INHIBITION OF COPPER CORROSION BY ORTHOPHOSPHATE: A MECHANISTIC STUDY

YU ZHE
(B.ENG., Qingdao Institute of Chemical Technology)

A THESIS SUBMITTED FOR THE MASTER DEGREE OF ENGINEERING
DEPARTMENT OF CHEMICAL AND BIOMOLECULAR ENGINEERING
NATIONAL UNIVERSITY OF SINGAPORE
2004
Acknowledgement

I am deeply indebted to my supervisor, Dr. Simo Olavi Pehkonen, for his invaluable advice and enthusiastic direction throughout the entire course of this project. His encouragements give me confidence to pass through the hardest time and I believe I am on the way to be an independent researcher under his patient supervision.

I also thank to Dr. Stanforth and Dr. Hong Liang for their help and advices. Dr Stanforth provided his knowledge and experience on adsorption and surface precipitation process of phosphate. Dr. Hong Liang provided the electrochemical instrument, which was the main tool in this research. Thanks are also extended to Mr. Zhang Xiaohui and Ms Daw Thin Thin Myint for their previous works, helps and advices.

I thank to Madam Chia Yuit Ching, Susan for the helps in handling the laboratory equipments, Mr. Li Sheng, for providing the willingly helps in the investigation of the morphology of sample surfaces with SEM, and Madam Fam Hwee Koong, Samantha helped in surface analysis with XPS and AFM..I also thank to National University of Singapore for providing the facilities and funds to conduct this project.

Lastly, I wish to express gratitude to my family members and friends for theirs understanding, support, and co-operation.
# Table of Contents

<table>
<thead>
<tr>
<th>Chapter</th>
<th>Introduction</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Copper Corrosion</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>Chemistry of Corrosion</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>Corrosion Control Strategies</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>Chemical Treatment</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>Phosphate</td>
<td>7</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Chapter 2</th>
<th>Literature Review</th>
<th>9</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>Proposed Mechanism for the Inhibitor Effect</td>
<td>9</td>
</tr>
<tr>
<td>2.1.1</td>
<td>General Information for Inhibition Mechanism</td>
<td>9</td>
</tr>
<tr>
<td>2.1.2</td>
<td>Inhibition Efficiency Evaluation Methods</td>
<td>12</td>
</tr>
<tr>
<td>Section</td>
<td>Title</td>
<td>Page</td>
</tr>
<tr>
<td>---------</td>
<td>-------</td>
<td>------</td>
</tr>
<tr>
<td>2.1.2.1</td>
<td>Gravimetric Method</td>
<td>12</td>
</tr>
<tr>
<td>2.1.2.2</td>
<td>Polarization Method</td>
<td>12</td>
</tr>
<tr>
<td>2.1.3</td>
<td>Organic Inhibitor</td>
<td>12</td>
</tr>
<tr>
<td>2.1.4</td>
<td>Surfactant</td>
<td>16</td>
</tr>
<tr>
<td>2.1.5</td>
<td>Polymer Coating</td>
<td>17</td>
</tr>
<tr>
<td>2.1.6</td>
<td>Inorganic Inhibitor</td>
<td>17</td>
</tr>
<tr>
<td>2.2</td>
<td>Phosphate as Corrosion Inhibitor</td>
<td>18</td>
</tr>
<tr>
<td>2.2.1</td>
<td>The Application of Phosphates</td>
<td>18</td>
</tr>
<tr>
<td>2.2.2</td>
<td>The Inhibition Mechanism of Phosphate</td>
<td>20</td>
</tr>
<tr>
<td>2.2.3</td>
<td>Relationship Between Phosphate and Microorganism</td>
<td>25</td>
</tr>
<tr>
<td>2.3</td>
<td>Electrochemical Approaches to Investigate Corrosion Inhibitors</td>
<td>25</td>
</tr>
<tr>
<td>2.3.1</td>
<td>Introduction to Electrochemical Kinetics</td>
<td>26</td>
</tr>
<tr>
<td>2.3.2</td>
<td>The Corrosion Potential</td>
<td>30</td>
</tr>
<tr>
<td>2.3.3</td>
<td>Polarization Methods</td>
<td>30</td>
</tr>
<tr>
<td>2.3.4</td>
<td>Electrochemical Impedance Spectroscopy (EIS)</td>
<td>32</td>
</tr>
<tr>
<td>2.3.4.1</td>
<td>Background on EIS</td>
<td>32</td>
</tr>
<tr>
<td>2.3.4.2</td>
<td>The Equivalent Circuit Model of EIS</td>
<td>35</td>
</tr>
<tr>
<td>2.3.4.3</td>
<td>Electrochemical Interpretation of Equivalent Circuit Elements</td>
<td>36</td>
</tr>
<tr>
<td>2.3.4.4</td>
<td>The Simulation of EIS data: Non-linear Least Squares Fitting</td>
<td>40</td>
</tr>
</tbody>
</table>
2.4 Other Approaches to Evaluate Corrosion Inhibitor Effect
2.4.1 General Introduction to the Surface Analysis Techniques
2.4.2 Application of Surface Analysis Techniques in Copper Inhibitor Research
2.4.3 Electrochemical Quartz Crystal Microbalance Technique

Chapter 3 Materials and Methods
3.1 Copper Coupons and Cleaning Process
3.2 Experimental Solutions
3.3 Monitoring Copper Concentrations
3.4 Monitoring Phosphorous Concentrations
3.5 Immersion Experiments
3.6 Electrochemical Measurements
3.7 Scanning Electron Microscopy Analysis
3.8 X-ray Photoelectron Spectroscopy Analysis

Chapter 4 Results and Discussion
4.1 Effect of Immersion Time
4.1.1 Electrochemical Impedance Spectroscopy
4.1.2 Polarization Results
4.1.3 Surface Morphology
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.1.4</td>
<td>Surface Composition</td>
<td>60</td>
</tr>
<tr>
<td>4.2</td>
<td>Effect of pH</td>
<td>63</td>
</tr>
<tr>
<td>4.2.1</td>
<td>Electrochemical Impedance Spectroscopy</td>
<td>64</td>
</tr>
<tr>
<td>4.2.2</td>
<td>Polarization Results</td>
<td>65</td>
</tr>
<tr>
<td>4.2.3</td>
<td>Surface Composition</td>
<td>67</td>
</tr>
<tr>
<td>4.2.4</td>
<td>Surface Morphology</td>
<td>71</td>
</tr>
<tr>
<td>4.2.5</td>
<td>Concentration of Leached Copper</td>
<td>73</td>
</tr>
<tr>
<td>4.3</td>
<td>Effect of Dosage</td>
<td>76</td>
</tr>
<tr>
<td>4.3.1</td>
<td>Polarization Methods</td>
<td>76</td>
</tr>
<tr>
<td>4.3.2</td>
<td>Surface Morphology</td>
<td>80</td>
</tr>
<tr>
<td>4.3.3</td>
<td>Concentration of Leached Copper</td>
<td>82</td>
</tr>
<tr>
<td>4.3.4</td>
<td>Control Experiments</td>
<td>83</td>
</tr>
<tr>
<td>4.3.4.1</td>
<td>Electrochemical Impedance Spectroscopy</td>
<td>82</td>
</tr>
<tr>
<td>4.3.4.2</td>
<td>Polarization Methods</td>
<td>84</td>
</tr>
<tr>
<td>4.3.4.3</td>
<td>Concentration of Leached Copper</td>
<td>85</td>
</tr>
<tr>
<td>4.4</td>
<td>The Mechanism of Orthophosphate Inhibition</td>
<td>88</td>
</tr>
<tr>
<td>4.4.1</td>
<td>Mechanism Proposed</td>
<td>88</td>
</tr>
<tr>
<td>4.4.2</td>
<td>Results and Discussion for the Proposed Mechanism</td>
<td>90</td>
</tr>
<tr>
<td>4.4.2.1</td>
<td>A Heterogeneous equilibrium is slowly established</td>
<td>90</td>
</tr>
</tbody>
</table>
4.4.2.2. Surface precipitation process 91

4.4.2.3. Desorption of Orthophosphate 93

Chapter 5 Conclusion 95

References 98
SUMMARY

First, the copper corrosion inhibitors and their inhibition mechanisms are introduced. The application and research related to phosphate are described based on the literature survey. Electrochemical approaches and other surface analysis methods that have been employed in inhibitor study are summarized.

Second, materials and methods used in the project were described. Copper coupons of 99.99% purity were immersed in orthophosphate solutions. Various techniques, Electrochemical Impedance Spectroscopy (EIS), Potentiodynamic Scan (PDS), X-ray photoelectron spectroscopy (XPS), Scanning Electronic Microscopy (SEM), Inductively Coupled Plasma - Atomic Emission Spectrometry (ICP-AES) and Inductively Coupled Plasma Mass Spectrometer (ICP-MS), were employed.

Third, the results of the study were presented and discussed. The experiment results of immersion time showed that the scale formed relatively rapidly in the first 15 days. The equivalent circuit model used to simulate the EIS spectra fit the data well and gave information on parameter $R_{ct}$, $R_{film}$ and $Z_{film}$. PDS and XPS results suggested that formation of Cu (I) and Cu (II) species varied with exposure time. In the early stage Cu (II) compounds was the main species while Cu (I) containing products appear with longer immersion time and retard anodic process. SEM images indicated that the pores of the 10-day immersion sample were ~ 0.5 μm in diameter. After 30-day immersion a compact scale structure appeared, which may be due to the cupric phosphate precipitation on the
copper surface. pH is one of the most significant parameters in copper corrosion control by orthophosphate. The inhibition efficiency is higher at low pH (90 percent at pH 7.2) than at high pH (40 percent at pH 8.4). Anodic passivation will occur naturally without addition of orthophosphate at pH of 8.4, if enough long reaction time was given. In the control experiment at pH of 7.2, it was found that anodic region in the polarization curves kept active even after 30 days and the leaching copper concentration was as high as 3.5 ppm. Several peaks in the polarization curve when 1.0 mg P/L orthophosphate was applied after 30 days at pH of 7.2 may indicate different anodic processes occurred at the solid/liquid interface. Based on the results on the dosage effect; addition of high amount of inhibitor will promote the anodic passivation. The growth of surface scale was related to the dosage of inhibitor, 1.0 mg P/L of orthophosphate helped to produce a less porous structure at pH of 7.2. A 0.2 mg P/L dosage at pH 7.2 or 8.4 exhibited similar effect as a 1.0 mg P/L dosage, based on the polarization results and the leaching copper concentration after 5 days. Addition of high amount of orthophosphate in the first stage (1–5 days) followed by a reduced dosage might be feasible to control corrosion. The mechanism research indicated that the corrosion inhibition of orthophosphate to copper is a pretty slow, heterogeneous process. Metal ions spike experiments and desorption of orthophosphate results provided evidence for a proposed 3 steps inhibition mechanism: adsorption-surface precipitation-equilibrium/desorption.
## Nomenclature

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>CPE</td>
<td>Constant phase element used to describe the response of the electrical double layer to the alternative current scan</td>
</tr>
<tr>
<td>DO</td>
<td>Dissolved Oxygen</td>
</tr>
<tr>
<td>O</td>
<td>Finite Warburg impedance for diffusion within finite length (Ω^{-1} s^{1/2})</td>
</tr>
<tr>
<td>$R_{ct}$</td>
<td>Charge transfer resistance (Ω cm²)</td>
</tr>
<tr>
<td>$R_p$</td>
<td>Polarization resistance (Ω cm²)</td>
</tr>
<tr>
<td>Z</td>
<td>Diffusion impedance (Ω cm²)</td>
</tr>
</tbody>
</table>
## List of Figures

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Figure 2.1</td>
<td>Simplistic conceptualization of factors influencing soluble copper concentrations at equilibrium after stagnation in waters dosed with hexametaphosphate.</td>
<td>22</td>
</tr>
<tr>
<td>Figure 2.2</td>
<td>Tafel Plot</td>
<td>28</td>
</tr>
<tr>
<td>Figure 2.3</td>
<td>The EIS spectra with infinite Warburg impedance</td>
<td>38</td>
</tr>
<tr>
<td>Figure 3.1</td>
<td>The configuration of three-electrode setup for electrochemical tests</td>
<td>48</td>
</tr>
<tr>
<td>Figure 4.1</td>
<td>A Nyquist Plot for different immersion times on copper corrosion at pH of 8.0, 1.0 mg P/L and 4.0 mg/L of chlorine added and the solution was replaced every 24 hours</td>
<td>50</td>
</tr>
<tr>
<td>Figure 4.2</td>
<td>An equivalent circuit to fit the EIS data for copper corrosion in the presence of chlorine, inhibited by orthophosphate</td>
<td>51</td>
</tr>
<tr>
<td>Figure 4.3</td>
<td>The relationships between resistance and immersion time, where R_p (EIS) was the polarization resistance extracted from EIS spectroscopy and R_p (TS) was calculated by Tafel slopes (Equation 2.1).</td>
<td>53</td>
</tr>
<tr>
<td>Figure 4.4</td>
<td>Steady state polarization curves for the copper coupons at pH of 7.2 after different immersion times, where 4.0 mg/L chlorine was added and replaced every 24 hours</td>
<td>56</td>
</tr>
<tr>
<td>Figure 4.5 (a)</td>
<td>Steady state polarization curves for the copper coupons at pH of 8.4 after different immersion times, where 1.0mg P/L and 4.0 mg/L chlorine were added and the solution was replaced every 24 hours.</td>
<td>57</td>
</tr>
<tr>
<td>Figure 4.5 (b)</td>
<td>Steady state polarization curves for the copper coupons at pH of 8.4 after different immersion times, where 4.0 mg/L chlorine was added and replaced every 24 hours, no inhibitor was present.</td>
<td>57</td>
</tr>
<tr>
<td>Figure 4.5 (c)</td>
<td>Steady state polarization curves for the copper coupons at pH of 8.4 after 30 days of immersion, where 4.0 mg/L chlorine was added and replaced every 24 hours.</td>
<td>58</td>
</tr>
</tbody>
</table>
Figure 4.6  The SEM micrographs of copper surface at pH of 8.0 after 10 days of immersion (a) x 5,000 (b) x 10,000; 35 days of immersion (c) x 5,000 (d) x 10,000. 1.0 mg P/L orthophosphate and 4.0 mg/L chlorine were added and the solution was replaced every 24 hours

Figure 4.7  Cu 2p (a), O 1s (b) and P 2p (c) XPS spectra of the protective film formed after 8 and 30 days of immersion at pH of 7.2, with addition of 1.0 mg P/L and 4.0 mg/L Chlorine

Figure 4.8  Cu 2p (a), O 1s (b) and P 2p (c) XPS spectra of the protective film formed after 8 and 30 days of immersion at pH of 8.4, with addition of 1.0 mg P/L and 4.0 mg/L Chlorine and the solution was replaced every 24 hours

Figure 4.9  A Nyquist Plot for different pH after 10 days of immersion, 1.0 mg P/L and 4.0 mg/L chlorine were added and the solution was replace every 24 hours

Figure 4.10  Steady state polarization curves for the copper coupons in solution after 30 days of immersion at different pH conditions, 1.0 mg P/L phosphate and 4.0 mg/L chlorine were added and the solution was replace every 24 hours

Figure 4.11  Cu 2p(a), O 1s (b), P 2p (c) and Cl 2p (d) XPS spectra of the protective film formed after 30 days of immersion at pH of 7.2, 8.0 and 8.4, 1.0 mg P/L and 4.0 mg/L chlorine were added and the solution was replaced every 24 hour

Figure 4.12  Cl 2p XPS spectra of the protective films formed after 30 days of immersion at pH of 7.2 and 8.4, 1.0 mg P/L and 4.0 mg/L chlorine were added and the solution was replace every 24 hour, (a) pH of 7.2; (b) pH of 8.4

Figure 4.13  The SEM micrographs of copper surface after 30 days of immersion, x10,000 (a) control experiment at pH of 7.2 (b) 1.0 mg P/L added at pH of 7.2 (c) control experiment at pH of 8.4 (d) 1.0 mg P/L added at pH of 8.4, 4.0 mg/L chlorine was added and the solution was replace every 24 hours

Figure 4.14  Effect of pH and inhibitor dosage to copper corrosion in 10 mM MOPS buffer solution, 4.0 mg/L chlorine, 0.2 mg P/L or 1.0 mg P/L added and replaced every 24 hours, exposure time 30 days, (a) pH of 7.2 ; (b) pH of 8.4
Figure 4.15 Steady state polarization curves for the copper coupons at pH of 7.2 and 8.4 after 2 days of immersion, where 4.0 mg/L chlorine was added and the solution was replaced every 24 hours, different dosages of orthophosphate were applied

