Full Length Research Paper

Corrosion inhibition of 316L stainless steel in plain tap water

Anaum Nawaz[1,2]*, A. Farooq[1,2], K. M. Deen[1,2], A. Inam[1], R. Ahmad[1] and I. H. Khan[1,2]

[1]Department of Metallurgy and Materials Engineering, CEET, University of the Punjab, 54590, Lahore, Pakistan.
[2]Corrosion and Corrosion Control Research Cell, Faculty of Engineering and Technology, University of the Punjab, 54590, Lahore, Pakistan.

The corrosion behavior of 316L stainless steel in the presence of various Cl^- ions concentrations at constant dose of Zinc orthophosphate (ZOP) containing inhibitor was investigated electrochemically by Tafel Scan, Potentiodynamic and Cyclic polarization. These techniques evaluated the probability of pitting to occur and the effect of ZOP inhibitor on pitting resistance. The corrosion inhibition by ZOP was considered due to formation of passive film which obstructed the approach of aggressive Cl^- ions at the surface. The effectiveness of ZOP containing inhibitor was found more pronounced at 100 ppm Cl^- ions concentration than at higher level. Increase in Cl^- ion concentration in solution not only shifted the pitting potential towards negative direction but also adversely affected the inhibitor efficiency which resulted in high corrosion rate.

Key words: Stainless steel, zinc orthophosphate (ZOP) inhibitor, cyclic polarization, Cl^- ions.

INTRODUCTION

One of the most popular grade of stainless steel is 316L that presents outstanding corrosion resistance, good mechanical properties and weldability. These properties are the principal reason why 316L is a primary material used in cooling water systems such as heat exchangers (American Iron and Steel Institute, 1974). High chromium content and comparatively low carbon content (<0.03%) and addition of molybdenum and nickel (2-3%) are chiefly responsible for excellent corrosion resistance properties in stainless steels, but the normal cooling water conditioning and design parameters are attributed to general corrosion stability of material such as conductivity, pH, temperature, alkalinity as well as nitrates, sulphate and most significantly chloride ions concentration (Deen et al., 2010; Petersen, 2009).

Devices used for efficient heat transfer from one fluid to another on whether they are directly connected or separated by a solid wall are heat exchangers. Heat exchangers associated with water cooling systems are extensively used in many industrial plants such as power production plants, food processing, chemical processing, air conditioning, and for domestic hot water (DHW) (Vasauskas and Baskutis, 2006). Excellent heat transfer

characteristics execution and compactness in design has extended widely their industrial applications as well (Joshi and Aravind, 2012). In cooling water system, water is used as cooling medium because of its availability, heat transfer capacity and effective cost. Natural water restrains many dissolved solid, organic matters and gasses as well as suspended solid and inorganic substances; at high temperature, the presence of these concentrations originates many severe corrosion problems in cyclic cooling systems (Puckorius and Cunningham, 1997; Srbislav et al., 2012).

So stainless steels grade are used in many process industries in which heating and cooling is a vital part of the process required for the material having high temperature resistance to oxidation and scaling, excellent heat transfer properties, and superior corrosion resistance with long service life. 316L stainless steels derive corrosion resistance by formation of thin passive

_____
*Corresponding author. E-mail: anaumnawaz29@gmail.com. Tel: +92-429-9232256; Fax: +92-429-9231159.

Table 1. Chemical composition of commercial grade 316L stainless steel.

Grade	Composition	C	Mn	Si	P	S	Cr	Mo	Ni	N
316L	(%)	0.03	2.0	0.75	0.045	0.03	18.0	3.0	14.0	0.10

film of protective oxides of chromium which act as a barrier between the surface and the environment. Breakdown of this protective film leads to localized corrosion failures such as pitting/crevice corrosion and the ability to repassivate determines the resistance to corrosion failure (Schmitt and Bedbur, 1984; Leckie and Uhlig, 1966).

