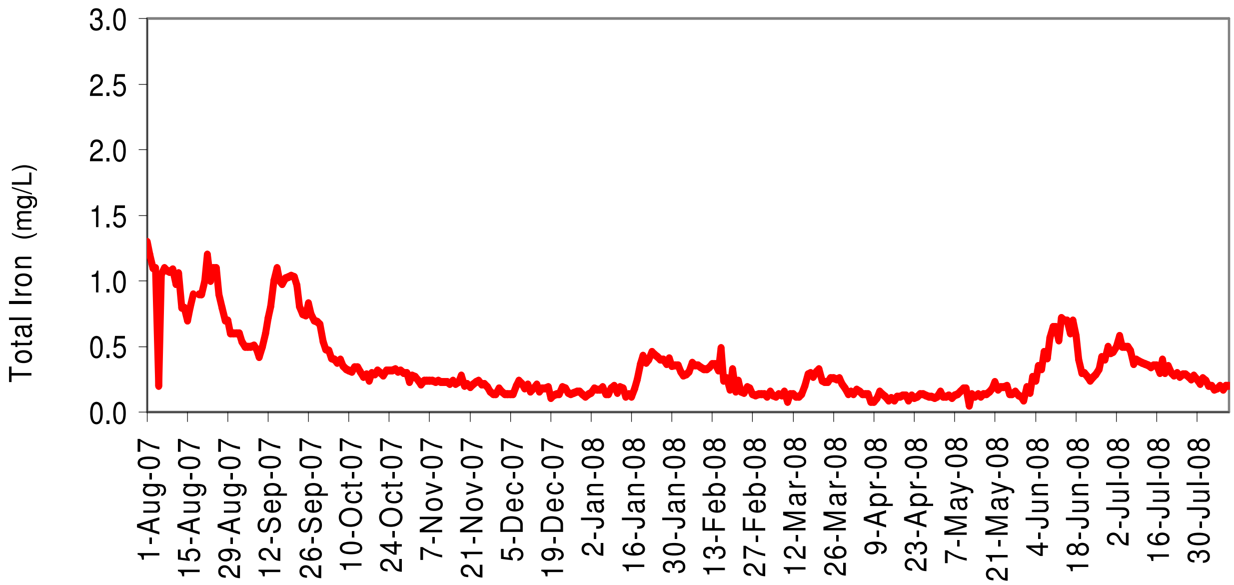

Figure 7. Total Iron versus time.

bags of sodium hydroxide (NaOH) to regain back the alkaline condition (Figure 5).

Turbidity of the water specified control treatment was given as 0 to 25 NTU (nephelometric turbidity units). Treatment result shows conformity to a great extent, also some deviations from standard were experienced within February, 2008 and June, 2008. Increased zinc, Fe and leakages into the system are possible causes of a corresponding increase in turbidity Figure 6.

Iron concentration over the period of treatment was excellently kept with the standard control limit given as 0 to 1.5 mg/L, hence not exposing the system to major corrosion (Figure 7).

Silica content in the treatment was effectively managed also within the control limit for recirculation cooling water of 0 to 150 mg/L. This is a major determinant for a good cycle of concentration (Figure 8).

Cycle of concentration over the period of treatment was majorly 4> COC>5, a value advised for good treatment. This is what informs the time lapse for blow-down and needed for replenishing of the system. The maximum operating COC for the tower is 6 (Figure 9). Langelier saturation index, a major indices for the prediction of corrosion tendency shows positive values <1.0 which shows good treatment with low corrosion tendency for the plant.