Figure 4.16 Steady state polarization curves for the copper coupons at pH of 7.2 after 2 days of immersion, where 4.0 mg/L chlorine was added and the solution was replaced every 24 hours, different dosages of orthophosphate were applied

Figure 4.17 Steady state polarization curves for the copper coupons at pH of 7.2 and 8.4 after 6 days of immersion, where 4.0 mg/L chlorine was added and the solution was replaced every 24 hours, different dosages of orthophosphate were applied

Figure 4.18 Steady state polarization curve for the copper coupons at pH of 7.2 after 30 days of immersion, where 4.0 mg/L chlorine was added and the solution was replaced every 24 hours, different dosages of orthophosphate were applied

Figure 4.19 The SEM micrographs of copper surface after 30 days of immersion at pH of 7.2 with different dosages of orthophosphate, x10,000 (a) control experiment (b) 0.1 mg P/L (c) 0.2 mg P/L (d) 0.1 mg P/L, 4.0 mg/L chlorine was added and the solution was replace every 24 hours

Figure 4.20 Effect of orthophosphate dosage to copper corrosion in 10 mM MOPS buffer solution at pH of 8.0 after 6 days of immersion, 4.0 mg/L chlorine and orthophosphate were added and the solution was replaced every 24hous

Figure 4.21 A Nyquist Plot for copper corrosion at different pH after 8 days of immersion, 4.0 mg/L chlorine was added and replaced every 24 hours, control experiment

Figure 4.22 Steady state polarization curves for the copper coupons at pH of 7.2 and 8.4 after different immersion times, where 4.0 mg/L chlorine was added and replaced every 24 h, control experiments

Figure 4.23 The 24 hour accumulated concentrations at pH of 7.2, 8.0 and 8.4, 4.0 mg P/L was added and replaced every 24 hours, control experiment
| Figure 4.24 | The 24 hour accumulated concentrations at pH of 7.2, 8.0 and 8.4 at the 34th days of immersion, 1.0 mg P/L and 4.0 mg P/L were added and the solution was replaced every 24 hours |
| Figure 4.25 (a) | Proposed adsorption process |
| Figure 4.25 (b) | Proposed precipitation process |
| Figure 4.25 (c) | Proposed equilibrium process |
| Figure 4.26 | Adsorption curves of different concentrations of orthophosphate at pH of 7.2 within 70 hours |
| Figure 4.27 | Spike experiment, shown as the phosphate surface coverage vs time, 300 ppb orthophosphate was initially added, different concentrations of copper ions were spiked |
| Figure 4.28 | Spike experiment, shown as the phosphate surface coverage vs time, 300 ppb orthophosphate was initially added, different concentrations of Ca^{2+} and Pb^{2+} ions were spiked |
## List of Tables

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Table 1.1</td>
<td>Galvanic series for common metals</td>
<td>5</td>
</tr>
<tr>
<td>Table 1.2</td>
<td>Commonly used phosphorous inhibitor compounds</td>
<td>8</td>
</tr>
<tr>
<td>Table 2.1</td>
<td>Possible drawbacks of phosphate based inhibitors perceived by water utilities (McNeill and Edwards, 2001)</td>
<td>18</td>
</tr>
<tr>
<td>Table 2.2</td>
<td>Reported minerals containing copper and orthophosphate</td>
<td>24</td>
</tr>
<tr>
<td>Table 2.3</td>
<td>Equilibrium reactions in copper solubility programs, and corresponding log K and β values</td>
<td>24</td>
</tr>
<tr>
<td>Table 2.4</td>
<td>Circuit elements used in circuit models</td>
<td>34</td>
</tr>
<tr>
<td>Table 2.5</td>
<td>Methods of surface analysis</td>
<td>42</td>
</tr>
<tr>
<td>Table 4.1</td>
<td>Elements of the equivalent circuit of pH of 8.0, 1.0 mg P/L and 4.0 mg/L chlorine at different immersion times</td>
<td>54</td>
</tr>
<tr>
<td>Table 4.2</td>
<td>The comparison of polarization resistance values calculated by EIS and Tafel Slopes</td>
<td>54</td>
</tr>
<tr>
<td>Table 4.3</td>
<td>Elements of the equivalent circuit after 10 days of immersion, 1.0 mg P/L and 4.0 mg/L chlorine were added the solution was replace every 24 hours at pH of 7.2, 7.6 and 8.4.</td>
<td>66</td>
</tr>
<tr>
<td>Table 4.4</td>
<td>The corrosion potential and corrosion current with different dosage of inhibitor at pH of 7.2 after 30 days of immersion</td>
<td>79</td>
</tr>
<tr>
<td>Table 4.5</td>
<td>The concentration (ppb) of phosphorous during desorption process. 200ppb and 400ppb orthophosphate was added initially until 72h. Then the copper coupons were immersed in the 10mM MOPS buffer solution at pH of 7.2. The leaching concentration of phosphorus is monitored by ICP-MS</td>
<td>94</td>
</tr>
</tbody>
</table>
CHAPTER 1
INTRODUCTION

1.1 Copper Corrosion

Corrosion is a major problem in most industrial sectors, affecting the performance of various materials. Failures due to corrosion have significant economic consequences in terms of repair and replacement costs, and have additional implications for both safety and environmental pollution.

Copper and copper-containing alloys have become the most widely used materials for plumbing systems since the early 1800s in UK (Skeat, 1969). They are ubiquitous due to excellent corrosion resistance, mechanical strength, and resistance to the external environment, as well as the ability to distribute water without contaminating it.

The main factors that may influence the corrosion rate of copper in the drinking water system are as follow:

1. the condition of the metal surface (deposits on the copper surface may introduce pitting corrosion);

2. the characteristics of the aqueous environment, including pH, oxygen concentration, organic matter, hardness, the concentrations of aggressive ions (Cl⁻, SO₄²⁻) and microbiological organisms;

3. Flow rate (high flow velocity of water will increase the oxygen access to the copper surface and remove the protective scales).
Copper rarely occurs naturally in drinking water, but can occur as a result of corrosion in the water system. In 1974, the U.S. Congress passed the Safe Drinking Water Act. This law requires EPA to determine safe levels of chemicals in drinking water, which do or may cause health problems. The Maximum Contaminant Level Goal for copper has been set at 1.3 parts per million (ppm), a value that the USEPA believes would not cause any of the potential health problems. In the UK the risking value of copper is set to 2.0 ppm from the Water Supply (water quality) Regulations (2000). Since copper contamination generally occurs from corrosion of household copper pipes, it cannot be directly detected or removed at the water source. Therefore, the USEPA requires water supplies to control the corrosiveness of their water if the level of copper at home taps exceeds the Action Level of 1.3 ppm.

1.2 Chemistry of Corrosion

Virtually, almost all kinds of corrosion reactions are electrochemical in nature. At the anodic sites on the metal surface, an oxidization reaction occurs:

\[
M \leftrightarrow M^{n+} + ne^{-} \quad (1.1)
\]

The redox reaction releases \( M^{n+} \) ions into the solution. The electrons will move from anode to cathode and may react with \( H^+ \) or \( O_2 \) (aq) as described in the following cathodic reactions:

\[
2H^+ + 2e^- \leftrightarrow H_2 \quad (1.2)
\]

which is referred to as the hydrogen evolution corrosion, or
\[ \text{O}_2 (\text{aq}) + 2\text{H}_2\text{O} + 4\text{e}^- \rightleftharpoons 4\text{OH}^- \quad (1.3) \]

if there is oxygen existing on the cathode area.

In the case of 1.3, the $M^{\text{m+}}$ will react further with $\text{OH}^-$ to form a metal hydroxide, which might also be oxidized into a more thermodynamically stable form.

The corroding piece of metal is described as a “mixed electrode” since simultaneous anodic and cathodic reactions are proceeding on its surface. The mixed electrode has a complete electrochemical cell on a metal surface.

This process is well summarized in Nimmo and Hinds’ study (2003):

1. Metals are involved and need a medium to move in (usually water)
2. Oxygen is involved and needs to be supplied
3. The metal has to be willing to give up electrons to start the process
4. A new product is formed and this may react again or could be protective of the original metal.
5. A series of simple steps are involved and a driving force is needed to achieve them.

Therefore, the most important action is to impede the corrosion process and to slow the corrosion reaction to a manageable rate.

**1.3 Corrosion Control Strategies**

It is essential for water supply plant personnel to be aware of the potential corrosion to occur and to develop an appropriate strategy in relation to design, materials selection,
environmental control, protection, monitoring and life assessment. Such strategies will reduce the likelihood of costly failure and unscheduled shut-down. Widely accepted control strategies are shown as below:

1. Selection of materials;
2. Coatings;
3. Chemical treatment;
4. Cathodic protection.

Metal with low corrosion potential (i.e., ranks low in the galvanic series) or those that form a protective oxide films on the surface to impede the redox reaction, such as aluminum.

The coatings may consist of another metal, for example, zinc or tin coating on steel and organic coatings, such as resins, plastics or paints.

Cathodic protection is an electrochemical method, which stifles the anodic reaction by using a DC power supply (impressed current), or by coating a more active metal on the original metal surface.

<table>
<thead>
<tr>
<th>Table 1.1 Galvanic series for common metals.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anode</td>
</tr>
<tr>
<td>-------</td>
</tr>
<tr>
<td>Magnesium</td>
</tr>
<tr>
<td>Aluminum</td>
</tr>
</tbody>
</table>
### Chemical Treatment

Inhibitors are used in a wide range of applications, such as the oil and gas exploration and production industry, the petroleum refining industry, the chemical industry, heavy industrial manufacturing industry and water treatment facilities. The total consumption of corrosion inhibitors in the United States has doubled from approximately $600 million in 1982 to nearly $1.1 billion in 1998. A particular advantage of corrosion inhibition is that it can be implemented or changed in situ without disrupting a chemical process.

The inhibitors usually play the corrosion mitigation role through forming a protective layer on the metal surface that limit the reaction at either anode or cathode. The following divides the inhibitors into three categories:

<table>
<thead>
<tr>
<th>Metal</th>
<th>Reaction</th>
<th>Potential (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zinc</td>
<td>Zn(s) → Zn^{2+} + 2e^-</td>
<td>+0.76</td>
</tr>
<tr>
<td>Steel or Iron</td>
<td>Fe(s) → Fe^{2+} + 2e^-</td>
<td>+0.44</td>
</tr>
<tr>
<td>Nickel</td>
<td>Ni(s) → Ni^{2+} + 2e^-</td>
<td>+0.25</td>
</tr>
<tr>
<td>Lead</td>
<td>Pb(s) → Pb^{2+} + 2e^-</td>
<td>+0.13</td>
</tr>
<tr>
<td>Copper/Brass</td>
<td>Cu(s) → Cu^{2+} + 2e^-</td>
<td>-0.345</td>
</tr>
<tr>
<td>Silver</td>
<td>Ag(s) → Ag^+ + e^-</td>
<td>-0.8</td>
</tr>
<tr>
<td>Platinum</td>
<td>Pt(s) → Pt^{2+} + 2e^-</td>
<td>-1.42</td>
</tr>
</tbody>
</table>

1. anodic inhibitor, which retards the anodic process; it is classified as a dangerous inhibitor, since it can cause pitting corrosion. Examples are chromate and nitrite as well as the precipitating film type as orthophosphate and silicate;

2. cathodic inhibitor, which suppresses the cathodic reactions by reducing available area for reactions. Examples include zinc, polyphosphate and carbonate alkalinity;

3. mixed inhibitor, which combines anodic and cathodic inhibitors to achieve the inhibition effect.

For the corrosion inhibition treatment of potable water, the commonly applied chemical inhibitors are silicate, polyphosphate, orthophosphate, zinc polyphosphate and zinc orthophosphate. The dosage of these chemicals is generally limited to at most 10 mg/L (National Sanitation Foundation, 1988).

The disadvantages of adding inhibitors are

1. once corrosion inhibitors are being used in a system it is difficult to stop their use;

2. in the future, the use of some common corrosion inhibitors may be restricted due to environmental impact and regulations.

1.5 Phosphate

It is well known that phosphorous is an essential element for the growth of algae and other biological organisms. The common forms of phosphorous that are found in aqueous solutions include orthophosphate, polyphosphate and organic phosphate. Either polyphosphates or orthophosphate are used in public water supplies as a means
of controlling corrosion (Table 1.2). It has been found that polyphosphate can be hydrolyzed in aqueous solutions and it can revert to the orthophosphate form:

$$\text{Na}_4\text{P}_2\text{O}_7 + \text{H}_2\text{O} \rightarrow 2\text{Na}_2\text{HPO}_4$$

This reaction is quite slow and the rate of conversion to orthophosphate is a function of temperature and increases rapidly as the temperature approaches the boiling point of water.

Table 1.2 Commonly used phosphorous inhibitor compounds.

<table>
<thead>
<tr>
<th>Name</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Orthophosphates</td>
<td></td>
</tr>
<tr>
<td>Trisodium phosphate</td>
<td>Na$_3$PO$_4$</td>
</tr>
<tr>
<td>Disodium phosphate</td>
<td>Na$_2$HPO$_4$</td>
</tr>
<tr>
<td>Monosodium phosphate</td>
<td>NaH$_2$PO$_4$</td>
</tr>
<tr>
<td>Polyphosphates</td>
<td></td>
</tr>
<tr>
<td>Sodium hexametaphosphate</td>
<td>Na$_3$(PO$_3$)$_6$</td>
</tr>
<tr>
<td>Sodium tripolyphosphate</td>
<td>Na$_5$P$<em>3$O$</em>{10}$</td>
</tr>
<tr>
<td>Tetrasodium pyrophosphate</td>
<td>Na$_4$P$_2$O$_7$</td>
</tr>
</tbody>
</table>
CHAPTER 2
LITERATURE REVIEW

2.1 Proposed Mechanism for the Inhibitor Effect

2.1.1 General Information for Inhibition Mechanism

Even though research on inhibitors has been carried on since the last half of the nineteenth century, the exact mechanism by which inhibition takes place on the metal is still not well understood.

Earlier, the evaluation of inhibitor effectiveness was based on a trial and error process, and the main scientific technique employed was to compare the loss in weight of samples. With the availability of modern computerized electrochemical and surface analysis instruments, more efforts are being directed towards probing the mechanisms of corrosion inhibition processes. A combination of electrochemical studies and surface analysis is well suited for elucidating the mechanism of corrosion inhibition.

The advent of modern surface analysis techniques, such as X-ray photoelectron spectroscopy, Auger electron spectroscopy and secondary ion mass spectroscopy make it possible to study the structure and composition of inhibitor films on metal surface in details.

Extensive basic studies about inhibitors and the factors governing the effectiveness have only been in progress for the last fifty years (Sastri, 1998). In general, descriptions of the inhibition mechanism invoke two processes in the action of the inhibitor on the metal surface: first, the transport of inhibitor to the metal surface,
followed by the chemical/physical interaction between the inhibitor and the metal surface.

When discussing copper corrosion inhibitors, most researchers will consider the surface product, such as oxides and metal salt into the mechanism of inhibitor actions. Although the naturally formed Cu$_2$O film has been recognized as a good barrier to copper corrosion, the addition of inhibitor will promote its protective properties. However, this further complicates the corrosion system by involving various processes.

The Anodic Process:

The widely accepted mechanism for anodic dissolution of copper proceeds in two steps:

$$\text{Cu} \rightarrow \text{Cu}^{+} + \text{e}^{-} \quad (2.1)$$

$$\text{Cu}^{+} \rightarrow \text{Cu}^{2+} + \text{e}^{-} \quad (2.2)$$

In the neutral aqueous environment, where oxygen is present, the overall reaction will proceed as follows:

$$\text{Cu} + \frac{1}{2} \text{O}_2 + \text{H}_2\text{O} \rightarrow \text{Cu}^{2+} + 2\text{OH}^{-} \quad (2.3)$$

This process is influenced by the copper ion diffusion; however when chloride ions are present in the solution, then the process will become:

$$\text{Cu}^{+} + \text{Cl}^{-} \rightarrow \text{CuCl}^{0} + \text{e}^{-} \quad (2.4)$$

$$\text{CuCl}^{0} + \text{Cl}^{-} \rightarrow \text{CuCl}_2^{-} \quad (2.5)$$

The dissolution process is controlled by the mass transfer of CuCl$_2^-$ from the electrode surface to the bulk solution. The reactions (2.4) and (2.5) together with the mass transfer of CuCl$_2^-$ have been used to explain the kinetics of copper dissolution in the
apparent Tafel region.