Protection mechanism by formation of oxide passive films compelled the presence of oxidizing environment but in the reducing environment such as the presence of chlorides ion, 316L stainless steel reveals the destructive form of corrosion due to breakdown of passive films particularly at elevated temperature. Intense concentration of Cl^- in solution and high temperature can decrease the critical pitting potential leading to the perforation of the surface exposed by localized corrosion attack (Hosni, 2014; Jiménez et al., 2014). For corrosion control to extend material's life, it is quite essential to study the effect of inhibitor for cooling water systems. The objective of the present work is to contribute to the study of the influence of zinc based orthophosphate inhibitor on 316L SS corrosion behavior. Inhibitor efficiency was evaluated at different Cl^- concentrations, that is, 40 ppm in tap water and 100 ppm, 200 ppm and 300 ppm, in the presence of 20 ppm zinc orthophosphate inhibitor by using electrochemical techniques.

EXPERIMENTAL DETAILS

For electrochemical testing, 1×1 cm^2 specimens of 316L SS used in this study were cut from a commercial grade heat exchanger plate. The chemical composition of 316L SS is given in Table 1.

The working surfaces of specimens were ground with grit size up to 600 silicon carbide paper, subsequently polished with Alumina power on polishing cloth and chemically cleaned and rinsed with distilled water. For working electrode, test specimens were placed on a copper plate and a cylinder of 6.25 mm diameter and 65 mm long was embedded on it by using polyester resin with an exposed area of 1 cm^2.

Four electrolyte solutions were prepared in tap water having different concentrations of Cl^- (100 ppm, 200 ppm, and 300 ppm) with constant dose of 20 ppm zinc based orthophosphate inhibitor in tap water for electrochemical testing.

The corrosion behavior of 316L SS was monitored using PC14/750 Potentiostat, and spectrum was studied using Echem analyst version 5.68. Electrochemical study was performed by analytical techniques, that is, Tafel scan, potentiodynamic, cyclic polarization and electrochemical impedance spectroscopy using three electrode cell working electrode of 316L SS, saturated calomel electrode as reference electrode, and graphite auxiliary electrode.

In Tafel scans, the sweep typically was applied from -250 mV to 250 mV vs. OCP with the scan rate of 1 mV/s. To determine the overall corrosion behavior, polarization of 316L SS was carried out in these electrolytes, at a sweep rate of 5 mV/s. The efficiency of zinc orthophosphate (ZOP) inhibitor at different chloride levels was evaluated from corrosion current by extrapolating Tafel region.

The following formula is used for the evaluation of inhibitor efficiency (Aydog and Aydinol, 2006):

$$IE\ \% = \frac{I_{corr} - I_{corr\ (inhibitor)}}{I_{corr}} \times 100 \qquad (1)$$

Where:

I_{corr} = Corrosion current at 40 ppm chloride level without inhibitor.

$I_{inhibitor}$ = Corrosion current at specific chloride level with 20 ppm inhibitor

Cyclic polarization scan was utilized to determine pitting susceptibility of 316L SS by polarizing the surface between -500 mV and 500 mV versus OCP respectively. Apex current density (10mA/cm^2) and apex potential (1200 mV versus OCP) was applied with a rate of 5.0 mV/sand, 2.5 mV/s during forward and reverse polarization scan respectively.

RESULTS AND DISCUSSION

Potentiodynamic studies

The cathodic and anodic curves of 316L SS in various chloride ions concentrations in tap water (100 ppm, 200 ppm and 300 ppm) with 20 ppm dose of zinc based orthophosphate inhibitor are shown in Figure 1. The results of polarization studies were collected in Table 2, which includes the E_{corr}, I_{corr}, corrosion rate and Tafel slope values.