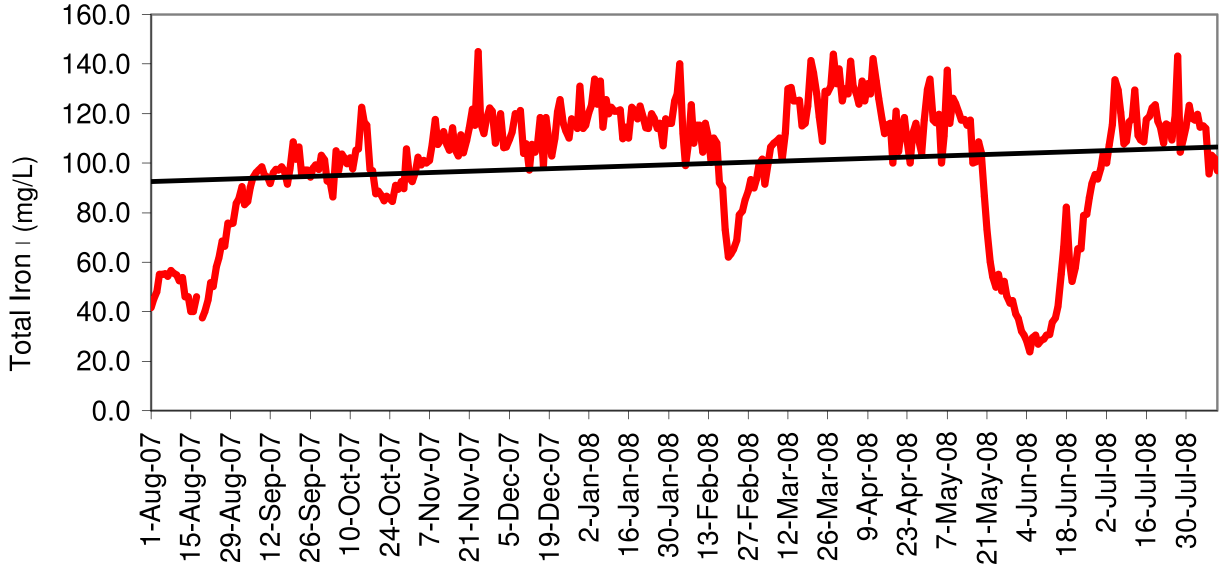

Figure 8. Plot of silica versus time.

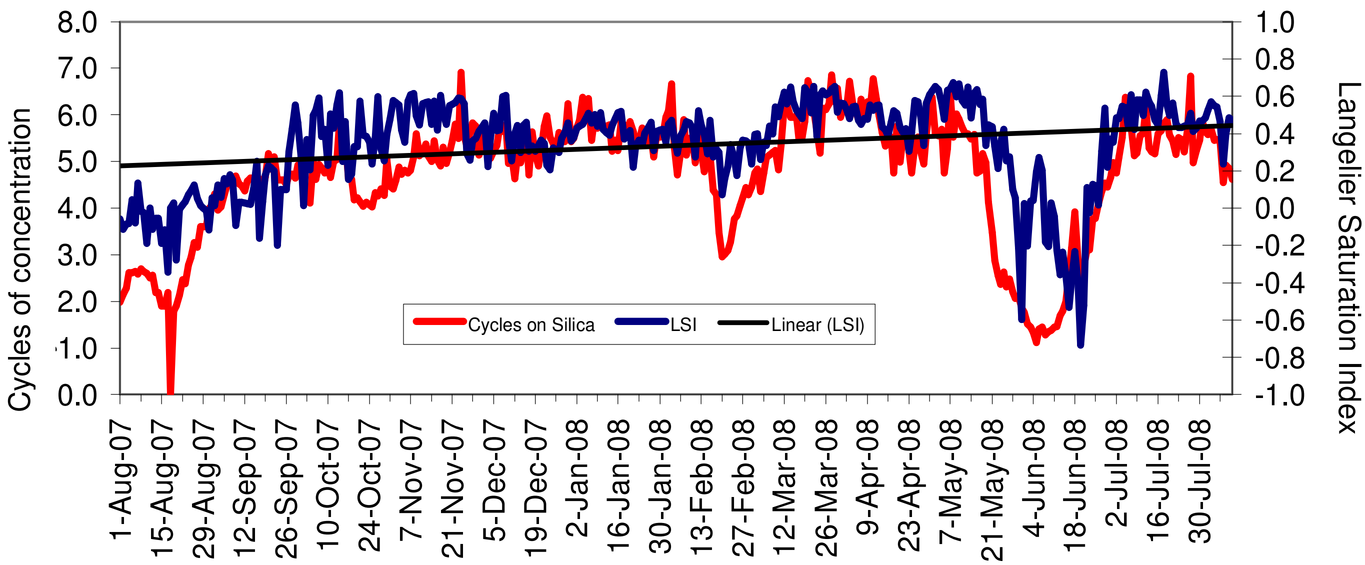

Figure 9. Cycles of concentration (based on silica) and Langelier saturation index versus time.

Aerobic bacteria count in the water from result shows low bacteria activity and invasion with values as low as 10<ABC<100 over the treatment period (Figure 10).