The Cathodic Process

The cathodic reduction of oxygen can be expressed either by a direct four-electron transfer as follows:

\[ \text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O} \]  \hspace{1cm} (2.6)

or by two consecutive two-electron steps involving a reduction to hydrogen peroxide first as follows:

\[ \text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O}_2 \]  \hspace{1cm} (2.7)

followed by a further reduction step (Jinturkar et al., 1984):

\[ \text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow 2\text{H}_2\text{O} \]  \hspace{1cm} (2.8)

No matter when the 4 electrons or 2 electrons process occurs, the transfer of oxygen from the bulk solution to the copper/solution interface will strongly affect the rate of oxygen reduction reaction.

Following introducing an inhibitor into the system, adsorption of the inhibitor molecule at the solid/liquid interface occurs, which changes the potential difference between the metal electrode and the solution due to the non-uniform distribution of electric charges. In a simple expression, the simple mechanism of organic inhibitors has been suggested as

\[ \text{Cu} + \text{Inhibitor} \rightarrow \text{Cu-Inhibitor film} \]  \hspace{1cm} (2.9)

The inorganics are believed to react with metal ions to precipitate as scale on the metal surface and the scale causes the corrosion inhibition.
In the following sections, the mechanisms for different types of inhibitors will be discussed in detail.

2.1.2 Inhibition Efficiency Evaluation Methods

2.1.2.1 Gravimetric method (weight loss method)

\[ IE = 100 \times \left( \frac{\Delta \omega \omega - \Delta \omega \omega}{\Delta \omega \omega} \right) \]  

(2.10)

where \( \Delta \omega \omega \) and \( \Delta \omega \omega \) are the weight losses of the specimens after immersion without and with inhibitors, respectively.

2.1.2.2 Polarization method

\[ IE = 100 \times \left( \frac{i^0 - i}{i^0} \right) \]  

(2.11)

\( i^0 \) and \( i \) are the corrosion current densities in the absence or presence of an inhibitor.

Meanwhile, according to the relationship between the corrosion current density and the charge transfer resistance, it is easy to deduce that:

\[ IE = 100 \times \left( \frac{R_p - R_p^0}{R_p^0} \right) \]  

(2.12)

\( R_p \) and \( R_p^0 \) are the charge transfer resistances or polarization resistances in the presence and absence of an inhibitor.

IE affects the surface coverage by inhibitors on the metal surface, assuming an adsorption mechanism for corrosion inhibition.

2.1.3 Organic Inhibitor

The inhibition efficiency of organic inhibitors strongly depends on the structure and chemical properties of the species formed under the experimental conditions. The
extent of adsorption is dependent upon the electronic structure of the metal and the inhibitor.

Among the organic inhibitors used for the protection of copper, N-heterocyclic compounds such as benzotriazole, indazole and mercaptobenzothiazole are the most effective ones, and have been investigated intensively.

Benzotriazole (BTA) has been used satisfactorily as a corrosion inhibitor for copper and copper alloys for more than 50 years (Proctor and Gamble Ltd. British Patent No.652339, 1947). The BTA-Cu-BTA-Cu film formed through the reaction between BTA and cuprous ions is believed to be useful in preventing copper staining and tarnishing. The inhibitor, which contains a nitrogen atom, can coordinate with copper through the lone pair of electrons to form complexes. Then complexes are generally believed to be polymeric in nature and form a protective film on the copper surface, which acts as a barrier to oxide film formation. The corrosion inhibition may also be due to physisorption or chemisorption onto the copper surface. Tommesani et al. (1997) investigated the inhibiting effect of 1,2,3-Benzotriazole (BTA) alkyl derivative films against copper corrosion in 3.5% NaCl neutral pH solutions, and postulated that the inhibitor retards the oxygen cathodic process. The film effectiveness increased with the alkyl chain length and coating treatment. A similar conclusion was made by Frignani et al. (1999), the introduction of aliphatic substituents into the benzene ring improve the inhibition effects of BTA by promoting the rapid formation of thicker, less defective and more hydrophobic, corrosion-resistant films onto the copper surface.

The benzotriazole/Cu system has been studied extensively by different techniques. In
the 1970s, Chin et al. (1973) conducted galvanostatic polarization to research the protective scale, where a direct current pulse technique was applied for the differential capacitance measurements. Hashemi and Hogarth (1988) applied surface techniques to establish a model for the inhibition mechanism. According to this model, disproportionation of the Cu (I) ions followed by the formation of a CuCl layer constitutes a suitable base for Cu-inhibitor complex formation. The thickness of the final complex layer is mainly governed by an intermediate stage of CuCl formation. 

Huynh et al. (2002a, 2002b) carried out the research about CBTA (carboxybenzotriazole) derivatives and found that the inhibition effect of alkyl esters of CBTA was influenced by pH. At lower pH (i.e., less than 8), the IE reached 96% and both the anodic and cathodic reaction were retarded. They attribute this phenomenon into the length of the alkyl chain, which performs different roles under different pH conditions. At lower pH van der Waals' forces of attraction contribute to the chemisorption process and at high pH values, the inhibition effect resulted from the formation of disordered polymeric films, as shown by the SERS measurement.

Yan and Lin (2000) conducted protective film research of 2-mercaptobenzoxazole in a NaCl solution. The point worth mentioning is the role of the electrolyte solution. They believe that the involvement of Cl$^{-}$ (Equations 2.4 and 2.5) promote the inhibition reaction, and the AES results supported this.

$$\text{CuCl}_2 + \text{MBO} \rightarrow \text{inhibition film} + 2\text{Cl}^- \quad (2.13)$$

It is also a common way to enhance the inhibition ability by modifying substituents and functional groups so that the inhibition mechanism is changed from the only
physical attached state to chemically adsorbed state. Subramanian et al. (2002) studied and compared the effect of adsorption of some azoles, including benzotriazole(BTA), mercaptobenzothiazole (MBT), benzimidazole (BIMD), mercaptobenzimidazole (MBIMD), and imidazole(IMD) on copper passivation in alkaline medium. These azoles showed a good linear fit to the Langmuir adsorption isotherm. More than 95% surface coverage (i.e., inhibition efficiency) was achieved under the experimental conditions. However, the triazole and its derivatives are replaced by the more environmentally friendly inhibitors, BTA for instance, which are excellent corrosion inhibitors, but highly toxic. Efforts are now being focused on the development of “green” corrosion inhibitors, the chemicals with satisfactory inhibition efficiency, but a low risk of environmental pollution. In the discharge water, the impact of inhibitors on the aquatic organism has not been fully understood, but it is well known that the chemical ingredients of the inhibitors are harmful to marine life. In Europe, the European Economic Community (EEC) has assigned the Paris Commission (PARCOM) with the task of providing environmental guidelines to corrosion inhibitors. The toxicity (LC$_{50}$ and EC$_{50}$), biodegradation (the duration over which the chemicals will exist in the environment) and bioaccumulation (the partition coefficient of chemicals between octanol/water phases, which can fairly accurately predict the organism cell membrane/water interface) are suggested by PARCOM to evaluate the environmental impact of corrosion inhibitors. Therefore, the research to environmental friendly inhibitors demands more attention and additional research.
Cicileo et al. (1999) studied the oxime group-contained organic inhibitor, salyciladoxime ($10^{-3}$ M + 0.1 M NaCl) and α-Benzoinoxime (a saturated solution). A polymeric Cu (II)-inhibitor complex composition was suggested by the measurement of XPS and FTIR. The XPS results also suggest that the composition of the protective film is the same from the first day to the ninth day, and the film became more compact with increasing time from SEM images.

The inhibition effect of BHAs in 0.5 M NaCl solution was studied by Shaban et al. (1998). A complex layer of the inhibitor and copper corrosion products with low solubility is proposed to account for the protective effect in chloride solutions. The most effective inhibitors based on the EIS result are $p$-Cl-BHA and $p$-N-BHA.

### 2.1.4 Surfactant

The structural property of a surfactant allows its application as an inhibitor to copper corrosion. Adsorption of surfactants is more complex than common inhibitors, it may absorb on a solid surface through electrostatic attraction or chemisorption depending on the charge of the solid surface and free energy of transferring hydrocarbons chains from water to the solid surface. Sufficiently high surfactant concentration under some conditions may adsorb strongly on the metal surface and form an organized structure, which can effectively prevent metal corrosion (Luo et al., 1998).

The inhibitive effect of a surfactant CTAB (cetyltrimethylammonium bromide) in aerated sulfuric acid solutions was investigated by Ma et al. in 2001. Based on the PDS results, the CTAB inhibits either the anodic reaction or the cathodic reaction, a
mixed-type inhibitor to copper corrosion in sulfuric acid. The long alkyl chains, n-cetyl, enable the CTAB offer better inhibition and the chemisorption of $\text{C}_{16}\text{H}_{33}\text{N} (\text{CH}_3)^+$ ions on the surface strengthened the compactness of the film with immersion time. In 2003, their research expanded on the different types of surfactant mechanism, such as the cationic surfactant CTAB, anodic surfactants SDS and SO as well as the nonionic surfactant TWEEN-80 and they proposed the adsorption models of surfactants on the copper surface.

2.1.5 Polymer coatings

Polymer coatings, such as PAP (polyaminophenol) film were studied by Guenbour et al. (2000). They concluded that

1. In the initial immersion stage, the electrolyte solution penetration in the coating defects cause an increase of capacitance of polymer film, but a decrease of resistance, both polarization resistance and polymer film resistance.

2. After longer immersion times (24h), the film resistance increases until a steady state is reached, which might be caused by the accumulation of corrosion products that sealed the pores of the polymer.

2.1.6 Inorganic Inhibitors

In contrast to organic inhibitors, the developments in this field have not reached the same level of sophistication as the organic inhibitors.

The mechanism of corrosion inhibition by oxyanions, chromate, molybdate and
tungstate, for instance, to mild steel has been clearly elucidated by the electrochemical techniques coupled with modern surface analysis techniques (Sastri, 1998). Other inorganic inhibitors (e.g., silicates, phosphates, chromates, arsenates and carbonates, etc.) are suggested to promote the formation of a precipitate on the metal surface, or possibly catalyzing the formation of a passive layer.

2.2 Phosphate as Corrosion Inhibitor

2.2.1. The Application of Phosphates

Phosphates can be applied as phosphoric acid, combinations of orthophosphoric acid, zinc orthophosphate and polyphosphate in many water treatment applications. The possible drawbacks of these phosphate-based inhibitors are shown in Table 2.1.

Table 2.1. Possible drawbacks of phosphate based inhibitors perceived by water utilities (McNeill and Edwards, 2001).

<table>
<thead>
<tr>
<th>Issue</th>
<th>Concerns</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phosphate-based inhibitors</td>
<td>- Increase in bacterial/microorganism/algal growth</td>
</tr>
<tr>
<td></td>
<td>- Increased phosphate loads in wastewater</td>
</tr>
<tr>
<td></td>
<td>- Effect of higher phosphate on industrial users</td>
</tr>
<tr>
<td>Zinc orthophosphate</td>
<td>- High zinc concentrations in wastewater sludges</td>
</tr>
<tr>
<td></td>
<td>- Effect of higher zinc on industrial users</td>
</tr>
<tr>
<td>Polyphosphate</td>
<td>- Possible increase in metal solubility</td>
</tr>
<tr>
<td></td>
<td>- Interference with the deposition of a protective calcium carbonate film</td>
</tr>
</tbody>
</table>

In United States, 53% of water utilities reported using the phosphate based inhibitor for copper corrosion control in 1992. About 33% of utilities dosing phosphate
inhibitors used either orthophosphate or zinc orthophosphate, while the remaining 67% dosed polyphosphate alone or a blend of polyphosphate or orthophosphate (Dodrill, 1992). A recent industry survey conducted by McNeill and Edwards (2002) showed that a dramatic increase in orthophosphate use and corresponding decrease in poly/orthophosphate blends, which is likely a positive trend given the potential for polyphosphate to increase soluble metal concentration in finished drinking water. It has been found that in some cases, polyphosphate can increase the concentrations of lead and copper in a water system instead of decreasing them. The factors that allow this detrimental phenomenon to occur have not been identified. Therefore, the use of polyphosphates for corrosion control is risky (Edwards, et al., 2002). The practical survey of polyphosphates was carried out by Cantor et al. (2000) based on three Wisconsin utilities. Their results uncovered possible negative consequences of using polyphosphate for corrosion control. And they strongly suggested that water utilities should conduct offline tests before using polyphosphate and full scale systems should be frequently monitored after polyphosphate addition.

In a USEPA survey of orthophosphate protection of copper and its alloys in drinking water distribution systems, Lytle and Schock (1996) found that orthophosphate demonstrated a satisfactory inhibition effect on lead leaching from brass pipes. It works as an “aging accelerator”, which means that the leaching of lead dramatically decreased and the duration for the stabilization of leached metal concentration was decreased. However, as for the inhibition effect on pure copper, the result was somewhat confusing. During the 140-day sampling at pH of 7.5, the coupon with a
dosage of 0.5 mg P/L exhibits slightly lower copper leaching than the one with no inhibitor added. And the higher dosage of orthophosphate (i.e., 3.0 mg P/L), does not show a better inhibition effect. A 1.0 mg P/L dosage of orthophosphate is obtained in the experiments based on the optimum dosage discussed in the literature. The effectiveness of the dosage varies based on the pH, NOM, temperature and DIC concentration (Sheihham and Jackson, 1981, Gregory and Hackson, 1984 and Colling, 1992).

Kilincceker et al. (2002) described the inhibition effect of phosphate ions in sulphate solutions within a wide pH range (i.e., 2.1, 7.2 and 12.3) and a wide temperature range (i.e., 293, 313, 333 and 353 K). They confirmed that orthophosphates are suitable for the protection of copper at low temperatures and at higher pH values.

2.2.2 The Inhibition Mechanism of Phosphate

Although phosphate-based inhibitors are widely applied in water utility corrosion control, very little is currently known regarding phosphate inhibition of copper corrosion by product release.

Earlier research on inhibition mechanism by Andrzejaczek (1979) employed gravimetric and potentiostatic techniques to investigate the inhibition effect of Na₃PO₄ in tap water to iron corrosion and found that phosphate is adsorbed in the form of positively charged colloidal particles on the cathode areas of the metal. The degree of coverage versus log [concentration] of orthophosphate ions shows a good agreement with Frumkin’s isotherm and the calculated standard free energy of adsorption to be
-28.8 kJ \cdot \text{mol}^{-1}.

Reiber (1989) and Schock (1995) postulated that the formation of \( \text{Cu}_3(\text{PO}_4)_2 \) or similar scale on the copper pipe surface controls the leaching of copper (Figure 2.1). The phosphate films appear to passivate the corroding surface by changing the fundamental nature of the anodic reaction while some corrosion inhibitors, especially organic chemicals, form a physical barrier to corrosion.

In discussions the effect of orthophosphate on drinking water cuprosolvency, Schock and Lytle (1995) hypothesized that the addition of orthophosphate might cause alteration of the nature or the growth rate of passivating films, or the kinetics of oxidation/reduction reactions at the copper pipe surface, and XRD measurements indicated that the copper pipe surface demonstrated substantial differences in appearance and mineralogy with and without the presence of 3 mg PO\(_4\)/L. Edwards et al. (2002) suggested that the addition of phosphate will produce a low solubility scale cupric phosphate on the pipe surface at short immersion times before the natural insoluble malachite scale eventually forms.
The inhibition mechanism of polyphosphate starts with polyphosphate being hydrolyzed into orthophosphate, which is the active part in the inhibition process. Szklarska-Smialowska and Mankowski (1967) described a two step mechanism, where the first step is the stimulation of the anodic dissolution process; the free Fe$^{2+}$ ions stimulate the hydrolysis of the polyphosphate to HPO$_4^{2-}$ and subsequently, the formation of a protective layer of calcium phosphate as follows:

$$2\text{HPO}_4^{2-} + 2\text{OH}^- + 3\text{Ca}^{2+} \rightarrow \text{Ca}_3(\text{PO}_4)_2 + 2\text{H}_2\text{O}$$

The source of hydroxyl ions is the cathodic reduction of oxygen. This cathode action of orthophosphate as an inhibitor of iron corrosion of iron in water was suggested by earlier researchers.

In Reiber’s (1989) study, the copper phosphate protective films were found to be labile
in low pH waters. Exposure to pH values less than 6 degrades the film, destroying its protective qualities within a matter of hours for either young or well aged phosphate films. Besides the pH that will greatly affect the protective property of phosphate films, other factors are also investigated recently, such as NOM. Li et al. (2004) found organic matter to markedly decrease the efficiency of orthophosphate corrosion inhibition for copper pipes in soft water. They thought that the decrease in dissolved oxygen due to the presence of organic matter might be a factor in increasing copper release. The age of the tested pipe also exhibits different copper leaching results. In the studies by Drogowska et al. (1992), a dosage of 1 mg P/L at DIC of 75 mg C/L and pH of 7.2 allows higher copper levels upon stagnation in aged (426-512 days) pipes than without orthophosphate, which suggests that orthophosphate may interfere with the normal corrosion scale oxidation and aging processes (Schock 1995, and Edwards et al., 2002).