With the increase on Cl^- ion concentration, the E_{corr} potential is shifted towards negative side and corrosion rate of 316L SS varies as the function of chloride ions activity in tap water. Chloride ions get adsorbed on the protective layer and formed complex with cations and hydroxides which breaks passive layers of oxides and
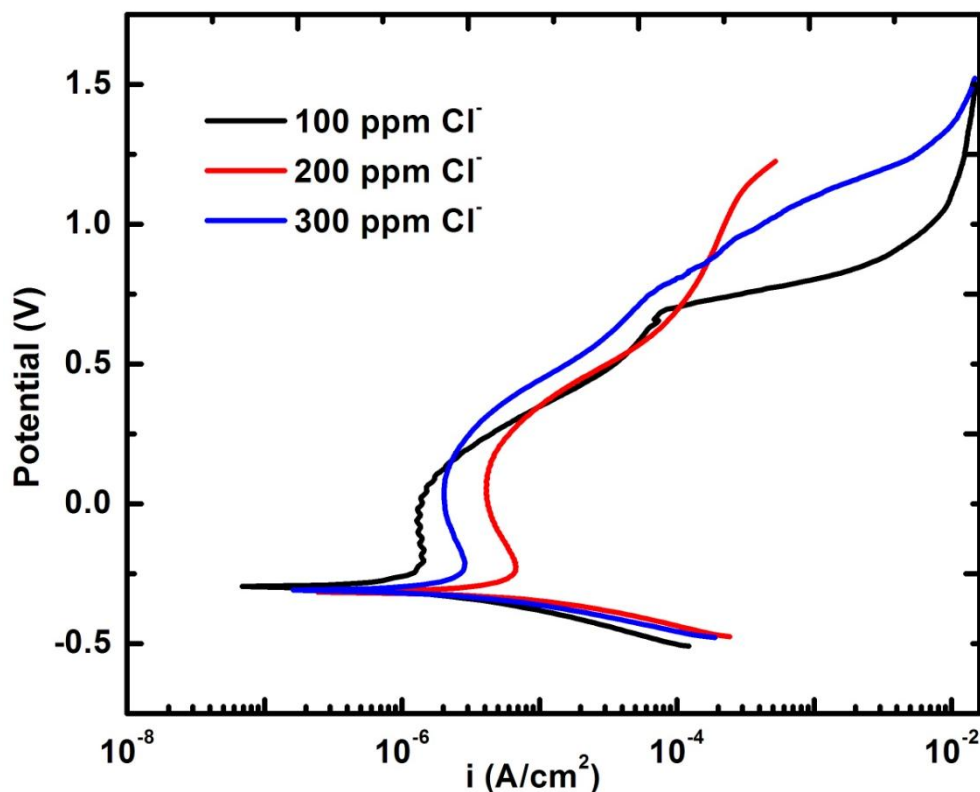
Figure 1. Potentiodynamic polarization curves for 316L SS in tap water containing different Cl⁻ concentrations.

Table 2. Electrochemical parameters within the tafel region of potentiodynamic for 316L Stainless steel in tap water with varying Cl⁻ concentrations .

Sample ID	$\beta_{a\ (V/decade)}$	$\beta_{c\ (V/decade)}$	$E_{corr\ (mV)}$	$I_{corr\ (A/cm^2)}$	Corrosion rate (mpy)
Tap water (100 ppm Cl⁻, 20 ppm ZOP)	1.00×10^{15}	66.3×10^{-3}	-297	1.35×10^{-3}	576×10^{-3}
Tap water (200 ppm Cl⁻, 20 ppm ZOP)	322×10^{3}	112×10^{-3}	-314	1.52×10^{-3}	633×10^{-3}
Tap water (300 ppm Cl⁻, 20 ppm ZOP)	1.0×10^{15}	45.80×10^{-3}	-310	19.9×10^{-3}	921×10^{-3}

increase the potential difference across the passive layer (Yusuke et al., 2007). The curve shift to the left at 100 ppm Cl⁻ concentration is caused by the reduction in the corrosion current. Corrosion current density increases with the increase in Cl⁻ amount which also enhance the hydrolyzation of metallic ion observed at high chloride ion concentration (200 ppm, 300 ppm) in containing tap water resulting in higher corrosion rate respectively (Khan, 2010).

Considering the effect of chloride ions, (ZOP) inhibitor efficiency was calculated which decreases with increase in chloride ions concentration (Figure 2). The inhibition action of ZOP inhibitor is due to formation of microscopic film which acts as barrier between surface and environment. Zinc based orthophosphate (ZOP) inhibitor tendency to film formation is rapid with less dispersing effect on corrosion products. The extent of inhibition can

be enhanced by increasing the amount of inhibitor with varying chloride ion values as shown in Figure 2. However, the inhibition efficiency is higher at 100 ppm low chloride ions concentration with shift in potential to positive side (Thomas, 1991).