Bioscan Count shows the count of active and non-active biocide in the water which reveals a good treatment been kept with the specified treatment limit of 0 to 10,000 (Figure 11).

In all of the above, the major deviations experienced were attributed to process leaks, from existing plant units by backflow to the tower (for example, olefins, polyethylene, polypropylene), critical exchangers leaks, hydrocarbon and oil leaks from seal of equipment etc. Control is however regained by trouble shooting, isolation of area of disturbance, creating necessary by-passes and treatment with continuous dose of appropriate chemicals.

Boiler result from olefins unit monitoring

Daily laboratory analysis result of boiler drums and steam condensates boiler feed water (BFW) and Quench water while monitoring the operation of the equipment itself and other ancillary units for example, dosing pumps. Due to the boiler being a steam generating unit, emphasis will be

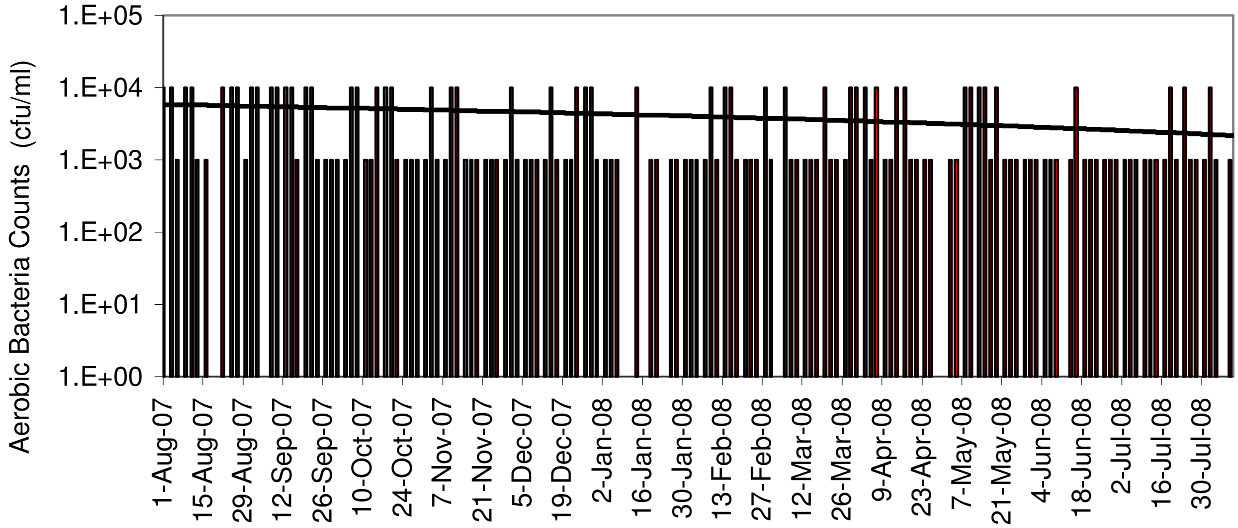

Figure 10. Aerobic bacteria counts versus time.