Some researchers try to establish copper release models in drinking water in view of thermodynamics, which incorporates the knowledge of Gibbs Free Energies of formation for copper and related chemical species. However, the information regarding equilibrium and solubility constants for many important copper compounds and complexes at temperatures other than 25°C is inadequate, in particularly, the carbonate complexes and phosphate species. Table 2.3 gives a list of some fundamental equilibrium reactions and constants were computed from the Gibbs Free Energy for copper and related species in aqueous environment. The information on the solubility of copper orthophosphate solids is scarce and almost no progress has been made in
identifying solids and determining solubility constants due to the absence of reliable thermodynamic data (Richard, 1970).

**Table 2.2** Reported minerals containing copper and orthophosphate.

<table>
<thead>
<tr>
<th>Compounds Name</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Libethenite</td>
<td>Cu₂PO₄(OH)</td>
</tr>
<tr>
<td>Cornetite</td>
<td>Cu₃PO₄(OH)₃</td>
</tr>
<tr>
<td>Reichenbachite/ Ludjibaite</td>
<td>Cu₅(PO₄)₂(OH)₄</td>
</tr>
<tr>
<td>Pseudomalachite</td>
<td>Cu₅(PO₄)₂(OH)₄ · 2H₂O</td>
</tr>
</tbody>
</table>


**Table 2.3** Equilibrium Reactions in Copper Solubility Programs, and Corresponding log K and β values.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Log K or β at 25°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu⁺ ↔ Cu²⁺ + e</td>
<td>-2.72</td>
</tr>
<tr>
<td>Cu²⁺ + H₂O ↔ CuOH⁺ + H⁺</td>
<td>-7.96</td>
</tr>
<tr>
<td>Cu²⁺ + 2H₂O ↔ Cu(OH)₂₀ + 2H⁺</td>
<td>-16.24</td>
</tr>
<tr>
<td>Cu²⁺ + 3H₂O ↔ Cu(OH)₃⁻ + 3H⁺</td>
<td>-26.90</td>
</tr>
<tr>
<td>Cu²⁺ + 4H₂O ↔ Cu(OH)₄⁻ + 4H⁺</td>
<td>-39.56</td>
</tr>
<tr>
<td>2Cu²⁺ + 2H₂O ↔ Cu₂(OH)₂²⁺ + 2H⁺</td>
<td>-10.58</td>
</tr>
<tr>
<td>3Cu²⁺ + 4H₂O ↔ Cu₃(OH)₄²⁺ + 4H⁺</td>
<td>-20.76</td>
</tr>
<tr>
<td>Cu²⁺ + H⁺ + CO₃⁻ ↔ CuHCO₃⁺</td>
<td>12.13</td>
</tr>
<tr>
<td>Cu²⁺ + CO₃⁻² ↔ CuCO₃⁰</td>
<td>6.82</td>
</tr>
<tr>
<td>Cu²⁺ + 2CO₃⁻² ↔ Cu(CO₃)₂²⁻</td>
<td>10.60</td>
</tr>
<tr>
<td>Cu²⁺ + CO₃⁻² + H₂O ↔ Cu(OH)CO₃⁻ + H⁺</td>
<td>-4.25</td>
</tr>
<tr>
<td>Cu²⁺ + CO₃⁻² + 2H₂O ↔ Cu(OH)₂CO₃⁻ + 2H⁺</td>
<td>-13.14</td>
</tr>
<tr>
<td>Cu²⁺ + 2H⁺ + PO₄³⁻ ↔ CuH₂PO₄⁺</td>
<td>21.09</td>
</tr>
<tr>
<td>Cu²⁺ + H⁺ + PO₄³⁻ ↔ CuH₂PO₄⁰</td>
<td>16.35</td>
</tr>
</tbody>
</table>
2.2.3 Relationship between phosphate and microorganism in drinking water

The concern of many water utilities that the use of phosphate-based corrosion inhibitors could stimulate biological growth in drinking water treatment systems, resulting in a regulatory noncompliance or a potential risk to public health. However, a survey of 31 public water systems in North America (LeChevallier et al., 1996) found that the use of phosphate based corrosion inhibitors was associated with lower distribution system coliform levels. In the project conducted by Olson et al. (1996), it has been suggested that system-wide reductions in corrosion reduce the area of habitat (i.e., tubercles in the pipeline) for biofilm microorganisms, thereby reducing regrowth potential. Similar conclusions were also drawn by Appenzenller et al. (2001).

2.3 Electrochemical Approaches to Investigate Corrosion Inhibitors

Since corrosion in aqueous solutions is an electrochemical process, electrochemical techniques can be used for investigating its mechanistic details. The suggested electrochemical mechanism of copper corrosion inhibition could be verified by different electrochemical approaches. Measurement of current-potential relationships
under controlled conditions can give information on corrosion rates, coatings and films, their passivity and the effectiveness of inhibitors. The main electrochemical techniques applied in inhibitor studies are the measurement of corrosion potential, polarization methods and AC impedance techniques.

2.3.1 Introduction to Electrochemical Kinetics

Electrochemical reactions in corrosion are heterogeneous, involving electron transfer reactions at a metal-solution interface. A simple three-step model in an electrochemical includes:

(a) Transport of reactant to the interface;
(b) Electron transfer reaction;
(c) Transport of product from the interface.

The overall rate of the reaction is determined by the slowest step among these. If the electron transfer rate is slower than the transport process, the overall reaction can be described by electrode kinetics and the reaction is under activation control. When the transport step is the slowest, then it is under mass transport control, and the equations of convective mass transport can be applied to describe the overall reaction rate.

Butler (1924) postulated a description of the relationship between the electrical current applied to the surface and the extent of polarization.

\[
i = i_0 \left[ \exp \left( \frac{\alpha A n F}{RT} \eta \right) - \exp \left[ - \eta \left( \frac{\alpha C n F}{RT} \right) \right] \right]
\]

where \( i \) is the applied current density (A/cm\(^2\)), \( F \) is the Faraday’s constant, \( R \) is the universal gas constant and \( T \) is the absolute temperature. Furthermore, \( \eta \) is the
overvoltage or overpotential, which measures the perturbation of the surface potential from the corrosion potential, or the degree of polarization. Moreover \( i_0 \) is the exchange-current density at the corrosion potential. When \( \eta = 0 \), \( i_0 = i_{\text{oxidation}} = i_{\text{reduction}} \), and the oxidative reaction rate equals the reductive reaction rate. The parameters of \( \alpha_A \) and \( \alpha_C \) are defined as anodic charge transfer coefficient and cathodic charge transfer coefficient, respectively. They are believed to represent the shape of the electron transfer energy barrier that develops at the reactive surface and might be envisioned as the fraction of the overvoltage consumed in pumping the electrons past the energy barriers at the corroding surface. From the tendency of anodic and cathodic Tafel slope values to vary, earlier researchers could justify the rate limiting factor to control the overall corrosion process (Reiber, 1989).

As the overvoltage becomes larger than 50mV, either positive or negative, the first or the second terms in the above equation will become negligible. Hence, a simple relationship between current, \( I \) and overvoltage, \( \eta \) is obtained:

\[
\eta = \beta \ln\left(\frac{i}{i_0}\right)
\]

This is in accordance with the equation by Tafel in 1904. The usual plot of overvoltage versus log[current density] is known as the Tafel Plot (Figure 2.2).
It is noteworthy that $\beta$ is constant for a given metal and chemical environment. Quantitatively, it represents the slope of an overvoltage versus \( \ln[i] \) curve and hence it is referred to as the Tafel slope. Tafel Slope is unique to the particular surface and the chemistry of the corrosion process. A single surface will display distinct anodic and cathodic Tafel slopes ($\beta_a$ and $\beta_c$). A large value of $\beta$ means that a surface polarizes readily and that a high overvoltage is required to bring about a particular rate of electron exchange. Furthermore, $\beta$ can be expressed in terms of the anodic/cathodic charge transfer coefficient, $\beta=2.3RT/\alpha nF$.

Stern and Geary estimated the value of $i_0$ from polarization curves when Tafel slopes are known and the degree of polarization falls within the linear polarization range (50 mV around the corrosion potential)

$$i_0=2.303[\beta_a\beta_c/ (\beta_a+\beta_c)] R_p$$
$R_p$ is the polarization resistance and equals $d\eta/d\iota$ when $\eta$ goes to zero.

Another important electrochemical fundamental equation is the Nernst Equation:

$$E = E_0 - (RT/nF) \ln Q$$

or

$$E = E_0 - (0.059/n) \log Q$$

$E_0$ is the standard electrode potential, measured relative to the normal hydrogen electrode (NHE) with all species at unit activity.

In the system studied herein, for the cathodic reaction (the reduction of oxygen):

$$E = 1.27 - (0.059/n) \log [O_2]$$

and $[O_2]$ stands for the activity of dissolved oxygen at the corroding copper surface and $n$ is for number of electron transfer equivalents, which is four in this case. When there is no current flow, the concentration of oxygen at the metal surface is equal to that in the bulk solution. However, a concentration gradient develops between the copper surface and the bulk solution when a current flows from anode to the cathode, thus promoting the change in surface potential, which can be given as follows

$$\Delta E = (0.059/n) \log ([O_2] / [O_2]_{(s)})$$

Here, $[O_2]_{(s)}$ refers to the oxygen concentration at the copper surface and is less than the concentration in the bulk solution due to mass transfer limitations. From the above equation, it is obvious that the larger difference between the surface and the bulk oxygen concentration, the greater the polarization. Therefore, a barrier that retards the transport process of oxygen will enhance the polarization by promoting the $O_2$ concentration difference.
2.3.2 The Corrosion Potential

Measurement of the corrosion potential is the easiest electrochemical test; and it also provides the least amount of mechanistic information. The measurement of $E_{corr}$ requires a stable reference electrode, a high impedance voltmeter and in most cases a suitable recording device.

The corrosion potential is helpful in elucidating the type of adsorption of organic inhibitors to the metal surface. However, the restriction of this technique must be considered carefully. The shift of the potential value to more noble or active direction can not serve as a dependable criterion of increasing or decreasing the corrosion rate. It is also true that corrosion inhibition may occur even without any shift on the electrode potential of the metal.

2.3.3 Polarization Methods

Polarization methods are often used for laboratory corrosion testing. These techniques can provide significant insight on the corrosion mechanisms, corrosion rates and the inhibitor behavior on the metal surface. Polarization methods involve changing the potential of the working electrode and monitoring the current, which is produced as a function of time or applied potential.

A simplification of the polarization resistance technique is the linear polarization technique proposed by Stern and Geary. They assume that the relationship between $E$ and $i$ is linear within a narrow range (50 mV) around the OCP. Polarization resistance
is defined as the resistance of the metal to oxidation during the application of an external potential:

\[ R_p = \left( \frac{\partial E}{\partial i} \right)_{i=0} \]

The value of \( R_p \) is measured as the slope of potential \( E \) versus current density \( i \) when \( i=0 \). However, the sweep rate that is used to determine \( R_p \) will cause inaccuracies in its value. If the sweep rate is too high, the experimental value of \( R_p \) will be too low and the calculated corrosion rate will be too high. The corrosion rate is directly related to \( R_p \) and can be calculated from it by knowing the anodic and cathodic Tafel slopes by the Stern-Geary equation.

Potentiodynamic polarization is a well-established electrochemical technique where a potential scan of 250 mV, both positive and negative, around the OCP is carried out. The current in this potential range varies logarithmically with the potential. The Tafel slopes of the anodic and cathodic reactions are obtained from the linear portions of the scan and together with the corrosion current, \( i_{\text{corr}} \), the corrosion rate can be calculated. The corrosion current is obtained from the plot where the two slopes join. In addition, the anodic and cathodic Tafel slopes can be used with \( R_p \) obtained from a linear polarization, and a corrosion rate could also be calculated. When investigating the behavior of corrosion inhibitors, the polarization curve can provide direct information about the inhibitor film on the electrode surface. By comparing the polarization curve for the blank case and the inhibitor added case, the type (anodic inhibition, cathodic
inhibition or mixed inhibition) of inhibition can be evaluated (Tommesani et al., 1997,

Cyclic voltammetry involves sweeping the potential in a positive direction until a
predetermined value of current or potential is reached, then the scan is immediately
reversed toward more negative values until the original value of the potential is
reached. In some cases, this scan is done repeatedly to determine changes in the
current-potential curve induced with scanning. From the research performed by
Subramanian and Lakshminarayanan (2002) and Ma et al. (2002) in the copper
corrosion inhibition system, the first anodic peak corresponds to the oxidation of
copper into a Cu$_2$O monolayer. The second and the third peaks are ascribed to be the
mulfilayer formation of CuO in parallel pathways, reverse scan of the fourth peak
corresponds to the cathodic reduction of CuO to Cu$_2$O while the fifth one is due to the
reduction of Cu$_2$O to Cu.

\[
2\text{Cu} + \text{H}_2\text{O} \rightarrow \text{Cu}_2\text{O} + 2\text{H}^+ + 2\text{e}^-
\]
\[
\text{Cu}_2\text{O} + \text{H}_2\text{O} \rightarrow \text{CuO} + 2\text{H}^+ + 2\text{e}^-
\]
\[
\text{Cu}_2\text{O} + 3\text{H}_2\text{O} \rightarrow 2 \text{Cu (OH)}_2 + 2\text{H}^+ + 2\text{e}^-
\]

Passivity has been related to the formation of a duplex structure Cu$_2$O/CuO and Cu
(OH)$_2$.

2.3.4 Electrochemical Impedance Spectroscopy (EIS)

2.3.4.1 Background on EIS
Electrochemical impedance is usually measured by applying a sufficiently small AC potential to an electrochemical cell and measuring the current through the cell. This is carried out so that the cell’s response is pseudo-linear. Linearity is described in more detail in a following section. In a linear or pseudo-linear system, the current response to a sinusoidal potential will be a sinusoid at the same frequency, but shifted in phase.

The excitation signal, which is expressed as a function of time, is also follows:

\[ E(t) = E_0 \cos(\omega t) \]

\( E_0 \) is the amplitude of the signal and \( \omega \) is the radial frequency (radians/second), and

\[ \omega = 2\pi f, \]

where \( f \) (Hertz) is the frequency.

In a linear system, the response signal \( I(t) \) is shifted in phase \( \phi \)

\[ I(t) = I_0 \cos(\omega t - \phi) \]

Using Euler’s relationship

\[ \exp(j\phi) = \cos\phi + j\sin\phi \]

It is possible to express the impedance as a complex function, and the potential is described as

\[ E(t) = E_0 \exp(j\omega t) \]

And current as

\[ I(t) = I_0 \exp(j\omega t - j\phi) \]

The impedance is then represented as

\[ Z = Z_0 \exp(j\phi) = Z_0 (\cos\phi + j\sin\phi) \]

EIS data is commonly analyzed by fitting it to an equivalent electrical circuit model.
To be useful, the elements in the circuit model should have a rational basis in the physical electrochemistry of the system. The Table 2.4 shows the most commonly employed elements in equivalent circuit models.

**Table 2.4** Circuit elements used in circuit models.

<table>
<thead>
<tr>
<th>Component</th>
<th>Admittance</th>
<th>Impedance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resistor</td>
<td>$1/R$</td>
<td>$R$</td>
</tr>
<tr>
<td>Capacitor</td>
<td>$j\omega C$</td>
<td>$1/j\omega C$</td>
</tr>
<tr>
<td>W(infinite diffusion)</td>
<td>$Y_0(j\omega)^{1/2}$</td>
<td>$1/[Y_0(j\omega)^{1/2}]$</td>
</tr>
<tr>
<td>O(finite diffusion)</td>
<td>$1/Y_0(j\omega)^{1/2} \text{ Coth}[B(j\omega)^{1/2}]$</td>
<td>$\text{Tanh}[B(j\omega)^{1/2}] / Y_0(j\omega)^{1/2}$</td>
</tr>
<tr>
<td>Q(CPE)</td>
<td>$Y_0(j\omega)^n$</td>
<td>$1/[Y_0(j\omega)^n]$</td>
</tr>
</tbody>
</table>

The impedance of a resistor is independent of frequency and has only a real component. Because there is no imaginary impedance, the current through a resistor is always in phase with the voltage.

The impedance of a capacitor decreases as the frequency is increased. Capacitors also have only an imaginary impedance component. The current through a capacitor is phase-shifted -90 degrees with respect to the voltage.