Overlay curves of Tafel for 316L SS in Cl⁻ containing tap water with 20 ppm zinc based orthophosphate (ZOP) inhibitor are shown in Figure 3. Corrosion current density (Icorr), corrosion potential (Ecorr), corrosion rate (mpy) and the Tafel lopes (βa and βc) computed from Tafel plots are given in Table 3.

More noble (less negative) corrosion potential was monitored at 100 ppm chloride ion concentration with 20 ppm inhibitor dosage attributing low corrosion rate. Addition of inhibitor has shifted the anodic polarization curve left and above, and the critical potential moves to more noble side (positive) by anodic inhibition (Guan,
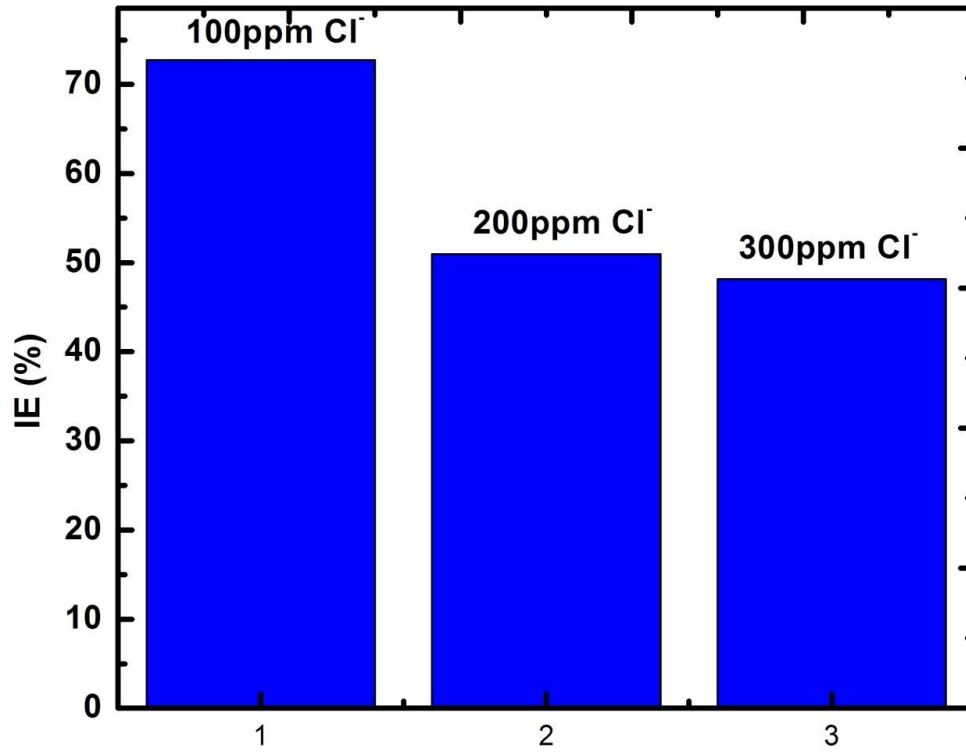
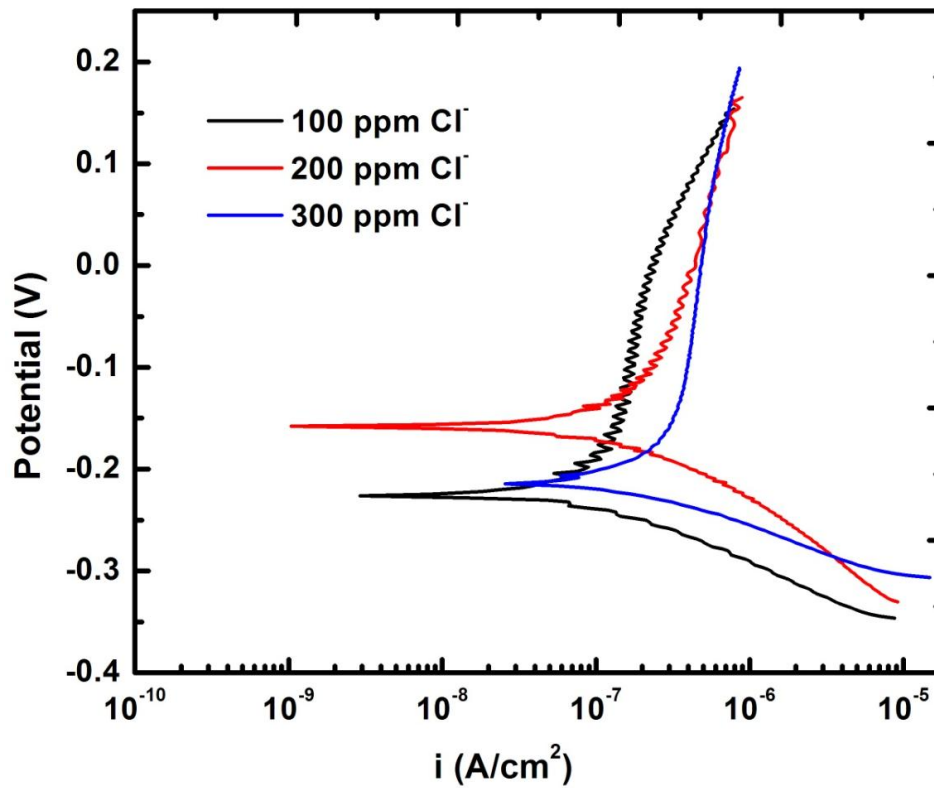**Figure 2.** ZOP inhibitor efficiency at various chloride ions level.

