CHAPTER 1

INTRODUCTION

1.1: Background

Deaerator in an equipment used to remove dissolved oxygen, carbon dioxide and other non-condensible gases from boiler feedwater [1]. Treated water containing dissolved oxygen is fed onto a contacting device where the water can be heated and contacted with steam which is also fed to the vessel. The steam heats the incoming treated water to around 250 °F (120 °C) and allows oxygen to escape (along with any small amount of uncondensed steam) to the atmosphere [2].

Due to the nature of this process, the internal wall of deaerator is highly exposed to corrosive environment. Cost effective solution to protect this surface is by coating this internal section of the deaerator. However, not all coating system successfully applied to this equipment which operated under immersed condition at high temperature up to 70 ^{o}C.

The degradation of the coating is usually result in blistering, loss of adhesion, softening or embrittlement. This require regular repair which is done during shutdown. Thus, there is a challenge in coating industry to develop new coating formulation system to overcome this limitation.

1.2: Problem Statement

Although coating is the most cost effective solution to deaerator corrosion protection, poor performance of the applied coating system requires regular repair which contribute to cost escalation. In order to overcome this problem, there is a need for a superior formulation to be used in this environment. A new formulation coating based on polyurea is claimed to be better than polyurethane in term of immersion in water at high temperature.

1.3: Objective and Scope of Study

The main objective of this project is to evaluate and analyze the performance of polyurea coating for internal section of deaerator which operates under water immersion at high temperature. The performance will be evaluated based on the results of several laboratory tests conducted by referring to American Standard of Testing Material (ASTM) testing and PETRONAS Technical Standards (PTS). Besides that, another objective of this project is to investigate degradation mechanism of the coating and to recommend optimum coating system to be applied under this condition.

CHAPTER 2

LITERATURE REVIEW

2.1: Corrosion Problems in Deaerator

Due to working principle, operation and environment of deaerator, this equipment is subjected to many problem associate with corrosion. If these problems occur continuously, it will become more serious and result in deaerator malfunction and breakdown. Section 2.1.1 until 2.1.3 discuss about corrosion problems normally found in deaerator.

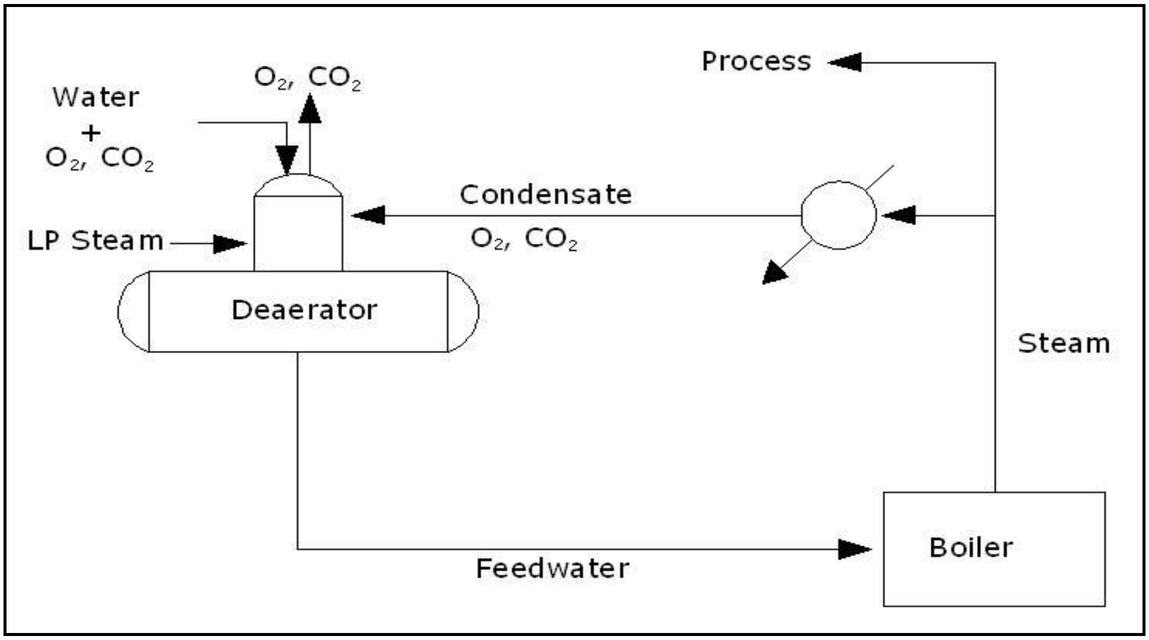


Figure 2.1: Deaerator Removes Corrosive Gases from Boiler Water

Figure 1 above shows process flow of water into the boiler together with deaerator unit which operates to remove gases dissolve in the water. These gases need to be removed from the feedwater because the presence of high oxygen level inside the system can lead to serious corrosion damage to the boiler. Carbon dioxide will lower the pH which causes the water to be acidic, and the rate of corrosion will be increased. Refer to Appendix 1 and Appendix 2 for a sketch of deaerator location in an operation.