EIS measurement results can interpret both the protective film structure and the kinetics of the process corresponding to copper dissolution. It can also be applied to monitor the changes in material properties with time and to separate the many impedance variables that account for the degradation of the surface (Mansfeld, 1981 and Kendig *et al*., 1983).
2.3.4.2 The Equivalent Circuit Model of EIS

Two-time constant:

The model discussed herein is the one involving two time constants due to the inhomogeneities in the electrode surface, expressed as depressed semicircles on the impedance plot. The high frequency semicircle is associated with the charge transfer resistance and double layer capacitance in the metal electrolyte interface, while the low frequency arc is due to the diffusive phenomenon in the finite thickness layer. This situation may be described by incorporating diffusion impedance in the finite length regime in the equivalent circuit.

In view of electrochemistry process occurring on the surface, the first time constant is attributed to the protective layer of the inhibitor on the surface and is described by the layer capacitance and the layer resistance, which is representative of the electrolyte reaching the metal substrate through a defect in the layer. The second loop is attributed to the charge transfer resistance and the double layer capacitance due to defects in the inhibitor layer. All the capacitances shown in the equivalent circuit have been modeled mathematically using a Constant Phase Element (i.e., CPE) to improve the fitness.

Several common equivalent circuits for a two-time constants model:

(a)

Equivalent circuits for modeling impedance data of the CuNi10Fe alloy by NADDT (Aljinovic et al., 2000). In the study on the polymer coated surfaces carried out by
Mansfeld (1993), the $Q_l$ and $Q_{del}$ was replaced by $C_l$ and $C_{del}$, the capacitance of coating film and surface double electrical layer, respectively (Yin and Wu, 1998).

(b)

![Equivalent Circuit Model](image)

An equivalent circuit model suggested by Jimenez-Morales et al. (1997), described the surface layers produced by nitrogen ion implantation.

(c)

![Equivalent Circuit Model](image)

(Hayon, et al., 2002 and Zhang.X. et al., 2002)

These models are typically used in studies of metal corrosion under organic coatings or protected by organic inhibitors (Armstrong and Wright, 1993, Thomopson and Campbell, 1995 and Miszczyk and Szalinska, 1995) in certain instances of localized corrosion and the systems, where surface layers may form during exposure to a corrosive environment (Oltra and Keddam, 1988) as well as the ion-implanted metal surface. In 1998, Yin and Wu applied EIS into resin-coated copper plates to conduct degradation experiments and trace the diffusion history of water molecules and electrolyte within the polymer films based on the variations of equivalent circuit parameters as a function of time.

### 2.3.4.3 Electrochemical Interpretation of the Equivalent Circuit Elements
**Electrolyte resistance**

The resistance of an ionic solution depends on the ionic concentration, the type of ions, temperature and the geometry of the area, in which current is carried. Although there is a mathematic equation for the calculation of electrolyte resistance based on electrode area, length and solution conductivity, it is more common and easier to obtain this parameter from fitting a model to experimental EIS data.

**Electrical Double Layer**

An electrical double layer exists at the interface between an electrode and its surrounding electrolyte. The double layer is formed as ions from the solution “stick” on the electrode surface.

The value of the double layer capacitance depends on many variables, including electrode potential, temperature, ionic concentrations, type of ions, oxide layers, electrode roughness, impurity adsorption etc.

**Charge Transfer Resistance**

\[
M \leftrightarrow M^{n+} + ne^-
\]

When electrons enter the metal and metal ions diffuse into the electrolyte, charge is being transferred. After simplification of the Bulter –Volmer equation, the expression for the charge transfer resistance becomes

\[
R_{ct} = \frac{RT}{nF}i^0
\]

**Warburg Impedance (Diffusion Phase)**

Diffusion could create impedance, known as the Warburg impedance. This impedance depends on the frequency of the potential perturbation. At high frequencies, the
Warburg impedance is small, since the reactants do not have to move very far. While at low frequencies, the reactants have to diffuse farther, thereby increasing the Warburg impedance. On the Nyquist plot, the infinite Warburg impedance appears as a diagonal line with a slope of 0.5 as shown in Figure 2.3. The corrosion of copper in aqueous solution, especially in neutral solution is composed of the oxidation of copper and the reduction of dissolved oxygen. The oxygen reduction is diffusion-limited and usually controls the rate of the entire corrosion reaction. The diffusion of dissolved oxygen from the bulk solution to the surface of the copper electrode causes the appearance of the Warburg impedance in the corresponding impedance diagram.

![Figure 2.3 The EIS spectra with infinite Warburg impedance.](image)

**Constant Phase Element (CPE)**

Originally the introduction of CPE was done to fit impedance data. It is common to obtain an EIS spectroscopy, where the center of the semicircle does not lay on the real axis. The depression of the capacitive semicircle observed may be treated as surface
nonhomogeneity of the polycrystalline solid electrode due to surface roughness (Delevie, 1965), to insufficient polishing and to corrosion, grain boundaries (Growcock and Jasinski, 1989), to impurities and to the fractal nature of the surface (Mulder and Sluyters, 1988).

In 1990, Rammet and Reinhard give a new concept to CPE that could be applied to describe the fractal nature of the interface. For a planar or smooth electrode, the non-Faraday process may be represented by a classical double layer capacitance; however, for a rough electrode, especially at high frequencies, the frequency dispersion of impedance is analogous to a nonuniform transmission line. Therefore such a non-Faraday response can be represented by a more general constant phase angle element (CPE), which is described by an empirical impedance function of the type as follows:

\[ Z_{\text{CPE}} = \left( \frac{1}{Y_0} \right) (j\omega)^n \]

1/\(Y_0\) is constant, \(Y_0\) is the magnitude of the CPE, \(\omega\) is the angular frequency (rad s\(^{-1}\)), \(n=\theta/(\pi/2)\), where \(\theta\) is the phase angle of the CPE.

The parameter \(n\) ranges from -1 to +1, when \(n=1\), it is described as capacitance; \(n=0\), resistance; \(n=0.5\), Warburg impedance, and \(n=-1\), inductance. Therefore, it may be considered as a parallel combination of a pure capacitor and a resistor that is inversely proportional to the angular frequency. Both \(Y_0\) and \(n\) are found to be temperature dependent parameters (Macdonald et al., 1982).

**Thickness of the Protective Film**

Manfeld (1993) suggested an equation to help in the calculation of film thickness
\[ C_c = \varepsilon \frac{\varepsilon_0 A}{d} \]

\( C_c \): capacitance of protective film

\( \varepsilon \): dielectric constant of film

\( \varepsilon_0 \): 8.85 \times 10^{-14} \text{ F} \cdot \text{cm}^{-1}

\( A \): test electrode surface area

\( d \): thickness of the film

Although \( \varepsilon \) is difficult to estimate, the change of \( C_c \) under different conditions can be used as an indicator of a change in the film thickness.

2.3.4.4 The Simulation of EIS Data: Non-Linear Least Squares Fitting

For most EIS simulations, a non-linear least squares fitting (NLLS) algorithm is used. NLLS starts with initial estimates for all the model parameters. Starting from this initial point, the algorithm makes changes in several or all of the parameter values and evaluates the resulting fit. If the change improves the fit, the new parameter value is accepted. If the change worsens the fit, the old parameter value is retained. Next a different parameter value is changed and the test is repeated. Each trial with new values is called iteration. Iterations continue until the goodness of the fit exceeds an acceptance criterion, or until the number of iterations reaches a limit.

Therefore, the choice for the set of starting parameters is very important as the number of iterations in the fitting procedure will depend strongly on the quality of this set. Moreover the choice of the proper equivalent circuit is crucial to a good fit result (Boukamp, 1986).
2.4 Other Approaches to Evaluate Corrosion Inhibitor Effect

Although there are many electrochemical techniques that can be applied to elucidate the electrochemical process occurring on the electrode surface, it is often difficult to interpret the complex information and there is no direct insight into what is occurring at a microscopic or molecular level on the electrode surface. Therefore, the surface analytical tools such as the spectroscopic and microscopic techniques are very helpful in the corrosion and corrosion inhibition analysis, as they provide supplementary information from a different perspective to overview the surface process.

2.4.1. General Introduction to the Surface Analysis Techniques

Surface techniques can be divided into two types based upon on the test conditions, one is the “ex situ” measurement, where tested coupons will be removed from the immersion solution and placed in an ultrahigh vacuum system, such as SEM, XPS and AES; the other is the “in situ” approaches, such as infrared (IR), Raman and Surface-Enhanced Raman Spectroscopy (SERS). Ideally, the best surface analytical technique is the one that can provide information concerning the chemical nature of the surface films in situ at the metal-solution interface. The potential drawback for many surface sensitive techniques lies in the fact that they are ex situ techniques. The various techniques involving electrons, photons and ions for surface analysis are summarized in Table 2.5.
### Table 2.5 Methods of surface analysis.

<table>
<thead>
<tr>
<th>Means of Probing</th>
<th>Method</th>
<th>Information Obtained</th>
<th>Monolayer Sensitivity</th>
<th>Probing Depth</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrons</td>
<td>Scanning electron microscopy (SEM)</td>
<td>Surface Topography</td>
<td>none</td>
<td>10 nm-1 μm</td>
</tr>
<tr>
<td>Electrons</td>
<td>Scanning transmission electron microscopy (STEM)</td>
<td>Image of the molecular structure, defect information</td>
<td>none</td>
<td>~1 μm</td>
</tr>
<tr>
<td>Electrons</td>
<td>Energy-dispersive X-ray analysis (EDX)</td>
<td>Elemental composition</td>
<td>none</td>
<td>1 μm</td>
</tr>
<tr>
<td>Electrons</td>
<td>Auger electron spectroscopy (AES)</td>
<td>Elemental composition</td>
<td>$10^{-2}$</td>
<td>1-2 nm</td>
</tr>
<tr>
<td>Electrons</td>
<td>Low energy electron diffraction (LEED)</td>
<td>Surface atomic structure</td>
<td>$10^{-3}$</td>
<td>1 nm</td>
</tr>
<tr>
<td>Photons</td>
<td>X-ray photoelectron spectroscopy (XPS)</td>
<td>Elemental composition, chemical bonding</td>
<td>$10^{-2}$</td>
<td>1-2 nm</td>
</tr>
<tr>
<td>Photons</td>
<td>UV photoelectron spectroscopy (UPS)</td>
<td>Valence band structure</td>
<td>$10^{-2}$</td>
<td>1-3 nm</td>
</tr>
<tr>
<td>Photons</td>
<td>Ellipsometry</td>
<td>Layer thickness</td>
<td>$10^{-1}$</td>
<td>1-100nm</td>
</tr>
<tr>
<td>Photons</td>
<td>Secondary ions mass spectrometry (SIMS)</td>
<td>Elemental composition</td>
<td>$10^{-5}$</td>
<td>1-2 monolayer</td>
</tr>
<tr>
<td>Magnetic Resonance</td>
<td>NMR and EPR</td>
<td>Chemical structure</td>
<td>undetermined</td>
<td>-</td>
</tr>
<tr>
<td>Thermal</td>
<td>Thermal desorption spectroscopy (TDS)</td>
<td>Adsorption states, adsorption energies</td>
<td>$10^{-1}$</td>
<td>1 monolayer</td>
</tr>
</tbody>
</table>


#### 2.4.2 Application of Surface Analysis Techniques in Copper Inhibitor Research

As benzotriazole (BTA) is the most intensively investigated inhibitor to copper corrosion, various surface analysis approaches have been applied to study its corrosion inhibition mechanism on the copper-solution interface.
Poling (1970) used Infrared Reflectance Spectroscopy to observe the protective film formed on copper surface by BTA. A copper-BTA complex and a film formed by BTA were detected. The spectrum of the BTA film on the copper surface is identical to the one of the Cu (I)-BTA complex.

XPS was also extensively employed in the Cu-BTA research. A strong N 1s peak and an enhanced C 1s peak as compared to the inhibitor-free surfaces suggested that a rapid adsorption of BTA on a cuprous oxide surface occurred with a formation of a Cu (I)-BTA complex, which will be oxidized to Cu (II)-BTA (Chadwick and Hashemi, 1977). XPS coupled with X-ray induced AES were employed to investigate the mechanism of BTA inhibition film formation on copper by Hashemi and Hogarth (1988). The combination of the two spectroscopic techniques proved to be quite powerful for such studies.

Aruchamy et al. (1990) used SERS to find that in the case of BTA, the inhibition action in an alkaline medium is due to the substitution of hydrogen of the –NH group of BTA and the formation of coordination links with the lone pair of electrons on one of the nitrogen atoms.

2.4.3 Electrochemical Quartz Crystal Microbalance Technique (EQCM)

When an alternating voltage is applied between two faces of a quartz crystal blade, the blade oscillates. The frequency of oscillation of a quartz crystal is highly sensitive to the mass supported by the two faces of the device. The in situ ECQM method could gather quick and vital information on the copper electrode behavior in aqueous
solutions. Its high sensitivity (of the order of ng/cm$^2$) to mass variations through the measurement of the vibration frequency of a quartz crystal over which a copper layer has been deposited enables the investigation of even a monolayer scale. A setback for this method is to distinguish between different processes taking place at the same time on the electrode surface (Shaban et al., 1995).

EQCM has been applied in measuring electrode corrosion and inhibitor adsorption. Differences in the inhibitor adsorption or metal dissolution velocities and the film thickness can be monitored simultaneously (Jope and Shell, 1995). Trachli et al. (2002) used ECQM to investigate the formation kinetics of the $p$-ATA film and determine the thickness of $p$-ATA film at a few micrometers. Frignani et al. (1999) found that the copper dissolution rate and the thickness of the protective film calculated by EQCM corresponded to the values deduced from EIS measurements.

Currently, the combination of electrochemical techniques and surface analysis methods are preferred to investigate the inhibitor behavior on copper corrosion.

EIS can probe the changing tendency of polarization resistance, double layer capacitance and diffusion resistance. PDS is employed to elucidate the cathodic or anodic process as well as the shift of OCP with immersion time and the surface analysis results can reveal the behavior (i.e., morphology, chemical composition and film thickness) of inhibitor ions on the copper surface.
CHAPTER 3

MATERIALS AND METHODS

3.1 Copper Coupons and Cleaning Process

99.9% pure copper coupons of CDA 110 type were from Metal Sample Company, Munford, Alabama, USA, with dimensions of 10 cm x 5cm x 2.8 mm (a surface area of 111.5 cm$^2$). These coupons were polished with No.180 and 600 sandpaper and then immersed in a HCl solution (4 parts deionized water + 1 part 37% HCl) for about 30 minutes at room temperature. Copper coupons were rinsed by three separately deionized water (DI water) baths to remove the acid from the coupons. The pH of the last water bath after removal of the coupons should be near 5.5, the same as normal DI water in equilibrium with carbon dioxide in the air. The coupons were rinsed with acetone to remove organic matter and then immediately immersed in the prepared solutions.

3.2 Experimental Solutions

Sodium dihydrogen phosphate monohydrate was prepared at concentrations of 100 mg P/L solution with 10 mM of MOPS (3-[N-Morpholino] propanesulfonic acid, sodium salt, from Sigma Chemicals, Inc.) as a buffer. In all the experiments, every copper coupon was immersed in 240 ml of solution, which is contained in a 250 ml HDPE plastic bottle. The mouth of the bottle was wide with a coupon surface/ solution volume ratio of 0.464 cm$^{-1}$ and was covered with a plastic laboratory film. The containers were put into a shaker bath to maintain the temperature and were shaken at 130 rpm to maintain
sufficient mixing. The solutions were replaced every 24 h to maintain the phosphate level, oxygen and carbon dioxide levels. The pH values of the solutions were measured with a pH meter from Fisher Scientific Company and were adjusted by adding either sodium hydroxide or nitric acid.

3.3 Monitoring Copper Concentrations

An aliquot of 10 ml was collected from the containers, adjusted to pH 2-3 and filtered through a 0.45 µm membrane filter (Whatman). To measure the copper concentration, the samples were analyzed with an Inductively Coupled Plasma- Atomic Emission Spectrometry (ICP-AES) spectrometer (Optima 3000) from Perkin Elmer Company. The detection limit of this instrument for Cu at 324.754 nm is 0.4 ppb.

3.4 Monitoring Phosphorous Concentrations

An aliquot of 10 ml was collected from the containers and adjusted to pH 2-3. To measure the phosphorous concentration, the samples were analyzed with an Inductively Coupled Plasma Mass Spectrometer (Elan 6100) from Perkin Elmer Company. The upper detection limit of this instrument for phosphorus is 200 ppb; therefore dilution and filtration (0.45 µm membrane filter from Whatman) are required

3.5 Immersion Experiments
To study the effect of exposure time on copper corrosion in the presence of orthophosphate, the measurements were conducted after immersion periods of 2, 4, 6, 8, 15 and 30 days at pH of 8.0.

