CHAPTER IX

Summary and Conclusion

The evolution of ennoblement in stainless steel is believed to precede the corrosion of the stainless steel conditions involved have been studied in freshwater with low-salt conditions. The occurrence of ennoblement process in freshwater has been studied. In the present study, the roles of natural and industrial biofilms on stainless steel have been studied. The role of biofilm at various temperatures was also analyzed.

The following conclusions have been derived from the present work.

i) The First chapter, a detailed review has been presented in the present work. This chapter mainly deals with the definition of corrosion followed by various forms of corrosion. Special emphasize is given to microbiologically influenced corrosion and the economic losses caused by MIC. The effect of various corrosion causing microorganisms such as sulphate reducing bacteria, iron oxidizing bacteria and manganese oxidizing bacteria and their morphology, biochemistry of each microorganisms are discussed in detail. The mechanistic aspects of corrosion of passive metals caused by ennoblement process are also dealt. Some recent research in the area of microbiologically influenced corrosion and some open problems for further research have been also discussed in this chapter. Besides, control the corrosion, an efficient corrosion inhibitor
should be able to bind irreversibly to the metal surface, provide good surface coverage and at the same time with very good biocidel effect. Besides, literature collection on corrosion and its control of cooling water has been carried out and presented in the first chapter. It raises a question that whether ennoblement occurs in industrial biofilm. Besides studies on electrochemical behavior of biofilm fill up the gap in literature.

ii) The Second chapter deals with aim and scope of the present study, which covers the importance of ennoblement process on passive alloys. Besides, it explains the literature survey on ennoblement process and it covered the role of biofilm on passive alloys and their roles on corrosion.

iii) The Third chapter is experimental procedures adopted in this research programme are presented in this chapter.

iv) The Fourth chapter is to evaluate the real electrochemical behavior of biofilm using employing GCE. The cathodic polarization curve of biofilm is similar to the cathodic polarization curve of MnO$_2$ coated stainless steel alloys noticed by Dexter and Maruthamuthu. The electrochemical behavior of biofilm was determined by accumulated biogenic MnO$_x$ where MnO$_2$ reduction only is the contributor for a reduction peak at 0 mV vs SCE. Cyclic voltammograms explained the role of biogenic MnO$_x$ and H$_2$O$_2$ on ennoblement process. Impedance revealed that the biofilm increases the kinetic and diffusion process on glassy carbon electrode where a loop at
higher frequency indicates the adsorption of biofilm on GCE surface. The present study explained the actual electrochemical behavior of biofilm.

v) The Fifth chapter presents the electrochemical behavior of biofilm investigated by employing FTO. The cathodic polarization curve of biofilm is similar to the cathodic polarization curve of biofilm covered stainless steel. The electrochemical behavior of biofilm was determined by accumulated biogenic MnO\textsubscript{x} where MnO\textsubscript{2} reduction only was the contributor for a reduction peak at 0 mV vs SCE. Cyclic voltammogram explained the redox behavior of biogenic MnO\textsubscript{x} and H\textsubscript{2}O\textsubscript{2} on ennoblement process. It can be claimed that biofouling was due to biomineralization of MnO\textsubscript{x} at the surface of the FTO by MOB was able to cause the increase of the free corrosion potential. It indicates that biofilm contributed to ennoblement process with n- type semiconducting oxide film. Impedance revealed that the biofilm increased kinetic and diffusion process on FTO where a loop at higher frequency indicated the adsorption of biofilm on FTO surface. FTIR concluded that biofilm contained organic molecules as extracellular polymeric substances (EPS) and inorganic metal oxides such as MnO\textsubscript{x}. In the present study, it was observed that the electron flow between n (FTO) -type and n (MnO\textsubscript{x} biofilm) -type semiconducting behavior.