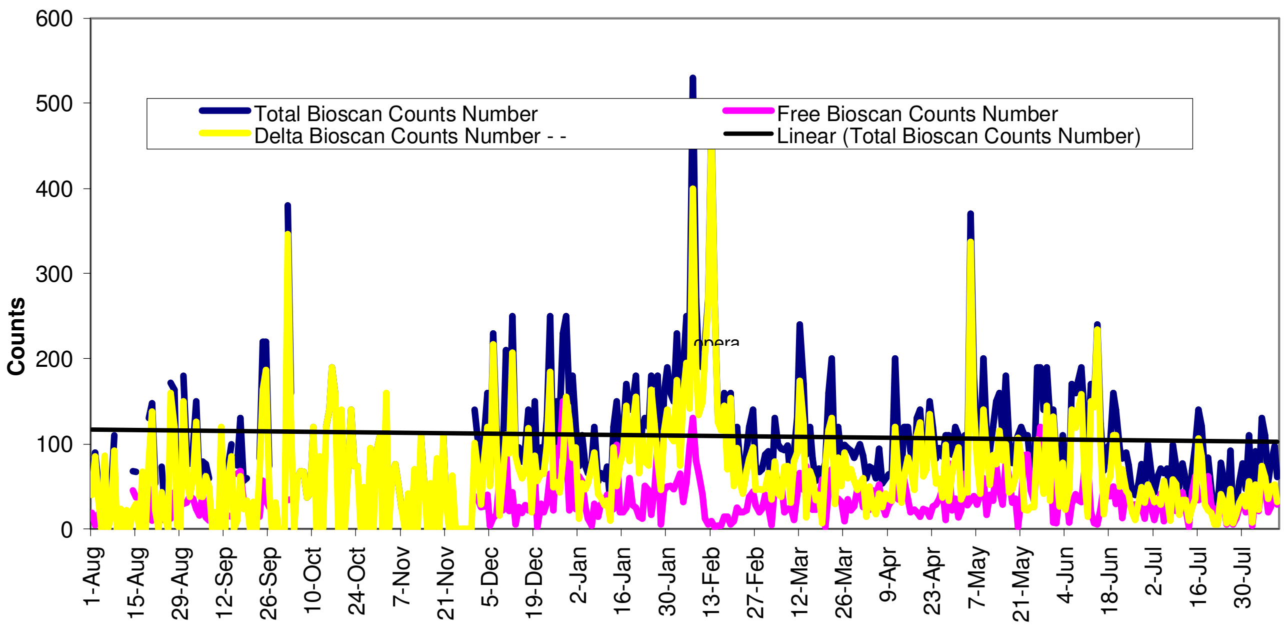

Figure 11. Bioscan counts versus time.

based majorly on boiler A steam. Boiler A pH within the period of monitoring and treatment conform to the treatment standard 8.0 to 8.5 (Figure 12).

Silica content in the boiler was kept as low as possible, standard control limit being 0.01 to 0.02 mg/L. Silica is not good for the boiler tubes and system; its carryover causes hotspot, reduced heat transfer surfaces, rupture, tube leakages and poor performance (Figure 13).

Ortho-phosphate level in the boiler was effectively managed within the control limit of 0 to 0.05 mg/L (Figure 14). The above result altogether shows a good treatment and handling of the boiler.

Exchanger's inspection, process unit passivation and general passivation from the cooling tower sump results are given in Tables 1 and 2.