Figure 3. Tafel curves for 316L SS in tap water containing varying amount of chloride ion concentration with 20 ppm ZOP inhibitor.

Table 3. Tafel polarization scans parametersfor 316L SS in the presence of 20ppm ZOP inhibitor.

Sample ID	$\beta_{a \text{ (V/decade)}}$	$\beta_{c \text{ (V/decade)}}$	$E_{corr \text{ (mV)}}$	$I_{corr \text{ (A/cm}^2)}$	Corrosion rate (mpy)
Tap water (100 ppm Cl⁻, 20 ppm ZOP)	1×10^{15}	82.10×10^{-3}	-23	175	11.55×10^{-3}
Tap water (200 ppm Cl⁻, 20 ppm ZOP)	1.738×10^{6}	114.2×10^{-3}	-158	315	20.78×10^{-3}
Tap water (300 ppm Cl⁻, 20 ppm ZOP)	1.818×10^{6}	71×10^{-3}	-213	333	21.95×10^{-3}
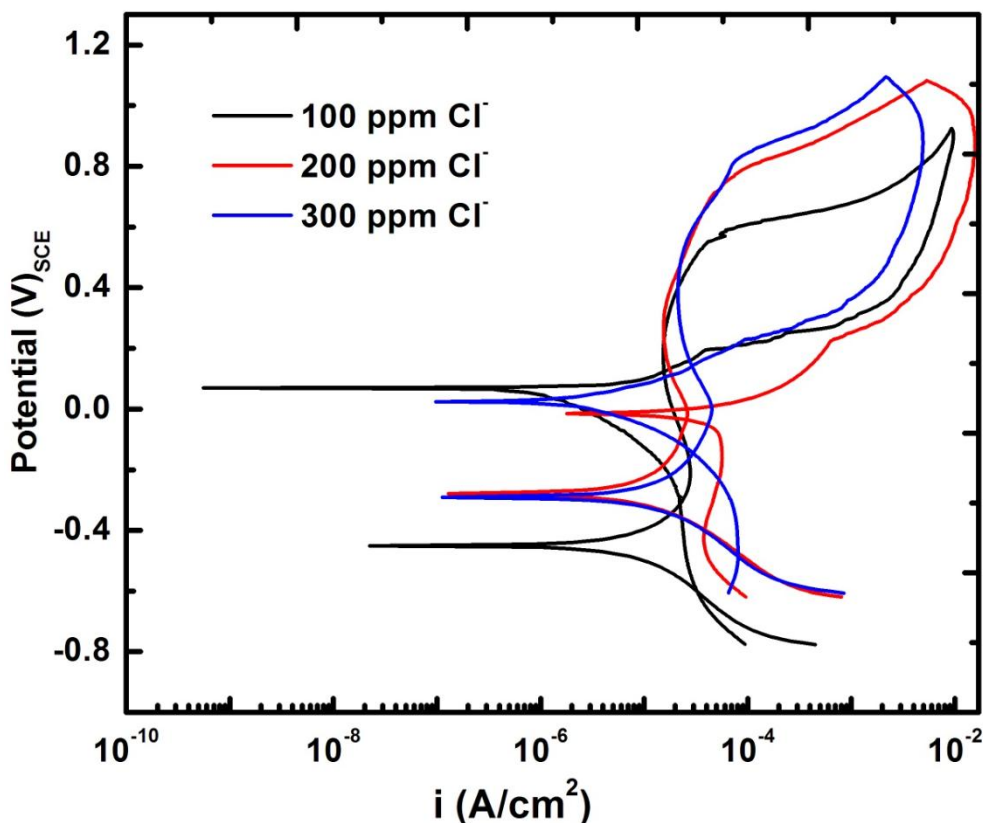
Figure 4. Cyclic polarization trend for 316L SS in tap water containing different Cl⁻ concentrations.