2.1.1: Pitting in Deaerator

Oxygen levels in just parts per billion dissolved in the feedwater stream for boilers and heat-recovery steam generators (HRSGs) can cause pitting and reduce the operating life of steam cycle components. That's why reliable steam plant operation relies on low dissolved oxygen levels in boiler and HRSG feedwater systems to limit pitting and related corrosion damage to carbon steel components, including deaerator vessels and storage tanks, piping, and boiler tubes [3].

Pitting corrosion is a very localized, non-uniform type of corrosion that appears as pinholes or shallow craters ("pits") in the steel surface. Pitting corrosion is sometimes difficult to detect, because layers of oxide or other scale may cover the "pits". It is recommended that some vessel surfaces be cleaned and spot-checked for pitting. This inspection is normally done in conjunction with MT and UT examination.

One cause of pitting is excessive dissolved oxygen in the water after extended periods with the unit off line or after filling the unit without sufficient oxygen scavengers and not placing the unit into operations. Pitting cannot occur in a properly operating deaerator during operation.

Pitting can occur in all areas of the deaerator but is most often found in the storage tank. Generally with good operating procedures including use of a deoxidizer and not filling the deaerator until the unit is ready to be placed into service, damage from pitting in utility deaerators is minimal [4].

2.1.2: Flow-accelerated Corrosion (FAC)

Flow-accelerated corrosion (FAC) may be defined as metal loss that occurs in carbon steel equipment when the normally protective magnetite (Fe_3O_4) layer is dissolved into a flowing stream of water or water and steam. The metal goes through continuous cycling of oxide layer production followed by loosening and dissolution into the turbulent stream. The oxide layer is not able to protect the metal, and the continuous loss of the oxide layer results in the steady loss of metal thickness.

There are four conditions that have been identified that are required for FAC to be active in components. These include:

1. **Water Chemistry**, the water in the system needs to be demineralized with a pH of less than 9.6
2. **Hydrodynamics**, turbulent flow is required.
3. **Materials**, low concentrations of chromium, molybdenum, and copper

4. **Temperature**, water temperature needs to be between 212F and 572F (100C-300C).

Temperature and flow are generally hard to change in an existing system so a change materials or water chemistry is generally believed to provide the best solution to FAC damage. Chemistry is often the most overlooked and possibly the easiest solution.

Two different types of FAC have been identified in utility equipment including deaerators, single phase and two-phase. The difference on which type of damage occur depends on if there is only water present of if there is a steam-water mixture present. The appearance of the damage will be different depending on which type of FAC caused the damage. Single-phase will have a scalloped appearance while two-phase FAC will have a tiger striped or horseshoe pit appearance. While most of the deaerator will be a reddish brown color, areas where FAC is active will appear to be grey like polished metal or have a black color.

FAC in deaerators occurs at locations where water is flowing with excessive velocity over a carbon steel pressure vessel shell, and is relatively common in large, horizontal deaerators in power plants. Steam enters the end of the deaerator vessel, flows under the tray enclosure, and in turn creates turbulent flow of the water in the bottom of the vessel. In several specific cases, the results have been dramatic - broad areas in the bottom section of the deaerator were characterized by a polished, scalloped and pitted surface.

Loss of metal thickness was extreme in some cases. In one case, cracks had begun to form along the lines of pits [4].

The deaerator removes oxygen just prior to feedwater entering the boiler economizer section of the HRSG, making conditions near the optimum (approximately 300F) for FAC damage to carbon steel components. Components with a change in flow direction--such as upper tube bends, piping elbows, and high-fluid-velocity regions in deaerator vessels--are especially vulnerable. Also, because operating pressures in deaerators are typically slightly above atmospheric, the vessel shell and head thicknesses required by ASME Code are relatively thin compared with those of higher-pressure vessels such as steam drums. If protective magnetite layers are damaged, a rapid wall thinning can occur in areas that are exposed to high local velocities under adverse water chemistry [4].

During the routine inspection of horizontal deaerators, advanced flow-accelerated corrosion is frequently discovered on the bottom of the heater vessel shell. Significant metal thickness is sometimes lost from the pressure shell as a result of this effect.