Application of relevant model

This comprises result from: deduction and calculation of

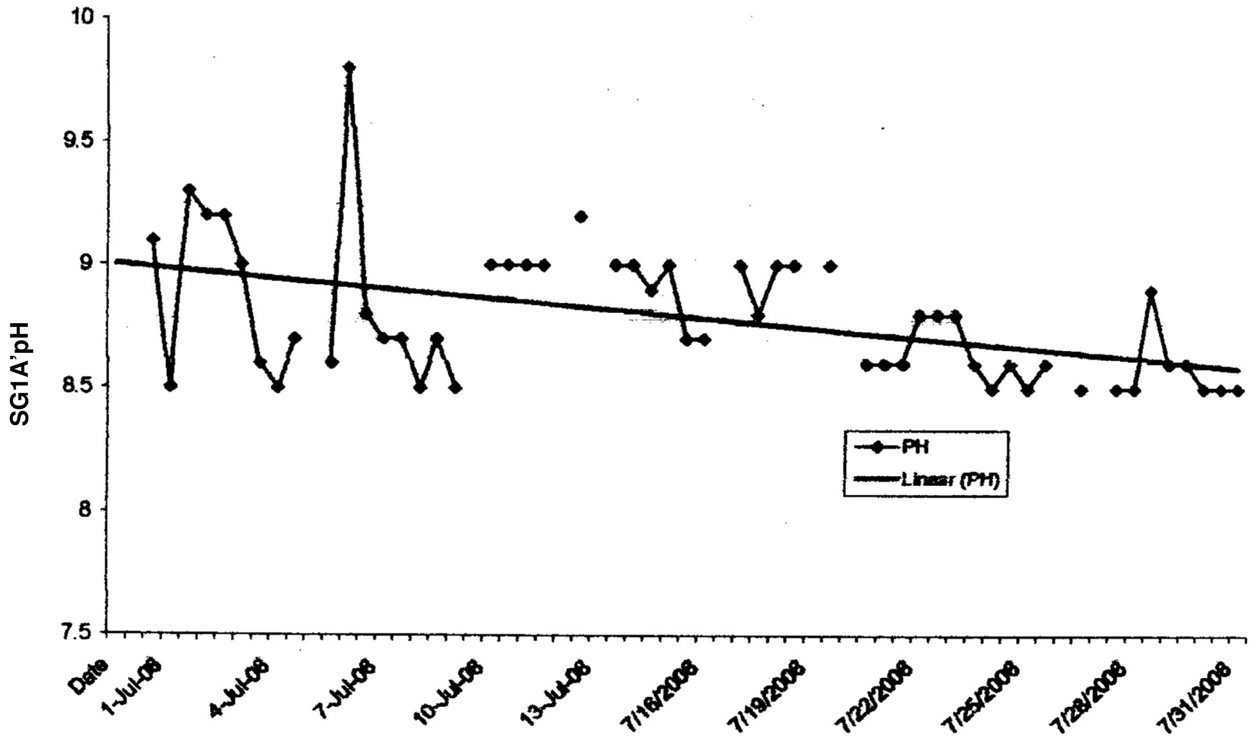

Figure 12. Boiler A steam pH versus time.

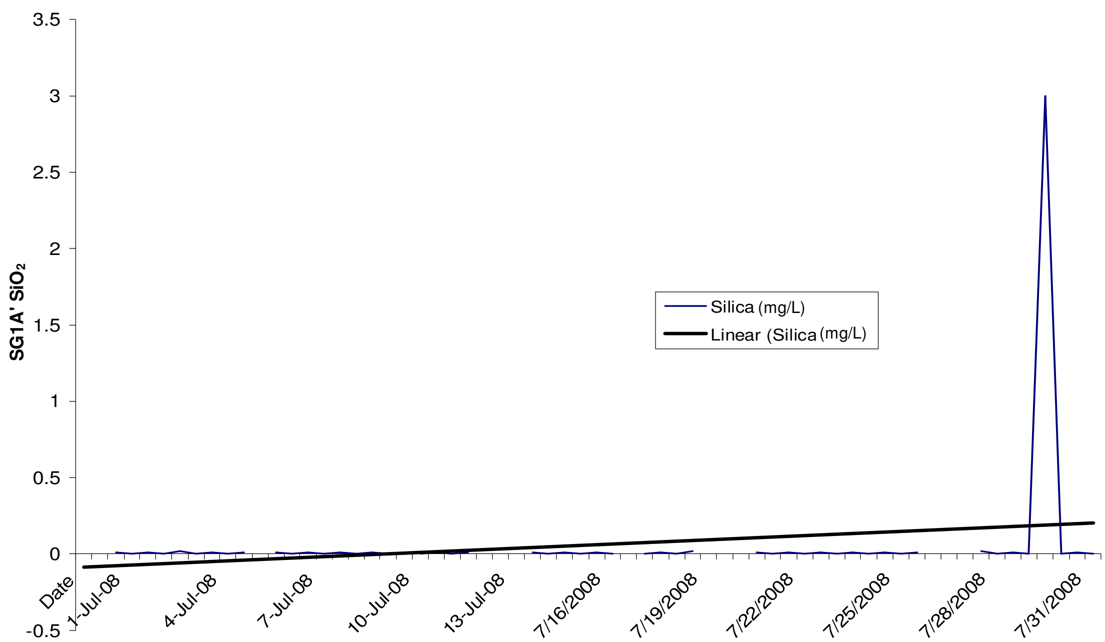

Figure 13. Boiler A steam A silica versus time.

Langelier saturation index (LSI), deduction and calculation of Reynar stability index (RSI), relationship between LSI and RSI, and relevance of the above and other models in predicting effectiveness of chemical inhibitors versus estimated corrosion rate.

Calculations

Langelier Saturation Index (LSI): The LSI index is calculated at two temperatures: 25°C (room temperature) and 82°C (cage wash cycle). The colder incoming water