The pH effect was investigated for three pH values of 7.2, 8.0 and 8.4, which are within the range of most water treatment plants.

Orthophosphate dosage of 0.1 mg P/L, 0.2 mg P/L, 1.0 mg P/L and 5.0 mg P/L were selected to perform the electrochemical experiments.

Low concentrations of phosphorous (50ppb–500ppb) were employed in the mechanistic research by ICP-MS.

### 3.6 Electrochemical Measurements

The electrochemical experiments were performed using a flat electrochemical cell as shown in Figure 3.1. In this cell, the test area and the solution volume were 13.2 cm² and 125 ml, respectively. An Ag/AgCl electrode was used as a reference electrode and a circular platinum electrode was used as a counter electrode.

A silver/silver chloride reference electrode was consisted of a silver wire, which was in a glass barrel. A silver chloride layer is grown on the wire. The barrel was filled with a suitable electrolyte solution, generally 3 M KCl, and was refillable.

Autolab/PGSTAT20’s Frequency Response Analyser (FRA) was used to perform the Electrochemical Impedance Spectroscopy scans, with the frequency range set from 5000 Hz to 2 mHz with a 5 mV AC amplitude around the OCP.
A General Purpose Electrochemical Scans (GPES) was used to conduct a linear polarization scan. Potentiodynamic scans (PDS) were carried out from -370 mV to +500 mV with scan rate of 0.2 mV/s. All electrochemical measurements were conducted after achieving the stabilization of an open circuit potential (i.e., OCP). The time to achieve stabilization depends on the experimental conditions, between 15 and 60 minutes. Occasionally stabilization was not obtained even after 1 hour.

![Electrochemical Set Up](image)

**Figure 3.1** The configuration of the three-electrode set up for electrochemical tests

### 3.7 Scanning Electron Microscope Analysis

The copper coupons after immersion were dried in air and cut into a 5 mm x 5 mm x 2.8 mm size. Subsequently, these coupons were stored in a dessicator to avoid continued oxidation from contact with air. JSM-5600 Scanning Electron Microscope (SEM) from JEOL Company (Tokyo, Japan) was used to study the morphology of the oxidized copper surfaces.
3.8 X-Ray Photoelectron Spectroscopy Analysis

XPS surface analysis was performed using the AXIS-His system from the Kratos Analytical Company (Kyoto, Japan) with Al K$_\alpha$ radiation (a photoelectron energy of 1486.6 eV) and an analyzer pass energy of 40 eV. Before the XPS measurements, the copper coupons after the immersion were air-dried and cut into 5 mm x 5 mm x 2.8 mm size and stored in a desiccator filled with nitrogen gas.
CHAPTER 4

RESULTS AND DISCUSSION

4.1 Effect of Immersion Time

4.1.1 Electrochemical Impedance Spectroscopy

The copper coupons were immersed in solutions containing 1.0 mg P/L phosphate and 4.0 mg/L chlorine (initially added and replaced every 24 h) at pH of 8.0 for different periods (2, 4, 6, 8, 15, and 30 days) to study the scale growth on the copper surface with time. The EIS results are shown in the Nyquist plot. The raw data from EIS have been multiplied by the measured electrode surface area of 13.2 cm².

![Figure 4.1](image)

**Figure 4.1** A Nyquist Plot for different immersion times on copper corrosion at pH of 8.0, 1.0 mg P/L and 4.0 mg/L chlorine were added and the solution was replaced every 24 hours.
From Figure 4.1, it is obvious that the arcs of the spectra increase with the immersion time. From the 2-day to 8-day, the semicircle enlarges rapidly, as compared with to 15-day to 30-day, which suggested that after 8 days of exposure, the thickening of the protective film was slow. This conclusion is supported by the simulation results of equivalent circuit elements listed in Table 4.1.

According to the equivalent circuit program suggested by Boukamp (1986), the circuit description code (CDC) in accordance with this electrode is illustrated as follows:

![Equivalent Circuit Diagram](image)

**Figure 4.2** An equivalent circuit to fit the EIS data for copper corrosion in the presence of chlorine, inhibited by orthophosphate.

Here, $R_{sol}$ is the solution resistance; $R_{ct}$ is the charge transfer resistance, which is also the corrosion resistance; $Q_{EDL}$ is the CPE of Electrostatic Double Layer; $R_{film}$, $Q_{film}$ and $Q_{film}$ are the film resistance, finite length diffusion element and CPE of the protection film, respectively. The bulk solution/EDL interface and EDL/electrode cannot be viewed as an ideal capacitor due to the presence of a dispersing effect, and the CPE (Constant Phase Element) is defined as:

$$Y = Y_0 (jw)^n$$

CPE is used widely to account for deviations brought about by surface roughness (Benedetti et al., 1995). $Y_0$ is the description of magnitude and n is the exponential term; both of them were found to be temperature dependent (Macdonald, 1982). The lower the value of n, the rougher the electrode surface, which may due to the corrosion
processes; similarly the higher n is characteristic for smooth surface during the inhibitor forming a compact protective film. When the exponential term of n=1, CPE plays a role as a capacitor (Boukamp, 1986).

In the equivalent circuit, the cotangent hyperbolic term “O” is used to describe the diffusion of mobile species through a thin layer, such as an oxide film, followed by a reaction at the electrode/layer interface (Benedetti et al., 1995). It is defined by the following:

\[ Y = Y_0 (jw)^{1/2} \tanh \left[ B (jw)^{1/2} \right] \]

The quotient of B divided by \( Y_0 \) has been accepted as the description for diffusion resistance of a finite length protective film. In the studied system, the \( O_{film} \) term reflects a diffusion process within the growing protective layer. It became increasingly difficult for the mobile species to diffuse from the bulk solution interface to the electrode surface due to compacting film, which blocks off the passage of free ions.

From the simulated results in Table 4.1, the resistance of the protective film of the 2-day immersion was 15.6 kohm, 6 days later, it increased to 55.4 kohm. From the 8\textsuperscript{th} - day to the 15\textsuperscript{th}-day, an increase of 12.1 kohm resistance was obtained, while only a 15.3 kohm was attained from the 15\textsuperscript{th} day to the 30\textsuperscript{th} day. The diffusion resistance of the protective film showed the same increasing tendency from Figure 4.3, where good logarithmic relationships between resistance values (\( i.e., R_{ct}, R_{film}, Z_{film} \)) and immersion times were indicated.
Figure 4.3 The relationships between resistance and immersion time, where $R_p$ (EIS) was the polarization resistance extracted from EIS spectroscopy and $R_p$ (TS) was calculated by Tafel slopes (Equation 2.1).
Table 4.1 Elements of the equivalent circuit of pH 8.0, 1.0 mg P/L and 4.0 mg/L chlorine were added after different immersion times.

<table>
<thead>
<tr>
<th>Time (-day)</th>
<th>2</th>
<th>4</th>
<th>6</th>
<th>8</th>
<th>15</th>
<th>30</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_{\text{sol}}$ (ohm)</td>
<td>141</td>
<td>130</td>
<td>101</td>
<td>153</td>
<td>127</td>
<td>171</td>
</tr>
<tr>
<td>$R_{\text{cl}}$ (kohm)</td>
<td>2.29</td>
<td>3.65</td>
<td>4.35</td>
<td>5.12</td>
<td>6.47</td>
<td>10.1</td>
</tr>
<tr>
<td>$Q_{\text{EDL}}$ $Y_0 \times 10^{-6}$ ($\Omega^{-1} s^n$)</td>
<td>32.7</td>
<td>37.7</td>
<td>21.6</td>
<td>41.0</td>
<td>40.5</td>
<td>29.4</td>
</tr>
<tr>
<td>$n$</td>
<td>0.84</td>
<td>0.86</td>
<td>0.85</td>
<td>0.82</td>
<td>0.84</td>
<td>0.85</td>
</tr>
<tr>
<td>$R_{\text{film}}$ (kohm)</td>
<td>15.6</td>
<td>33.6</td>
<td>30.8</td>
<td>55.4</td>
<td>67.5</td>
<td>82.8</td>
</tr>
<tr>
<td>$Q_{\text{film}}$ $Y_0 \times 10^{-6}$ ($\Omega^{-1} s^n$)</td>
<td>41.4</td>
<td>44.8</td>
<td>35.5</td>
<td>58.8</td>
<td>31.5</td>
<td>49.6</td>
</tr>
<tr>
<td>$n$</td>
<td>0.83</td>
<td>0.88</td>
<td>0.87</td>
<td>0.87</td>
<td>0.86</td>
<td>0.91</td>
</tr>
<tr>
<td>$O_{\text{film}}$ $Y_0 \times 10^{-6}$ ($\Omega^{-1} s^{0.5}$)</td>
<td>228</td>
<td>135</td>
<td>118</td>
<td>135</td>
<td>157</td>
<td>108</td>
</tr>
<tr>
<td>$B$ ($s^{0.5}$)</td>
<td>9.33</td>
<td>9.16</td>
<td>9.75</td>
<td>10.7</td>
<td>13.2</td>
<td>11.1</td>
</tr>
<tr>
<td>$Z_{\text{film}}$ (kohm)</td>
<td>41</td>
<td>67</td>
<td>76</td>
<td>79</td>
<td>83</td>
<td>102</td>
</tr>
<tr>
<td>$R_p$ (kohm)</td>
<td>7.44</td>
<td>12.1</td>
<td>14.9</td>
<td>16.1</td>
<td>15.6</td>
<td>19.8</td>
</tr>
</tbody>
</table>

The tendency of polarization resistance is to increase rapidly during the first several days and then to slow down. The values of $R_p$ (TS) calculated by the polarization method are also obtained; the similar increasing tendency with time corresponds to the results extracted from the EIS spectra as presented in Figure 4.3.

$$R_p = (\beta_a + \beta_c) / [2.3i_{\text{corr}} (\beta_a + \beta_c)]$$  \hspace{1cm} (Equation 2.1)

Table 4.2 The comparison of polarization resistance values calculated by EIS and Tafel Slopes.

<table>
<thead>
<tr>
<th>Time (-day)</th>
<th>2</th>
<th>4</th>
<th>6</th>
<th>8</th>
<th>15</th>
<th>30</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_p$ (kohm)(EIS)</td>
<td>7.44</td>
<td>12.1</td>
<td>14.9</td>
<td>16.1</td>
<td>15.6</td>
<td>19.8</td>
</tr>
<tr>
<td>$R_p$ (kohm) (Tafel Slopes)</td>
<td>14.3</td>
<td>20.3</td>
<td>25.8</td>
<td>21.4</td>
<td>29.5</td>
<td>43.2</td>
</tr>
</tbody>
</table>
The values of the diffusion impedance, $Z_{\text{film}}$ (=B/Yo), also showed a similar changing behavior. The value of exponential term n in description of $Q_{\text{film}}$ showed a slight increase, which was consistent with the electrode surface becoming smoother with time also observed from the SEM images.

Another important equivalent circuit element is the charge transfer resistance, reflecting the corrosion rate of the copper electrode. The larger the $R_{\text{ct}}$, the more difficult for the ions to transfer through the interface, thus the corrosion rate decreases. The $R_{\text{ct}}$ increase from 2.29 kohm to 10.1 kohm meant that the corrosion rate decreased with exposure time in solution with orthophosphate. As illustrated in Table 4.1, charge transfer resistance was relatively small as compared to the diffusion resistance, $Z_{\text{film}}$, therefore the diffusion process may dominate the whole corrosion process.

### 4.1.2 Polarization Results

The potentiodynamic scan curves of copper coupons in 10 mM MOPS buffer solutions at pH of 7.2 are presented in Figure 4.4. For the short immersion times (6 days), there is no obvious anodic or cathodic “polarization valley” appearing, the curves are similar to that obtained from the “no inhibitor” samples. However, for the coupon with 1.0 mg P/L added, 30-day exposure time, there is a dramatic decrease in the anodic current compared to the curve without an inhibitor. The wide range of the passive region from -50 mV to +180 mV, where the current density declined rapidly with an increase in potential, may be attributed to the behavior of phosphate ions on the copper surface and the formation of the copper phosphate film, and thickening of this film (Benedetti et al., 1995). Therefore, the addition of 1.0 mg P/L orthophosphate will retard the anodic process in the electrochemical reaction, with a 30-day exposure required at pH of 7.2.
The cathodic polarization curves under all conditions do not change, while a slightly positive shift in the corrosion potential is observed when phosphate is added.

The influence of immersion time at pH of 8.4 is presented in Figure 4.5. When phosphate was added, a narrow anodic passive valley appears from +80 mV to +300 mV as early as the second day; while the passivition behavior does not appear in the control experiment even after 6 days. This may indicate that at higher pH values (i.e., 8.4); the passivation state of the anodic reaction can be reached after sufficient long reaction times if no orthophosphate is dosed (Fig 4.5 (c)). The addition of phosphate will retard the whole process at the early times when comparing the two-day curves in Figure 4.5 (a) and (b).
Figure 4.5 (a) Steady state polarization curves for the copper coupons at pH of 8.4 after different immersion times, where 1.0mg P/L and 4.0 mg/L chlorine were added and the solution was replaced every 24 hours.

Figure 4.5 (b) Steady state polarization curves for the copper coupons at pH of 8.4 after different immersion times, where 4.0 mg/L chlorine was added and replaced every 24 hours, no inhibitor was present.
4.1.3 Surface Morphology

SEM surface analysis was performed for 10-day and 30-day exposure times at pH 8.0 under the same solution conditions as the experiments described earlier. The completely different surface configuration of Figure 4.6 (b) and (d) suggested the inhibition effect of orthophosphate was associated with immersion time. The pores of the 10-day immersion sample were ~ 0.5 µm in diameter, however, after the 30-day immersion, no pores on the surface were observed, instead a scale structure was observed, which may be due to the cupric phosphate precipitation on the copper surface. The formation of this precipitated film protected the copper surface from aggressive ions, such as Cl\(^-\) and OH\(^-\).
Figure 4.6 The SEM micrographs of copper surface at pH of 8.0 10 days of immersion (a) x 5,000 (b) x 10,000; 35-day immersion (c) x 5,000 (d) x 10,000, 1.0 mg P/L orthophosphate and 4.0 mg/L chlorine were added and the solution was replaced every 24 hours.
4.1.4 Surface Composition

The changes in the scale composition as a function of immersion time were determined by XPS on the copper surface after 10 days and 30 days of immersion time at pH of 7.2 and 8.4, respectively.

The peaks centered at 932.5 eV and 952 eV represent Cu$_2$O or pure elemental copper. The Cu (II) compounds exhibit peaks around 933.8 eV (CuO) and 935 eV (CuCO$_3$ or Cu (OH)$_2$). A noticeable Cu (I) compound appears after 30 days of immersion compared to the surface composition of 10 days at pH of 7.2 from the Figure 4.7 (a). This might indicate that the Cu (I)-containing species are the cause of “passivation valley” on the polarization curves of 30 days (Figure 4.4). From the diagram of 4.8 (a), the spectra of Cu 2p at pH of 8.4, both Cu (I) and Cu (II) peaks are present, which correspond to the polarization results if the Cu (I) is assumed to be the passivating scale.

According to the XPS spectra and the polarization results, The Cu (I)-containing compounds are important to control the passivation process. From the spectra of O 1s, the CuO (529.6eV) is the main copper oxide species and P 2p signal was present regardless of the stagnation time at pH of 7.2. Therefore, the Cu (I)-P species play the inhibiting role at pH of 7.2, the fluctuation of anodic valley peaks may result from the reaction between Cu (I) species and phosphate ions. At pH of 8.4, the spectra of Cu$_2$O are observed (Figure 4.8 (b)), and phosphate exists either after 10 days or 30 days of immersion. Both phosphate and Cu$_2$O perform an inhibiting effect on the anodic process. The formation and thickening of Cu$_2$O is quite slow.
Figure 4.7  Cu 2p (a), O 1s (b) and P 2p (c) XPS spectra of the protective film formed after 8 and 30 days of immersion at pH of 7.2, with the addition of 1.0 mg P/L and 4.0 mg/L of chlorine.
Figure 4.8 Cu 2p (a), O 1s (b) and P 2p (c) XPS spectra of the protective film formed after 8 and 30 days of immersion at pH of 8.4, with the addition of 1.0 mg P/L and 4.0 mg/L of chlorine.
Therefore, the formation of Cu₂O, CuO, CuCO₃, Cu (OH)₂ and other Cu (I) and Cu (II) species, such as Cu₃P, Cu₃(PO₄)₂ varied with the exposure time. In the early stages the Cu (II) compounds are the main species regardless the pH condition, while the Cu (I)-containing product will appear as the immersion time increases and retards the anodic process. The addition of orthophosphate will promote the anodic passivation process by forming Cu₃P, Cu₃(PO₄)₂ etc. on the copper surface, and therefore reduce the time required for copper passivation.