FAC is metal loss that occurs in carbon steel equipment when the normally protective oxide layer is dissolved into the flowing stream of water and / or steam. The metal goes through continuous cycling of oxide layer production followed by loosening and dissolution into the turbulent stream. The oxide layer is not able to protect the metal, and the continuous loss of the oxide layer results in the steady loss of metal thickness.

Upon entry into the bottom portion of the heater vessel, the areas subject to FAC are immediately obvious – bright, polished patches of metal that are easily identified on the vessel shell below the tray area. These areas are also characterized by severe pitting.

Figure 2.2: Typical Location of FAC at Bottom of Heater Shell

Normally, a protective oxide layer forms on all carbon steel internal surface to inhibit further corrosion. In the case of FAC, water that flows with excessive velocity and / or turbulence continually dissolves the oxide layer. Thus the local areas in the heater vessel subject to FAC are exposed to water with such flow characteristics [5]. Refer Appendix 3 to Appendix 6 for more image of FAC occurs in deaerator.

2.1.3: Other Forms of Corrosion in Deaerator

Besides pitting and flow accelerated corrosion, deaerator can also be subjected to corrosion fatigue and intergranular corrosion. Corrosion fatigue, which is defined as the reduction of fatigue resistance due to the presence of a corrosive medium. In corrosion fatigue, cracking results from the combination of a corrosive environment and cyclic stress [6].

Intergranular corrosion of deaerator made of stainless steel. When stainless steel internal components are fabricated from grades containing greater than 0.03% carbon (i.e. other than “L” grades), they become susceptible to sensitization. Although deaerators do not operate at elevated temperatures, during welding or post-weld heat treat the material may be sensitized. At temperatures between 800°F and 1600°F , carbon can diffuse to the grain boundaries and precipitate out as chromium carbide, thus depleting the boundaries of chromium. The corrosion resistance of the grain boundaries is then dramatically reduced [4].

Corrosion in deaerator is a very serious problem. This problem must be control to ensure that service life of deaerator can be maintained. Serious corrosion problem can lead to equipment malfunction and jeopardize the safety of the workers. There are numbers of corrosion prevention methods available today. Cathodic protection, coating, corrosion inhibitor, proper material selection and equipment design are the most commonly used method to control corrosion. Among all of these methods, coating is the most flexible method because it can be used in nearly all environments depending on the quality and performance of the coating material used for that application. Section 2.2 discuss further on coating as corrosion protection.

2.2: Coating as corrosion protection

Prevention by coating is the most popular as it is very cost effective. Coating applied on the metal surface of deaerator provides physical barriers to corrosion. The coating must be nonreactive in the corrosive environment and resistant to mechanical damage that exposes the bare metal to the corrosive environment.

Besides become the cost effective corrosion prevention method, coating also come with wide variety of option. However, the formulations of current coating material are limited to normal condition only. Most of the coating failed when subjected to extreme environment. Therefore, the needs for new formulation emerge.

2.2.1: Coating for Internal Section of Deaerator

Interior part of deaerator is normally lined with high quality baked epoxy lining [7-8]. Baked epoxy is designed for extreme immersion service with resistance to acid, alkaline, salt and water. They are resistance to wide range of pH environment, typically in storage tank, process and transport equipment [9].

2.2.2: Limitation of polyurethane coating

Polyurethane presents the best compromise between cost and quality, but is limited by the application performance. The polyurethane system is susceptible to blistering when the substrate contains more than five per cent humidity. This is due to competition between hydroxyl-polyols and water for the reaction with an isocyanate group. The humidity content of the environment and the application temperature are limiting factors for polyurethanes and other chemically reacting systems. New formulation which produces polyurea is said to be a good candidate to break the limitation of applying Polyurethane coating [10]. As illustrated in Figure 4, application of polyurethane is limited to low relative humidity and application temperature. Hybrid polyurethane can be applied at higher relative humidity. On the other hand polyurea coating have the highest application temperature and relative humidity.