2007). Significant effect of chloride ions was also observed on corrosion current density of 316L stainless steel (Table 3), though the lower value of I_{corr} at 100 ppm was the result of protective layer formed by ZOP inhibitor improving the resistance to pitting. Further increase in chloride concentration (200 ppm, 300 ppm) of the anodic polarization curve slips down (Figure 3). The transfer of corrosion potential towards negative (active) side and increase in corrosion current density depicted at high concentration of chloride than TW-100.ZOP inhibitor shifted the potential to noble side by increasing the pitting resistance, but the increase in chloride level lowered the inhibitor efficiency.

Cyclic polarization

Cyclic polarization curves for 316L SS in inhibitor containing tap water with chloride ions are shown in Figure 4. The representative cyclic polarization curve is including cathodic polarization curve, tefal region and passive region followed by the reverse scan to depict the behavior of 316L SS in Cl⁻ containing tap water. Possibility of pitting was investigated by hysteresis loop during reverse scan in cyclic polarization (Ahmad, 2006).

A positive loop during reverse anodic scan was observed at 100 ppm Cl⁻ level characterizing the chloride ions attack on surface causing pitting corrosion. At 100 ppm Cl⁻ concentration in tap water, the current density was relatively lower and the pitting tendency was more positive (0.88 mV) than the protection tendency (0.57 mV) as given in Table 4. The increase in corrosion current density was observed above the E_{pit} potential as the result of pitting initiation process (Liu et al., 2010). The presence of inhibitor in tap water and increasing

Table 4. Electrochemical Kinetics parameters of cyclic polarization scan for 316L SS in the presence of 20ppm ZOP inhibitor.

Sample ID	$E_{corr1\,(mV)}$	$E_{corr2\,(mV)}$	I_{crit} (A/cm^2)	$E_{pit\,(mV)}$	$E_{prot\,(mV)}$	E_{pit}-$E_{corr1\,(mV)}$	E_{prot}-E_{corr1} (mV)
Tap water (100 ppm Cl⁻, 20 ppm ZOP)	-0.45	0.07	4.18×10^{-6}	0.43	0.123	0.88	0.57
Tap water (200 ppm Cl⁻, 20 ppm ZOP)	-0.27	-0.015	4.36×10^{-6}	0.61	0.0018	0.88	0.27
Tap water (300 ppm Cl⁻, 20 ppm ZOP)	-0.289	0.0294	6.80×10^{-6}	0.49	0.137	0.7	0.426

chloride level with an exceptional behavior was depicted having relatively smaller positive loop by reverse polarization and the difference between the pitting potential and protection potential was less due to localized corrosion reactions at the surface and the formation of passive film by phosphate ions (PO_4^{-3}) inhibitor (ZOP) with iron in the system.