4.2 Effect of pH

Since the aquatic speciation of chlorine and phosphate are influenced by acid-base chemistry, it is necessary to carry out studies at different pH values to evaluate the effect of water pH on orthophosphate inhibition efficiency.

Chlorine is one of the most widely employed disinfectants in water utilities; it is also known as an aggressive corroding species attacking the copper pipe. The equilibrium is as follows (Snoeyink and Jenkins, 1980).

\[ \text{HClO} \leftrightarrow \text{H}^+ + \text{ClO}^- \quad \text{pK}_a=7.5 \]

Hong and Macauley (1998) presented a two-step mechanism at pH less than 7.5, where HClO is the predominant chlorine species. Firstly HClO approaches a fresh copper surfacesite, forming an intermediate surface complex; then the dissolution of the oxidation product from the surface takes place.

For orthophosphate,

\[ \text{H}_3\text{PO}_4 \leftrightarrow \text{H}^+ + \text{H}_2\text{PO}_4^- \quad \text{pK}_a=2.1; \]
\[ \text{H}_2\text{PO}_4^- \leftrightarrow \text{H}^+ + \text{HPO}_4^{2-} \quad \text{pK}_a=7.2; \]
\[ \text{HPO}_4^{2-} \leftrightarrow \text{H}^+ + \text{PO}_4^{3-} \quad \text{pK}_a=12.3 \]
The thermodynamically possible cupric complexes with phosphate are libethenite, $\text{Cu}_2(\text{PO}_4)(\text{OH})$; Cornetite, $\text{Cu}_3(\text{PO}_4)(\text{OH})_3$; reichenbachite, $\text{Cu}_5(\text{PO}_4)_2(\text{OH})_4$; and pseudomalachite, $\text{Cu}_5(\text{PO}_4)_2(\text{OH})_4\cdot\text{H}_2\text{O}$ (Schock and Lytle, 1995). $\text{Cu}_3(\text{PO}_4)_2$ is barely soluble in water, according to the small solubility product of the following reaction:

$$\text{Cu}_3(\text{PO}_4)_2(\text{s}) \leftrightarrow 3\text{Cu}^{2+} + 2\text{PO}_4^{3-} \quad \text{log } K = -36.86$$

The solubility of the cupric ion is around 3 ppb in pure water, if the above solid governs it. In an aqueous solution containing phosphate, the solubility of cupric will therefore be insignificant.

### 4.2.1 Electrochemical Impedance Spectroscopy

Firstly, electrochemical experiments were conducted at three pH values of 7.2, 7.6 and 8.4, where the dosage of orthophosphate was 1.0 mg P/L, chlorine dosage was 4.0 mg/L and a 10-day immersion time was employed for all the experiments.

The arc of the EIS spectra obtained at pH of 7.2 was much smaller than the one at pH of 8.4 (Figure 4.9). The same equivalent circuit model is used to fit the spectra and the simulation results are listed in the Table 4.3. Although the charge transfer resistance, $R_{ct}$, increases from 2.48 kohm at pH of 7.2 to 6.37 kohm at pH of 8.4, it is 10 times smaller than the diffusion resistance, $Z_{film}$, which increases from 24.7 kohm to 102 kohm, respectively. The diffusion occurring within the protective film still predominately controls the entire process under different pH conditions, with stronger diffusion impedance at higher pH. The value of $n$, which describes the electrostatic double layer roughness, was 0.79, 0.85 and 0.96 for pH of 7.2, 8.0 and 8.4. This tendency suggested that the EDL behaved as a capacitor with increasing pH. At pH of 8.4, it exhibited characteristics close to a capacitor ($i.e.$, $n=0.96$).
4.2.2 Polarization Results

The potential dynamic scan curves of copper coupons in 10 mM buffer solutions at pH of 7.2, 8.0 and 8.4 with the addition of 1.0 mg P/L as an inhibitor after 30 days of exposure are presented in Figure 4.10. The corrosion potential increases from -88 mV at pH of 7.2 to +23 mV at pH of 8.4. The current at the corrosion potential declines one order of magnitude (from $4.6 \times 10^{-6}$ amperes to $3.8 \times 10^{-7}$ amperes) at pH of 7.2 if 1.0 mg P/L orthophosphate is employed. The calculated inhibition efficiency ($i.e., IE$) based on corrosion current is $\sim 91\%$. A slight decrease in the corrosion current from $4.3 \times 10^{-7}$ amperes in the inhibitor free solution to $2.6 \times 10^{-7}$ amperes when 1.0 mg P/L orthophosphate was added is observed at pH of 8.4; the inhibition efficiency is $\sim 40\%$. 

**Figure 4.9** A Nyquist Plot for different pH values after 10 days of immersion, 1.0 mg P/L and 4.0 mg/L chlorine were added and the solution was replace every 24 hours.
Table 4.3 Elements of the Equivalent Circuit after 10 days of immersion, 1.0 mg P/L and 4.0 mg/L chlorine were added and the solution was replaced every 24 hour at pH of 7.2, 7.6 and 8.4

<table>
<thead>
<tr>
<th></th>
<th>$R_{sol}$</th>
<th>$R_{ct}$</th>
<th>$Q_{EDL}$</th>
<th>$n$</th>
<th>$R_{film}$</th>
<th>$Q_{film}$</th>
<th>$n$</th>
<th>$O_{film}$</th>
<th>$B$</th>
<th>$Z_{film}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(ohm)</td>
<td>(kohm)</td>
<td>$Y_0*10^{-6}$</td>
<td></td>
<td>(kohm)</td>
<td>$Y_0*10^{-6}$</td>
<td></td>
<td>$Y_0*10^{-6}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH 7.2</td>
<td>175</td>
<td>2.48</td>
<td>18.5</td>
<td>0.79</td>
<td>11.9</td>
<td>81.5</td>
<td>0.88</td>
<td>278</td>
<td>6.78</td>
<td>24.7</td>
</tr>
<tr>
<td>pH 7.6</td>
<td>132</td>
<td>4.17</td>
<td>53.1</td>
<td>0.85</td>
<td>27.8</td>
<td>24.7</td>
<td>0.82</td>
<td>162</td>
<td>9.90</td>
<td>61.1</td>
</tr>
<tr>
<td>pH 8.4</td>
<td>166</td>
<td>6.37</td>
<td>212</td>
<td>0.96</td>
<td>73.3</td>
<td>29.7</td>
<td>0.87</td>
<td>102</td>
<td>10.4</td>
<td>102</td>
</tr>
</tbody>
</table>
Therefore, orthophosphate plays a significant role to control copper corrosion at lower pH values.

![Graph showing steady state polarization curves for varying pH conditions.](image)

**Fig 4.10** Steady state polarization curves for the copper coupons after 30 days of immersion at different pH conditions, 1.0 mg P/L phosphate and 4.0 mg/L chlorine were added and the solution was replaced every 24 hours.

### 4.2.3 Surface Composition

The changes in the scale composition with pH were determined by XPS measurements at the copper surface after 30 days of immersion at pH of 7.2, 8.0 and 8.4.

From Figure 4.11, the first distinct peak around 932–933 eV suggests the existence of Cu$_3$P (932.2 eV), Cu$_2$O (932.5 eV) and CuO (933.6 eV), the second peak around 935 eV may be strong evidence for CuCO$_3$ (935 eV) and Cu(OH)$_2$ (935.1 eV). Both cupric and cuprous ions were precipitated onto the copper surface regardless of the pH value after one month.
According to the XPS of O1s, which proved that at pH of 7.2 cupric oxide CuO, with a binding energy of 529.6 eV was the dominant oxidant. At pH of 8.4, cuprous compounds, such as Cu$_2$O (530.5 eV) were the main dominant species. While for pH of 8.0, it was a mixture of cuprous and cupric species, the transitional pH regime being between pH of 7.2 and 8.4. This finding is in accordance with that of Hong and Macauley (1998), who concluded that at pH value lower than 7.5, HClO was capable of directly attacking the copper surface to form cupric scales, such as CuO, Cu(OH)$_2$, CuCO$_3$ and Cu$_2$(OH)$_3$(CO$_3$).

Based on P 2p XPS results, all three pH values suggested a considerable amount of phosphate on the copper surface. While in the spectra of Cl 2p, a weak signal of chloride was detected only at pH of 7.2. A possible explanation was that after a long immersion period, the surface at pH of 8.4 was well protected by copper precipitates, such as Cu$_2$O, Cu$_3$P, Cu$_3$ (PO$_4$) and few free copper ions were able to escape from the coupon surface to bulk solution through the protective film, and the opportunity for Cl$^-$ seizing the free copper ions was pretty small at pH of 8.4. This assumption is also valid to interpret the results of Figure 4.12, the weak signal of CuCl$_2$ (199.2 eV) present at pH of 7.2 for short and long immersion periods. But for pH of 8.4, the existence of Cl 2p peak is only evident in the short-term experiment.
Figure 4.11 Cu 2p (a), O 1s (b), P 2p (c) and Cl 2p (d) XPS spectra of the protective film formed after 30 days of immersion at pH of 7.2, 8.0 and 8.4, 1.0 mg P/L and 4.0 mg/L chlorine were added and the solution was replaced every 24 hours.
Figure 4.12 Cl 2p XPS spectra of the protective films formed after 30 days of immersion at pH of 7.2 and 8.4, 1.0 mg P/L and 4.0 mg/L chlorine were added and the solution was replace every 24 hours, (a) pH of 7.2; (b) pH of 8.4.

4.2.4 Surface Morphology

SEM surface analysis was performed on copper coupons under pH 7.2 and pH 8.4 after 30 days of immersion. The roughly honeycombed surface free of the inhibitor at pH of 7.2 (Figure 4.13 (a)) indicates that the copper coupon was seriously deteriorated. The addition of 1.0 mg P/L orthophosphate helps to product a relatively smooth film on the surface within a month. It is noticeable that the surface is in a good state either with or without inhibitor at pH of 8.4.

These SEM results (Figure 4.13 (c) and (d)) suggest that the surface at pH of 8.4 is well protected by copper precipitates, Cu₂O, Cu₃P, Cu₃ (PO₄)₂, CuCO₃ etc. according to the XPS analysis. A compact surface film successfully prevents the leaching of copper ions to the bulk solution, as well as the attack of Cl⁻ or OH⁻ ions. This may explain why the Cl 2p signal disappears after 30 days of immersion at higher pH.
values (Figure 4.13 (b)).

The porous structure at pH of 7.2 could be viewed as the pathway for aqueous ions, such as Cu$^+$, Cu$^{2+}$, H$^+$, OH$^-$, ClO$^-$, HClO, Cl$^-$, CO$_3^{2-}$ and their complexes. When orthophosphate is added, both H$_2$PO$_4^-$ and HPO$_4^{2-}$ are present in the solution. The reactions between copper and phosphate ions and a slow growth of the precipitation film may establish the protective scale, such as the image in Figure 4.13 (b), a relatively smooth surface with small pores (a diameter of about 0.2 µm) uniformly distributed.

(a) control experiment at pH of 7.2

(b) 1.0 mg P/L added at pH of 7.2
Figure 4.13 The SEM micrographs of copper surface after 30 days of immersion, x10,000 (a) control experiment at pH of 7.2 (b) 1.0 mg P/L added at pH of 7.2 (c) control experiment at pH of 8.4 (d) 1.0 mg P/L added at pH of 8.4, 4.0 mg/L chlorine was added and the solution was replace every 24 hours.

4.2.5 Concentration of Leached Copper

The effect of pH on the inhibition effect of orthophosphate is also studied by monitoring the leached copper concentration at different pH values. At pH of 7.2, the leached copper concentration is around 0.5 ppm in comparison to the 3.5 ppm in the inhibitor-free solution from the fifth day to the 30th day (Figure 4.14 (a)). The time to reach a steady state of copper leaching to the solution is around 5~6 days. Related to the information obtained from the polarization behavior (Figure 4.4) and XPS
measurements (Figure 4.7), it could be concluded that at lower pH values \((i.e., \ 7.2)\), a longer time is required for the formation of a tough protective scale on the copper surface and this scale is efficient to control copper leaching to the bulk solution by preventing the aggressive ion action. The inhibition effect as measured by the gravimetric method is nearly 86 percent in this case, similar to the result calculated by the polarization method, 91 percent.

However, at pH of 8.4 (Figure 4.14 (b)), the inhibition performance is not as good as that at pH of 7.2. The leached copper concentration has declined to 0.7 ppm even without the addition of orthophosphate after 24 hours of exposure. From the fifth day to the 30th day, the concentration values are well controlled at under 0.3 ppm, which is below the USEPA criteria of 1.3 ppm. It is noticeable that the concentration values are constant after the fourth day when the inhibitor was added, but it reaches a steady state after 8 days when no inhibitor is applied. This observation corresponds to the conclusion from Section 4.1, that the addition of orthophosphate will reduce the time required for the copper passivation process.
Figure 4.14 Effect of pH and inhibitor dosage on the copper corrosion in a 10 mM MOPS buffer solution, 4.0 mg/L chlorine, 0.2 mg P/L or 1.0 mg P/L were added and the solution was replaced every 24 hours, exposure time is 30 days, (a) pH of 7.2 ; (b) pH of 8.4.

Therefore, pH is one of the most significant parameters in copper corrosion control by
orthophosphate. The inhibition efficiency is more satisfactory under low pH conditions than at the high pH values. The passivation of the anodic process will occur naturally without the addition of orthophosphate at pH of 8.4, if sufficiently long reaction times are allowed. However, neutral water is better for drinking purpose. At pH of 7.2, it is obvious that the anodic region in the polarization curves stay active even after 30 days. The anodic passivation duration is reduced when the inhibitor is added. Several peaks at 1.0 mg P/L orthophosphate after 30 days may describe different anodic processes, such as chemical reaction or the diffusion of active reactants as well as the charge transfer occurring within the electrical double layer.

4.3 Effect of Dosage

Although the importance and practical meaning of controlling the dosage of orthophosphate in drinking water are well known, the quantitative study is rather limited. A dosage of 1.0 mg P/L is obtained in the experiments based on the optimum dosage discussed in the literature, and the effectiveness of the dosage varies with pH, NOM, temperature, DIC concentration and the surface state of the copper plumbing.

4.3.1 Polarization Methods

The influence of orthophosphate dosage at pH of 7.2 and 8.4 after 2 days of immersion is presented in Figure 4.15. The solid lines stand for the scan results for pH of 7.2 and dotted lines for pH of 8.4. Control experiments 0.2 mg P/L and 1.0 mg P/L orthophosphate applied experiments were conducted at the two pH values. Within two days of immersion, the anodic curves stay active regardless the dosage of
orthophosphate at pH of 7.2; however, the passivation characteristics are exhibited at pH of 8.4 when 1.0 mg P/L was added. No such peaks like that were found during the control experiment and at lower concentrations (0.2 mg P/L of orthophosphate added) at pH of 8.4. This suggests that the addition of 1.0 mg P/L orthophosphate at this pH promotes the inhibition of the anodic reaction. When a larger amount of orthophosphate, 5.0 mg P/L, was applied at pH of 7.2, a noticeable anodic valley appears (Figure 4.16) after 2 days of exposure.

A polarization scan for 6 days of immersion is also conducted as shown in Figure 4.17. In contrast to the nearly superpositioned curves after 2 days, there is a slight increase in the corrosion potential when an inhibitor is applied for 6 days of immersion at pH of 7.2. The addition of 0.2 mg P/L orthophosphate at pH of 8.4 begins to exhibit its passivating role to the anodic process after 6 days of immersion.

Figure 4.15 Steady state polarization curves for copper coupons at pH of 7.2 and 8.4
after 2 days of immersion, where 4.0 mg/L chlorine was added and the solution was replaced every 24 hours, 0.2 mg P/L and 1.0 mg P/L of orthophosphate were applied.

Figure 4.16 Steady state polarization curves for copper coupons at pH of 7.2 after 2 days of immersion, where 4.0 mg/L chlorine was added and the solution was replaced every 24 hours, different dosages of orthophosphate were applied.
Figure 4.17 Steady state polarization curves for the copper coupons at pH of 7.2 and 8.4 after 6 days of immersion, where 4.0 mg/L chlorine was added and the solution was replaced every 24 hour, different dosages of orthophosphate were applied.