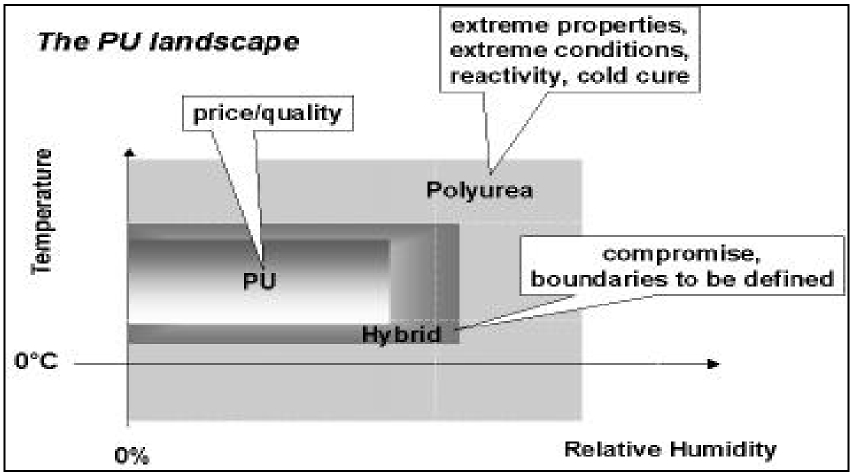


Figure 2.3: Applicability of the Different PU Chemistries

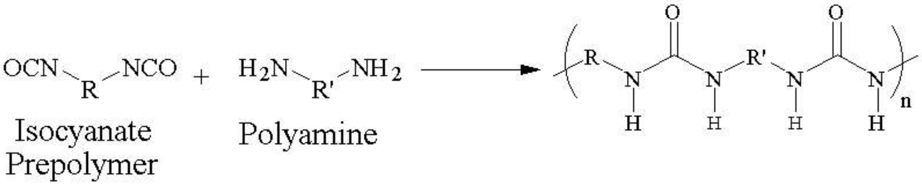


Figure 2.4: Polyurea Formulation

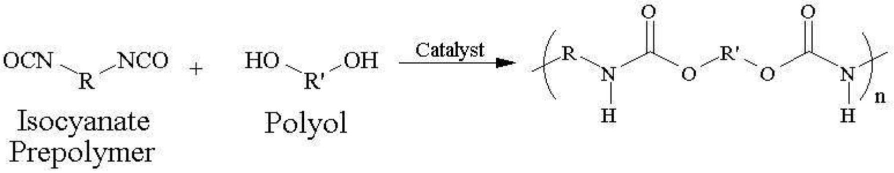


Figure 2.5: Polyurethane Formulation

Figure 5 and Figure 6 show the coating formulations for polyurethane and polyurea coating respectively. Polyurea based thick film coatings encompass a diverse group of products. A pure polyurea is the combination of isocyanate with a long chain amine, excluding the hydroxyl reactive sites. For reference, pure polyurethane coatings are formulated using an isocyanate combined with hydroxyl-containing polyols.

2.2.3: Evaluation of coating performance

After the test was conducted, the specimen will be observe and examine to evaluate its performance. The first direct evaluation is the observation of any coating defect. Apart from that, the specimen can be examined under microscope or Scanning Electron Microscope (SEM) to gain more insight on change of coating microstructure that lead to the defect initially observed.

Another evaluation technique is using Electrochemical Impedance Spectroscopy. Electrochemical Impedance Spectroscopic techniques can be used to determine the quantity of water that has penetrated the coating, from this it is possible to gauge the solubility of the coating. The data obtained from EIS measurements can be correlated directly to allow analysis of the following phenomena:

1. Blister formation [11]
2. Water permeation
3. Swelling, of the coating
4. Loss of adhesion, including delamination
5. Corrosion

The uptake of water in organic coatings can be determined directly from capacitance measurement. The dielectric constants of organic coating are generally small, and hence it is normal for them to be an order of magnitude smaller than that of water which has a dielectric constant around 80 at ambient temperatures. For this reason, the absorption of small amount of water can significantly effect the capacitance of the film. The capacitance of the organic coating can be determined directly from the dielectric constant of the coating ε, the dielectric constant of a vacuum ε_o, the thickness d, of the dielectric and the surface area, A:

Low frequency data collected using EIS shows considerable sensitivity and variation to changes in the impedance / phase angle – due to the uptake of water. From the data collected, it is apparent that different coating thickness will affect dramatically the effectiveness of the coating to an aggressive environment.

Direct use of EIS techniques will enable manufacturers and researchers to determine detailed information about the properties of these coating in conditions which will reflect the environments of the detail application, giving detailed data relating to the performance and quality of the coating in term of potential adhesion loss [12].

2.2.4: Coating System Approval Process Flow

In order to determine whether polyurea coating can be accepted or not, coating system approval process flow which specify in PETRONAS Technical Standard (PTS) was follow. There are nine (9) numbers of coating testing to be carried out depending on the application and process that the equipment or structure will undergo. For internal section of deaerator, water immersion test are required. See Appendix 9 for list of test specify in PTS [13].