Further increase in chloride level (200 ppm) and in tap water increased the potential difference between Pitting Potential (E_{pit}) and Protection Potential (E_{prot}) which consorted to the breakdown of the protective film on the surface. At 300 ppm chloride level, the shift in curve to left and above was the result of resistance to pitting by 316L SS due to development of protective layer, but the overall uniform corrosion was more dominant in this case. Over all zinc based orthophosphate (ZOP), the inhibitor retarded the pitting tendency of the substrate but the increase in chloride concentration affected the inhibitor efficiency.

Conclusion

- The ZOP inhibitor efficiency was comparatively better at 100 ppm chloride ions concentration.
- It was deduced that further increase in chloride level accelerated the pitting tendency of 316L stainless steel, and the effectiveness of the inhibitor was relatively poor.
- It was further investigated that higher dose of the inhibitor could suppress the aggressiveness of higher chloride ions concentration.

REFERENCES

Ahmad Z (2006).Principles of corrosion engineering and corrosion control. Elsevier.

American Iron and Steel Institute (1974).Steel products manual: stainless and heat resisting steels. Washington: The Institute.

Aydog GH, Aydinol MK (2006). Determination of susceptibility to Intergranular corrosion and electrochemical reactivation behavior of AISI 316L type stainless steel. Corro. Sci., 3565–3583.

Deen KM, Virk MA, Haque CI, Ahmad R, Khan IH (2010). Failure investigation of heat exchanger plates due to pitting corrosion. Eng. Failure Anal., 17: 886-893.

Gehan K, Lockey A, Rao M (1991).Chemical Treatments to Control Corrosion in Open Cooling Water Systems. Corrs. Assoc., Corrosion. 91: 15.

Guan X (2007). Impact of zinc orthophosphate inhibitor on distribution system water quality.

Hosni ME (2014). Influence of temperature on the pitting corrosion behavior of AISI 316L in chloride-CO2 (sat.) solutions. Mater Design, 59: 339–343.

Jiménez MJ, Turias IJ, Trujillo FJ (2014). An automatic pitting corrosion detection approach for 316L stainless steel. Mater Design, pp. 642–648.

Joshi NM, Aravind RP (2012). A method to increase flexibility of plate heat exchanger through analysis of flow resistance, heat transfer and pressure drop having different surface profiles. Int. J. Adv. Eng. Res. Stud., pp. 108-111.

Kelly RG, Scully JR, Shoesmith DW, Buchheit RG (2002). Electrochemical techniques in corrosion science and engineering.

Khan IH (2010).Corrosion Technology.AFAQ.

Leckie HP, Uhlig HH (1966). Environmental Factors Affecting the Critical Potential for Pitting in 18–8 Stainless Steel. J. Electrochem. Soc., pp. 1262-1267.

LIU Z, CHENG X, Shengjie X (2010). Effect of Chloride ion on 316L Stainless steel in cyclic cooling water. Acta Metall., 23: 431-438.

Malik AU, Kutty M, Siddiqi NA, Andijani IN, Ahmad S (1990). Corrosion studies on SS 316L in low pH High chloride product water medium.

Petersen B (2009).Guideline of Water quality for copper brazed plate heat exchangers. Danf. Dist. Heating, pp.1-8.

Puckorius PR, Cunningham B (1997). Cooling water technology advanced course. Int.l water Conf. Pittsburgh.

Schmitt G, Bedbur K (1984). Proc. 9th International Congress on Metallic Corrosion, Toronto, Canada, p. 112.

Srbislav BG, Branislav M, Dragan M, Dragan P (2012). Experimental determination of fouling factor on plate heat exchangers in district heating system. Ener. Buildings, 50: 204–211.

Thomas JY (1991). The use of zinc for corrosion Control in open cooling systems. Association of water technologies, Inc. Spring convention & Exposition.

Vasauskas V, Baskutis S (2006). Failures and fouling analysis in heat exchangers. Mech., 5: 24-31.

Yusuke T, Nishikata A, Tsuru T (2007).Pitting corrosion mechanism of Type 304 stainless steel under a droplet of chloride solutions. Corro. Sci., 1394–1407.