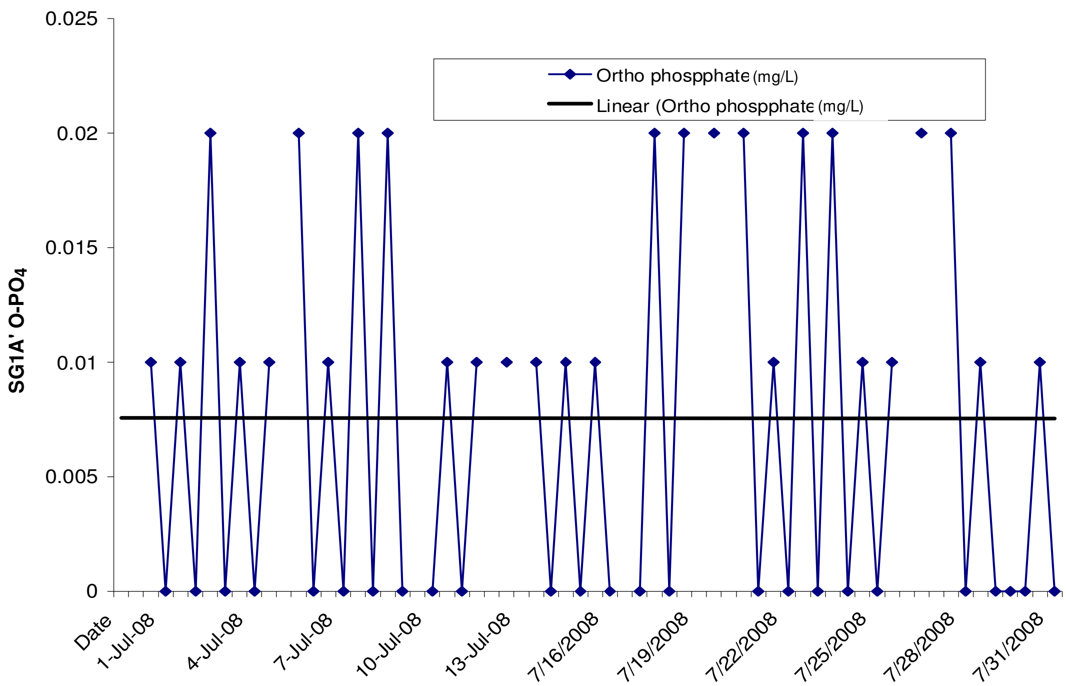

Figure 14. Boiler A steam A ortho-phosphate versus time.

will warm to room temperature in the manifolds. Residual water in the rack manifold can be heated to 82°C when the rack is in the cage washer. At this process conditions, the following data were obtained.

Water analysis: pH = 7.5, TDS = 320 mg/L, Calcium = 150 mg/L (or ppm) as $CaCO_3$ and Alkalinity = 34 mg/L (or ppm) as $CaCO_3$.

LSI formula: LSI = pH - pH_s, pH_s = (9.3 + A + B) - (C + D) where: A = (Log_{10}[TDS] - 1)/10 = 0.15, B = -13.12 × Log_{10}(°C + 273) + 34.55 = 2.09 at 25°C and 1.09 at 82°C, C = Log_{10}[Ca^{2+} as $CaCO_3$] - 0.4 = 1.78, D = Log_{10}[alkalinity as $CaCO_3$] = 1.53.

Calculation at 25°C: pH_s = (9.3 + 0.15 + 2.09) - (1.78 + 1.53) = 8.2, LSI = 7.5 - 8.2 = - 0.7, hence no tendency to scale calculation at 82°C, pH_s = (9.3 + 0.15 + 1.09) - (1.78 + 1.53) = 7.2, LSI = 7.5 - 7.2 = + 0.3, hence slight tendency to scale, also, for chemical treatment program at Indorama process operation, practically LSI from empirical data is calculated automatically by direct system unit computations and reported on daily basis as follows:

LSI=[PH-(9.4-LOG(Ca)-0.94*LOG(M.Alk)+LOG(Conduct)/10.7+3.24*EXP(-(65*1.8)+32)/191)]

The controlling parameters were some of the major parameters upon which researcher "Pisigan" based his corrosion rate prediction model equation.

Reynar stability index (RSI)

The Reynar stability index (RSI) attempts to correlate an empirical database of scale thickness observed in municipal water systems to the water chemistry. Like the LSI, the RSI has its basis in the concept of saturation level. Reynar attempted to quantify the relationship between calcium carbonate saturation state and scale formation. Applying the formula below, the Reynar index takes the form:

RSI = 2(pH_s) - pH

At the same condition as that applicable to LSI, RSI can also be determined as follows:

At 25°C, pHs = 8.2, RSI = 2(8.2) – pH, At 82°C, pHs = 7.2, RSI = 2(7.2) – pH

Hence, RSI can be determined, taking direct measurement of the water PH=7.5, RSI = (2(8.2) -7.5) – 2(7.2) – 7.5), RSI = 8.9 – 6.9 = 2.0. Where pH is the measured water pH, and pHs the pH at saturation in calcite or calcium carbonate, thus applying the above values to Indorama Plc cooling water treatment process gives an operating data temperature of; supply temperature = 32°C, return temperature = 44°C. Average LSI and RSI by applying the above formula, all conditions been normal it was obtained that: LSI = pH - pH_s, pH_s = (9.3 + A + B) - (C + D) where: A = (Log_{10}[TDS] - 1)/10 = 0.15, B = -13.12 x Log_{10}(°C + 273) + 34.55 = 1.96 at 32°C and 1.74 at 44°C, C = Log_{10}[Ca^{2+} as $CaCO_3$] - 0.4 = 1.78,

Table 1. Chemical composition of cooling water treatment chemical.

OPO_4 (Ortho-phosphate)	**Carbon steel corrosion inhibitor**	**Anodic and cathodic**
HPS (Co-polymer)	Dispersant for iron scale formation	-Control scale formation. -Stabilizes salt of zinc phosphate and calcium phosphate from precipitating.
HEDP(Organic phosphonates)		-Calcium carbonate stabilizer. -Control salts formation to avoid scaling.
TTA (Tolytriazole)	Copper alloy corrosion inhibitor	-Forms Cu-azole passive film on copper alloys.
Flogard MS6208 on the other hand contains:		
Zn (Zinc)	Carbon steel corrosion inhibitor	Cathodic

Table 2. Effect of analyses parameters in cooling water and controls.

S/N	Analytes	High effect	Low effect	Control action
1	Zinc (Zn)	Environmental	Cathodic corrosion from deposit	Optimize dosage
2	Phosphate (PO_4)	Precipitation to form salt deposit	Ineffective corrosion inhibition	Optimize dosage
3	Calcium and Magnesium hardness	Scaling	Corrosion	High- initiate blowdown, low- optimised dosage to maintain natural inhibition from film
4	PH	Fouling/Scaling, removal of surface protective film	Corrosion	Low- dose suitable quantity of caustic soda
5	Conductivity	Better performance	Poor performance	Monitor cycle of concentration
6	Total Iron	Deposition/Scaling/Corrosion	Under control	Maintain pH and auto-phosphate treatment range
7	Turbidity	Possibility of leakage or interference	Better	High-check for leakages and contain it by dosing dispersant; Initiate blowdown
8	Silica	Good, gives high cycle of concentration (COC)	Not good	Minimise blowdown rate and check for leakages and possible loss of water
9	Chloride	Could form $CaCl_2$ salt with calcium and weak acid with hydrogen causing pH depression and possible corrosion		Optimise the dose of dispersant to stabilise salt formation and inhibit possible corrosion
10	Bioscan	High biocide activity	Low biocide activity	Ensure sufficient oxidising and non-oxidising treatment
11	Aerobic bacteria count	Excess bio-activity	Low bio-activity	Ensure sufficient oxidising and non-oxidising treatment
12	Free residual Chlorine (Cl_2)	Form weak acid with loose hydrogen/possible corrosion	Insufficient dose of Calcium hypochlorite/increased bio-activity	Maintain sufficient dose of calcium hypochlorite or other supplement for example, liquid bromine

D = $\log_{10}$[alkalinity as $CaCO_3$] = 1.53.

Note: Cooling water design treatment data for operation of Indorama Plc Cooling Tower is given by the range 8.0 to 8.2. Hence for Indorama treatment parameter:

Calculation at 32°C: pH_s = (9.3 + 0.15 + 1.96) - (1.78 + 1.53) = 8.1, LSI = 8.0 - 8.1 = - 0.1; hence no tendency to scale.

Calculation at 82°C: pH_s = (9.3 + 0.15 + 1.74) - (1.78 + 1.53) = 7.7, LSI = 8.0 - 7.7 = + 0.1; hence slight tendency to scale.

Also Average Reynar stability index (RSI) is calculated as follow: At 32℃, pHs = 8.1, RSI = 2(8.1) – pH; At 44℃, pHs = 7.9, RSI = 2(7.9) – pH. Hence, RSI can be obtained, taking direct measurement of the water pH=8.0, RSI = (2(8.1) -8.0)–2(7.9) – 8.0). RSI = 8.2-7.8 = 0.4.