A long-term (30 days) experiment was carried out at pH of 7.2 to evaluate the effect of orthophosphate dosage (Figure 4.18). Firstly, the corrosion potential shifts positively and the anodic current decreases with an increasing dosage of the inhibitor. The anodic process stays active in the solution that is free of inhibitor even after 30 days, but the passivation valley appears when 0.2 mg P/L was added. As for the dosage of 1.0 mg P/L orthophosphate, three sharp peaks were observed, the current reaches as low as 8.4 x 10^{-8} amperes at a potential around 50 mV from Table 4.4. The corrosion current decreases by a factor of 10 compared with the no inhibitor case.
Table 4.4 The corrosion potential and corrosion current with different dosages of inhibitor at pH of 7.2 after 30 days of immersion.

<table>
<thead>
<tr>
<th>Corrosion Potential (mV)</th>
<th>Corrosion Current (A)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control experiment</td>
<td>-130</td>
</tr>
<tr>
<td>0.2 mg P/L added</td>
<td>-90</td>
</tr>
<tr>
<td>1.0 mg P/L added</td>
<td>-88</td>
</tr>
</tbody>
</table>

Figure 4.18 Steady state polarization curves for copper coupons at pH of 7.2 after 30 days of immersion, where 4.0 mg/L chlorine was added and the solution was replaced every 24 hours, different dosages of orthophosphate were applied.

4.3.2 Surface Morphology

SEM surface analysis was conducted on copper coupons at pH of 7.2 after 30 days of immersion with different amount of orthophosphate (Figure 4.19). The different between the control experiment to the 1.0 mg P/L surface is obvious; the porous structure disappears gradually with an increase in orthophosphate dosage.
(a) control experiment

(b) 0.1 mg P/L

(c) 0.2 mg P/L
Figure 4.19 The SEM micrographs of the copper surface after 30 days of immersion at pH of 7.2 with different dosages of orthophosphate, x10,000 (a) control experiment (b) 0.1 mg P/L (c) 0.2 mg P/L (d) 1.0 mg P/L, 4.0 mg/L chlorine was added and the solution was replace every 24 hours.

4.3.3 Concentration of Leached Copper

In view of environmental impact, the smaller dosage of orthophosphate the better for practical water utility applications. Although a dosage of 1.0 mg P/L has been suggested for an optimal choice based on earlier literature, Figure 4.20 indicates that a dosage of 0.2 mg P/L performs similar inhibition efficiency as 1.0 mg P/L from the third day at pH of 8.0.

This can also been seen in Figure 4.14, where the 0.2 mg P/L of orthophosphate was employed for 30 days of immersion at pH of 7.2 and 8.4, the nearly superpositioned concentration curves of 0.2 mg P/L and 1.0 mg P/L addition after 5 days may suggest that a high dosage (i.e., 1.0 mg P/L) of orthophosphate could be applied during the few days of corrosion control, and then the reduced dosage (i.e., 0.2 mg P/L) also can maintain the same effect.
Figure 4.20 Effect of orthophosphate dosage on copper corrosion in 10 mM MOPS buffer solutions at pH of 8.0, 4.0 mg/L chlorine and orthophosphate were added and the solution was replaced every 24 hours.

4.3.4 Control Experiments

4.3.4.1 Electrochemical Impedance Spectroscopy

The copper coupons were immersed in a solution free of orthophosphate at pH of 7.2, 8.0 and 8.4. Figure 4.21 shows the EIS behavior after 8 days of exposure. The semicircle at pH of 7.2 is much smaller than that at the high pH conditions. A characteristic of infinite length diffusion appears as a diagonal line with a slope of 0.5 and may be evidence that the surface scale is quite porous and cannot exhibit protective characteristics at this pH. The arcs at pH of 8.0 after 8 days of immersion are smaller than the two-day case that was immersed in a 1.0 mg P/L orthophosphate solution. The EIS spectra at pH of 8.4 shows a similar shape and size as the 4-day
copper exposed to the 1.0 mg P/L inhibitor solution at pH of 8.0 (Figure 4.1).

![Nyquist Plot](image)

**Figure 4.21** A Nyquist Plot for different pH values of copper after 8 days of immersion to inhibitor-free solution, 4.0 mg/L chlorine was added and replaced every 24 hours.

The EIS results of control experiments support the idea that at lower pH, the corrosion of copper continues active even after 8 days, while it dramatically slows down at pH of 8.0 and 8.4 via the formation of finite length diffusion impedance, which might be due to the formation of Cu (I)-containing compounds, which have been confirmed to inhibit the corrosion.

**4.3.4.2 Polarization Methods**

The polarization study of control experiments at pH of 7.2 and 8.4 after different immersion times shows that the corrosion potential shifts positively from -128 mV to 0 mV. The anodic current is always lower at the high pH and passivation occurs after 30
days of exposure in the solution that is free of inhibitor.

**Figure 4.22** Steady state polarization curves for copper coupons at pH of 7.2 and 8.4 after different immersion times, where 4.0 mg/L chlorine was added and replaced every 24 hours, control experiments without orthophosphate.

### 4.3.4.3 Concentration of Leached Copper

A 24-hour leached copper concentration in the control experiment was measured on the first day of immersion. From Figure 4.23, the copper leaches rapidly when no inhibitor is added, especially at pH of 7.2, the copper concentration increased from 0.5 ppm at 30 minutes to 3.8 ppm after 24 hours.
Figure 4.23 The 24 hour accumulated concentrations at pH of 7.2, 8.0 and 8.4, control experiment without orthophosphate.

Meanwhile, the concentration of leached soluble copper (filtered) did not change dramatically after 24 hours for the samples taken at the 34th day immersion solution when 1.0 mg P/L orthophosphate was used (Figure 4.24). The concentration curves at pH of 8.0 and 8.4 are relatively steady with a slight fluctuation; an increase from 200 ppb to 500 ppb in 24 hours at pH of 7.2 is observed. Based upon the 24-hour short immersion period scale results, the protective film on the copper surface can control the leaching of copper on a daily dosage.
Figure 4.24 The 24 hour accumulated concentrations at pH of 7.2, 8.0 and 8.4 on the 34th day of immersion, 1.0 mg P/L and 4.0 mg P/L were added.

Therefore, the addition of large amount of inhibitor will promote the anodic passivation process, such as 5.0 mg P/L at pH of 7.2 and 1.0 mg P/L at pH of 8.4 after two days of exposure according to the polarization curves. The growth of surface scale is related to the dosage of the inhibitor, the 1.0 mg P/L orthophosphate helps to produce a less porous structure at pH of 7.2. However, in view of the minimum environmental impact and reducing the scale on pipe surfaces caused by orthophosphate, a 0.2 mg P/L dosage from pH of 7.2 to 8.4 provides similar protective effect as the 1.0 mg P/L either from the polarization methods or the leached copper concentration measured by ICP after the first five days. The addition of large amount of orthophosphate during the first stage (i.e., 1~5 days) and then reducing the dosage should be feasible to control copper corrosion, as well as to meet the environmental
regulations of phosphate discharge.

4.4 The Mechanism of Orthophosphate Inhibition

The complex behavior of orthophosphate on copper surface in the aqueous environment has not been investigated as intensively as the organic inhibitors, whose inhibition mechanism has been widely accepted as the physisorption or chemisorption on the surface. Earlier researchers believed that orthophosphate on copper is an adsorption process (Andrzejaczek, 1979), however, more and more evidence in the recent years from electrochemical and concentration monitoring measurements suggest that the orthophosphate produces a low solubility scale of cupric phosphate on the pipe surface at short immersion times before the naturally insoluble malachite scale eventually forms (Reiber, 1989, Schock, 1995 and Edwards. et al., 2002). In this section, a simple 3-step mechanism is put forth at pH of 7.2, the pH of neutral drinking water.

4.4.1 Mechanism proposed

Steps1. Incoming \( \text{H}_2\text{PO}_4^- \) and \( \text{HPO}_4^{2-} \) ions form surface complexes with copper ions on the solid surface. Concentration of P should reduce rapidly in the first stage to form the initial layer; other aqueous anions such as \( \text{ClO}^- \) and \( \text{OH}^- \) react with copper ions.
Figure 4.25 (a) Proposed adsorption process

Steps 2. Adsorbed phosphate will then act as a sorption site for dissolved copper and they form a ternary complex (surface precipitation). The copper concentration should decline, since the corrosion is controlled by the phosphorus adsorbed in step 1. A monolayer film is formed to reduce the leaching of copper directly from the copper coupon; the adsorbed phosphate will also react with dissolved copper in the liquid phase.
Figure 4.25 (b) Proposed precipitation process

Steps 3. The formation of Cu₃(PO₄)₂ or a similar scale on copper surface. At pH of 7.2, where H₂PO₄⁻ and HPO₄²⁻ are the predominant forms of orthophosphate, the formation of copper multi-hydrogen phosphate compounds is also possible. This may be a reason for the slow kinetics illustrated by experiment results.

Figure 4.25 (c) Proposed equilibrium process

Figure 4.25 The proposed inhibition mechanism of orthophosphate on copper.

4.4.2 Results and Discussion for the Proposed Mechanism

4.4.2.1. A Heterogeneous equilibrium is slowly established

Figure 4.26 shows the adsorption curves when different concentrations of orthophosphate were initially added within 70 hours. At 100 ppb and 200 ppb of orthophosphate, the surface coverage reaches a constant value after only 20 hours of reaction, which might indicate that this dosage is not sufficient to control the release of copper.

When 300–500 ppb of orthophosphate is applied, the kinetics has not reached an
equilibrium even after 70 hours of reaction. This may be due to a slow release of copper after a period of time; a gradual rearrangement of phosphate ions adsorbed on the surface to form the ternary surface precipitates. Adsorption experiments cannot give a satisfactory explanation for this phenomenon.

Surface coverage = \left[ P(0 \text{ min}) - P(\text{specified time}) \right] / P(0 \text{ min})

![Figure 4.26 Adsorption curves of different concentrations of orthophosphate at pH of 7.2 within 70 hours of immersion.](image)

**4.4.2.2. Surface precipitation process**

To study in more detail of the complex surface precipitation process, the spike methods suggested by Ler and Stanforth (2003) is employed. From Figure 4.27, the copper spike was added after 30 hours. It results in a rapid increase in the amount of P absorbed (surface coverage) with the subsequent adsorption kinetics following a similar reaction kinetics pattern as the control experiment, where only 300 ppb of orthophosphate was initially applied.
Figure 4.27 Spike experiment, shown as the phosphate surface coverage vs. time, 300 ppb orthophosphate was initially added. Different concentrations of Cu$^{2+}$ ions were spiked into the system.

Based upon the solubility product $\log K$ of calcium phosphate $\text{Ca}_3(\text{PO}_4)_2$ (-28.6), copper phosphate $\text{Cu}_3(\text{PO}_4)_2$ (-36.8) and lead phosphate $\text{Pb}_3(\text{PO}_4)_2$, -42.1), Ca$^{2+}$ and Pb$^{2+}$ metal ions spike experiments are illustrated in Figure 4.28.

When lead was spiked after 30 hours, it demonstrated a similar reaction kinetic profile as copper did (Figure 4.27). But for calcium, it is noticeable that the addition of Ca$^{2+}$ did not affect the surface coverage of phosphate.

According to the solubility products of the respective solids, lead and copper are the first ions to precipitate with phosphate on the metal surface and react with soluble phosphate in solution. This may be evidence of the ternary complex (i.e., precipitation) on the metal surface.
Figure 4.28 Spike experiment, shown as the phosphate surface coverage vs. time, 300 ppb orthophosphate was initially added, different concentrations of Ca\(^{2+}\) and Pb\(^{2+}\) ions were spiked into the system.

4.4.2.3. Desorption of Orthophosphate

The desorbed phosphate concentration is quite low after sufficient long immersion time (72 h) in buffer solutions at pH of 7.2 (Table 4.5), this may be the result of the dissolution of the phosphate-containing scale. The leached concentration of phosphate is in accordance with the original phosphate concentration. When 400 ppb of orthophosphate was initially added, the measured orthophosphate after 72 hours is also higher than the concentration in the 200 ppb spike experiment. This may indicate that the ions produced by the dissolution of solids can undergo further reactions.
Table 4.5 The concentration (ppb) of phosphorous during desorption process. 200ppb and 400ppb orthophosphate was added initially until 72 h. Then the copper coupons were immersed in the 10 mM MOPS buffer solution at pH of 7.2. The leaching concentration of phosphorus was monitored by ICP-MS

<table>
<thead>
<tr>
<th>Time</th>
<th>200ppb initially added</th>
<th>400ppb initially added</th>
</tr>
</thead>
<tbody>
<tr>
<td>72h</td>
<td>33</td>
<td>47</td>
</tr>
<tr>
<td>96h</td>
<td>13</td>
<td>35</td>
</tr>
<tr>
<td>112h</td>
<td>9</td>
<td>22</td>
</tr>
</tbody>
</table>
CHAPTER 5
CONCLUSIONS

The inhibition effect of orthophosphate on copper corrosion in drinking water distribution systems was studied in this project. The experiment results showed that a scale formed on copper surface relatively rapidly during the first 15 days. The equivalent circuit model used to simulate the EIS spectra fit data well and yielded information on several parameters, such as the charge transfer resistance $R_{\text{ct}}$, which varied from 2 to 10 kohm and the protective film resistance $R_{\text{film}}$, which varied from 15 to 80 kohm when the immersion time is from 2 to 30 days at pH of 8.0. Diffusion within the protective film was found to play a significant corrosion-limiting role according to the $Z_{\text{film}}$ change tendency with time. PDS and XPS results suggested that the formation of Cu$_2$O, CuO, CuCO$_3$, Cu (OH)$_2$ and other Cu (I), Cu (II) species varied with exposure time. In the early stages, Cu (II) compounds were the main species regardless of pH, while Cu (I)-containing product will appear at longer immersion times and retards the anodic process. The addition of orthophosphate promoted the anodic passivation process by forming Cu$_3$P, Cu$_3$ (PO$_4$)$_2$, etc., and reduced the duration required for copper passivation. SEM images indicated that the pores of the 10-day immersion sample were ~ 0.5 µm in diameter, however, after the 30-day immersion, a compact scale structure appeared, which may be due to the cupric phosphate precipitation on the copper surface. The formation of this precipitated film protected the copper surface from aggressive ions, such as Cl$^-$ and OH$^-$. 
It is known that pH is one of the most significant parameters in copper corrosion control by orthophosphate. The inhibition efficiency is more satisfactory at low pH (90 percent at pH of 7.2) than that at high pH (40 percent at pH of 8.4). The passivation of the anodic process will occur naturally without the addition of orthophosphate at pH of 8.4, if a sufficiently long reaction time (30 days) is allowed. In the control experiment at pH of 7.2, it was found that the anodic region in the polarization curves stayed active even after 30 days, and the leached copper concentration was as high as 3.5 ppm. Several peaks in the polarization curve when 1.0 mg P/L orthophosphate was applied after 30 days at pH of 7.2 indicate different anodic processes, such as chemical reactions and the diffusion of active reactants as well as the charge transfer occurring within the solid/liquid interface.

From the result and discussion of the dosage effect, the addition of large amounts of the inhibitor will promote the anodic passivation process, such as 5.0 mg P/L at pH of 7.2 and 1.0 mg P/L at pH of 8.4 after two days of exposure based on the polarization curves. The growth of surface scale was related to the dosage of the inhibitor, a 1.0 mg P/L orthophosphate helped to produce a less porous structure at pH of 7.2. However, in view of the minimum environmental impact and reducing the scale thickness on copper pipe surfaces, a 0.2 mg P/L dosage at pH of 7.2 to 8.4 exhibited a similar effect as the 1.0 mg P/L did from the polarization results and the leached copper concentration measured by ICP after 5 days of immersion. Therefore, the addition of large amounts of orthophosphate in the first few days and then reducing the dosage
should be feasible to control corrosion, as well as to meet the environmental regulations of phosphate discharge.

The simple mechanistic research indicated that corrosion inhibition by orthophosphate on copper surfaces was a rather slow heterogeneous process. Metal-ion spike experiments and desorption of orthophosphate results provided evidence of the proposed 3-step inhibition mechanism, adsorption, surface precipitation and equilibrium.

As the suggestion to the application of orthophosphate by water utilities, they also should conduct off-line tests before using orthophosphate to determine the optimum dosage according to the local water quality and the physical characteristic of copper plumbing.
REFERENCES


Ler, A. and R. Stanforth. Evidence for Surface Precipitation of Phosphate on Goethite,


Sastri, V.S. Corrosion Inhibitors: Principles and Applications, John Wisley & Son Ltd,


Standards Number 60 and 61, Drinking Water Chemicals and System Components-Health Effects, National Sanitation Foundation, Ann Arbor, 1988.


Trachili, B., M. Keddam, H. Takenouti. and A. Srhiri. Protective Effect of Electopolymerized 3-amino 1, 2, 4-triazole Towards Corrosion of Copper in 0.5M NacCl, Corrosion Science, 44, pp. 997-1008. 2002.