vi) The Sixth chapter presents the evaluation the electrochemical behavior of natural biofilm on 316L stainless steel, alloy C276 and Nickel 200 at 30 °C. The potential shifts towards nobler direction were noticed when
exposed in the freshwater such as 316L stainless steel, alloy C276 and Nickel alloy 200. Electrochemical behavior of passive alloys especially 316L SS was entirely different from other passive alloys. CV response of biofilm covered 316L SS revealed a redox behavior of MnO₅, whereas alloy C276 and Nickel 200 did not exhibit such behavior. The redox behavior was due to free flow of electron between biogenic MnO₅ biofilm and passive film. FTIR spectrum of natural biofilm on passive alloy indicated the presence of MnO₅ - stretching, bending and wagging vibrations. It may be concluded that the shifting of open circuit potential (ennoblement) of passive alloys observed was due to the interaction between manganese biofilm and bacterially produced peroxide. This process was also influenced by the electronic structure of the passive (oxide) film. The biofilm covered 316L SS was due to the ease of electron flow between the passive film (Fe₂O₃) and the MnO₅ biofilm, which were both n-type. In contrast, on alloys such as alloy C276 and Nickel 200 with passive films having a low concentration of free electrons, MnO₅ reduction was more difficult, resulting in a reduced amount of ennoblement in the presence of manganese biofilm. When manganese biofilm was present, however electrons were supplied to the p-type oxide film for chromium / nickel ion reduction. There was a good agreement with cyclic voltammograms and Mott-Schottky plots. The natural biofilm encouraged the ennoblement process (E_{max}) on passive alloy and changed the behavior of surface oxide film.

vii) The **Seventh chapter** deals with the influences of temperature on the electrochemical behavior of natural biofilm on 316L stainless steel. The
ennoblement was caused by natural biofilm formation on SS 316L from freshwater at 30 °C. $E_{\text{max}}$ changes were similar to that of bacterial density decrease on their surfaces with temperature (40 °C & 50 °C). The influence of bacterial concentration depended on pH, temperature and dissolved oxygen were determined using cells grown in freshwater environment, in which biochemical speciation was defined. The characteristics of biofilm adsorption influenced on $E_{\text{max}}$ and temperature dependence during the adsorption process was seen. There were close correlations between the biofilm formation on 316L SS and ennoblement of their shifting potential at various temperatures. Ennoblement process on 316L SS was encouraged by natural biofilm at 30 °C only while increasing the temperature the ennoblement process was not seen at 50°C.

The Eighth chapter deals with the influences of temperature on the electrochemical behavior of Industrial biofilm on 316L stainless steel. With the addition of ATMP and ZnSO$_4$ inhibitor system, the bacterial density was reduced at temperatures at 40 °C and 50 °C in industrial biofilm on 316L SS. The count of bacteria in industrial biofilm was lower compared to natural biofilm. The positive shift could be noticed on 316L SS while in the presence of ATMP and ZnSO$_4$ in freshwater. Industrial biofilm formed was due to the absence of manganese oxide deposition. There was no ennoblement process in industrial biofilm on 316L SS at 30 °C to 50 °C. Antibacterial activity of ATMP was a result of a synergistic effect of the removal of cations (Mn$^{2+}$ ions) and the chemical nature of the used phosphonate molecule. The film may consist of ATMP-Fe$^{2+}$ complex and Zn(OH)$_2$. The anodic reaction was controlled by the formation of
ATMP-Fe$^{2+}$ complex. The cathodic reaction was the generation of OH$^-$ which was controlled by the formation of Zn(OH)$_2$ on the cathodic sites of the metal surface. This accounted for the synergistic effect of ATMP-Zn$^{2+}$ system. Inhibitor treated biofilm on 316L SS did not encourage the ennoblement process. ATMP + Zn$^{2+}$ inhibitor system prevented the MnO$_2$ deposition by utilizing Mn$^{2+}$ chemical stabilization and antibacterial activity to control biomineralization process. ATMP + Zn$^{2+}$ system controlled the changes in the passive film and bacterial growth in cooling water system.

In the present study, with the applications of the principles of electrochemistry, microbiology, biotechnology and corrosion, a focus has been thrown on MOB attachment on stainless steel reported. This work may pave many ways for the scientists in various disciplines to find the solutions for manganese deposition in the heat exchanger tubes and on the process equipments in industries. This is a global problem threatening the safety measures and economy of countries worldwide and more importantly a challenging environmental and health concern. The present study concluded that ennoblement process was encouraged by natural biofilm at 30°C only, while increasing the temperature the ennoblement process could not take place. In industrial biofilm the ennoblement process at 30°C to 50°C was not seen.

In the present study, the roles of “real-time” problem of industrial biofilm on 316L stainless steel have been investigated by electrochemical techniques. The significant improvements in electrochemical techniques allowed the development of new methods for field assessment of microbiologically influenced corrosion (MIC) in
industrial systems. The present investigator believes that the present investigation will be useful for cooling water and process industries.