Conclusion

A combination of models (for example, corrosion inhibitor and scale inhibitor models) can be used to optimize the ratio of ingredients in a blended formulation. Corrosion rate and inhibitor 2 dosage models can provide guidelines to assist an experienced cooling system professional in optimizing treatment rates and controllable operating parameters. As with any predictive tool, the models are a supplement to experience - not a substitute for it.

Corrosion and Fouling in Indorama petrochemical plant has been effectively managed and kept at minimal level from continuous chemical dosage treatment, of inhibitors, oxidising and non- oxidising biocide given to cooling water that runs through the entire plant. Installed corrosion rate from coupon result has been kept as low as 1.5 mpy.

Process equipment that forms the network of the plant as boilers, exchangers, heaters etc receives adequate protection due to general passivity initiated from the cooling tower forming resistance passive film to corrosion and microbial invasion against scale tendency and eventual fouling. Chemical consumption in treatment of cooling water and olefins operation has been excellent. Necessary modifications still further need to be implemented to improve performance. Daily challenges faced that has to do with control of parameters and arresting of emergency situations were adequately managed through surveillance inspection, troubleshooting and reporting of incidences. Leakages were traced, pumps were shut, and optimizations in chemical dosage were carried out as occasion demands.

The fouling observed is as a result of a number of factors pertaining to both the treatment of the cooling water, and the design and engineering of the plant and exchangers. This further highlights the need for a well-managed and maintained treatment programme, for additional monitoring as detailed above and for ongoing review of results with a view to implementing continuous improvement. A great stride has been achieved as a testimonial of efficiency in cooling water monitoring while improvement plans are still necessary to fully be on top of olefins monitoring programme. Predictive models, theories, Index and empirical relationship applied in the research agrees with the treatment regime approved for the chemical treatment program in place of Indorama Plc. Average circle of concentration (COC) during treatment was between 4 to 5. Average LSI and RSI values have been between -0.1 to 0.3 and 0.3 respectively. This shows low corrosive tendency and reduction in heavy scale tendency for possible fouling.

CONTRIBUTION TO KNOWLEDGE

This research work has been able to ascertain the suitability of cooling water treatment as a medium for control of corrosion, scaling and bio-fouling in Petrochemical plant. If this is maintained consistently, increased efficiency and improved performance will be the result. This will further extend the useful life on Petrochemical plant. For future consideration the standard treatment must be sustained while some improvement procedure and necessary modification may be useful. One of such modification needed for Indorama Plc Petrochemical plant is ‘true sense’ but for the cost which would be a major limitation, new set of chemicals that goes with true sense will be introduced and dosage opted for example, SPECTRUS BD15001E, CONTINUM AEC3192, INHIBITOR AZ101, GENGARD GN7004 and SPECTRUS NX 1422. Some parameters treatment range shall be reviewed upward and dosage possibly increased for example, free residual chlorine formerly 0.3 - 0.6 mg/L to 0.6 - 1.0 mg/L, Orthophosphate formerly 4 - 6 mg/L to 8 - 10 ppm, Zinc formerly 0.8 - 1.2 mg/L to 0.7 - 0.8 mg/L. Dose of Spectrus OX909 will be reduced to optimize cost and dosing of calcium hypochlorite will be increased to span 4 to 5 h for good retention in the system against Bio-activity.

Operation of cooling tower and monitoring of olefins operations has been quite successful and also challenging. This informs certain modifications to further improve the operation and service delivery as applicable to both cooling tower and olefin monitoring. The supposed modifications some of which has commenced implementation are presented below: increase dosage of calcium hypochlorite to increase the killing effect of biocides, reducing the rate of blow-down so that oxidising biocides and bio-dispersant can stay longer in the system for effective treatment and maintainance of an optimum cycle of concentration, change and modification in the entire treatment programme. Dosage of non-oxidising chemical on a weekly spread basis, as against fortnight step-up of free residual chlorine treatment ranges from 0.3 - 0.6 to 0.6 - 1.0. Possibly warehouse is hired for chemical storage for stock control purpose. Similarly, for Olefins: installation of new dosing pumps, modification of some dosing point and possible changes occur. Introduction of support chemical petroflo 21Y621 to complement petroflo 22y630 for adequate control of pH in the system and monitoring increased to cover 24 h for adequate service delivery.

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