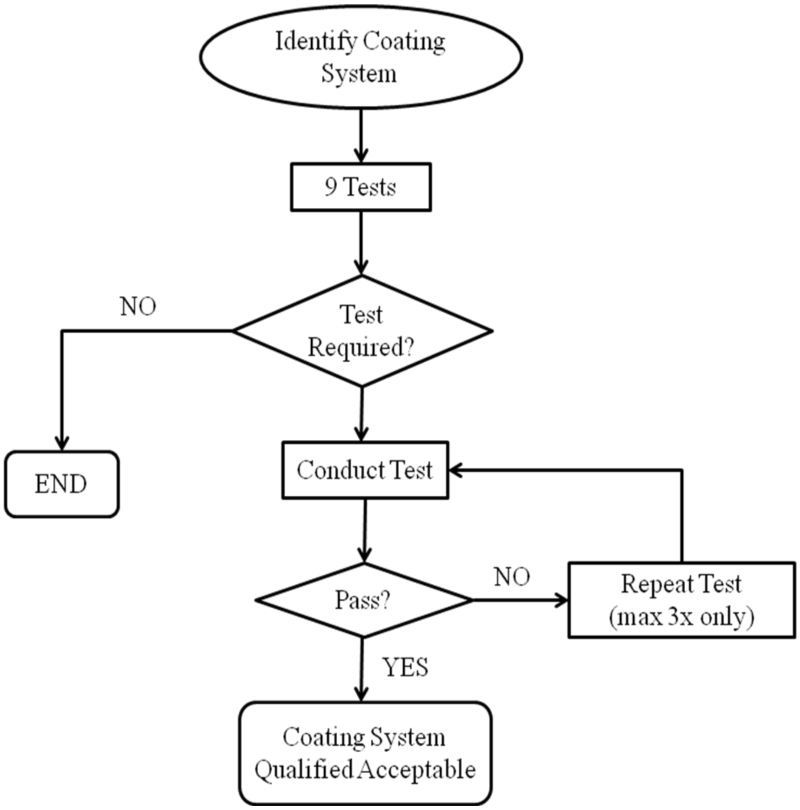


Figure 2.6: Coating System Approval Process Flow

2.3: List of coating test conducted

A lot of coating tests were conducted by company of individual generally with the objective to evaluate the quality, performance and suitability of the coating system to be applied to the required environment as well as to examine the performance of new coating formulation. Below, are list of tests conducted under immerse conditions but in different immersion environment, coating system and dry-film thickness. Results from these testing were used as a reference to estimate the output of my coating testing.

2.3.1: Corrosion Coating for High Temperature Water Immersion Service

This test program has been done in the years 1997-1999 before the start of the Kristin project. The aim of the program was to find candidate system for submerged used for temperature up to 200^{o}C. The design temperature was 162^{o}C and involved short term excursions up to 175^{o}C. The test program had been done in the years 1997-1999 before the start of the Kristin project.

The main qualification testing for an immersed system is covered in two types:

- Cathodic disbondment test at maximum operational temperature
- Ageing testing to verify that the lifetime of the product

The test sample were coated carbon steels plates (150 mm x 200 mm x 5 mm) with coating on both sides and the edges. The test plates were placed in heated and pressurized autoclaves.

- Test temperatures: 140, 160, 180, 200^{o}C.
- Test pressure: 30 bar (sea water with oxygen). the water was change every month to provide new oxygen supply.
- Samples were inspected after 1, 3, and 6 months.

For cathodic disbondment test, Epoxy-phenolic, solvent free coating with 400-500 microns DFT was found to be the best candidate for this test while for accelerated ageing testing, phenolic with 350 microns DFT was recommended for the surface treatment on the project [14].

2.3.2: Water Immersion Testing of Metal Protective Paints-Influence of Bare Metal Areas

Objective of this test s to study the influence of bare metal on or in contact with the test panel under water immersion at 25°C.

Seven raw linseed oil paints were prepared with seven widely recognized metal protective paint pigments. Single coat of each of the seven paints were spray on both sides of six steel panels resulting a total of 42 test specimens. The paint films were allowed to dry for 3 weeks under room conditions before the test were started. Finally, holes of 1.17mm in diameter were drilled into the backs of two panels of each paint. The depth was about half the panel thickness. The area of bare metal exposed was slightly over 1mm^2. Circular area of 78.5mm^2 were laid bare on a one side of two other panels of each paint. Thus two sets of the test panel were completely coated on all sides, two sets had bare metal areas of about 1mm^2 and 2 had bare metal areas of about 78.5mm^2 on each panel [15].

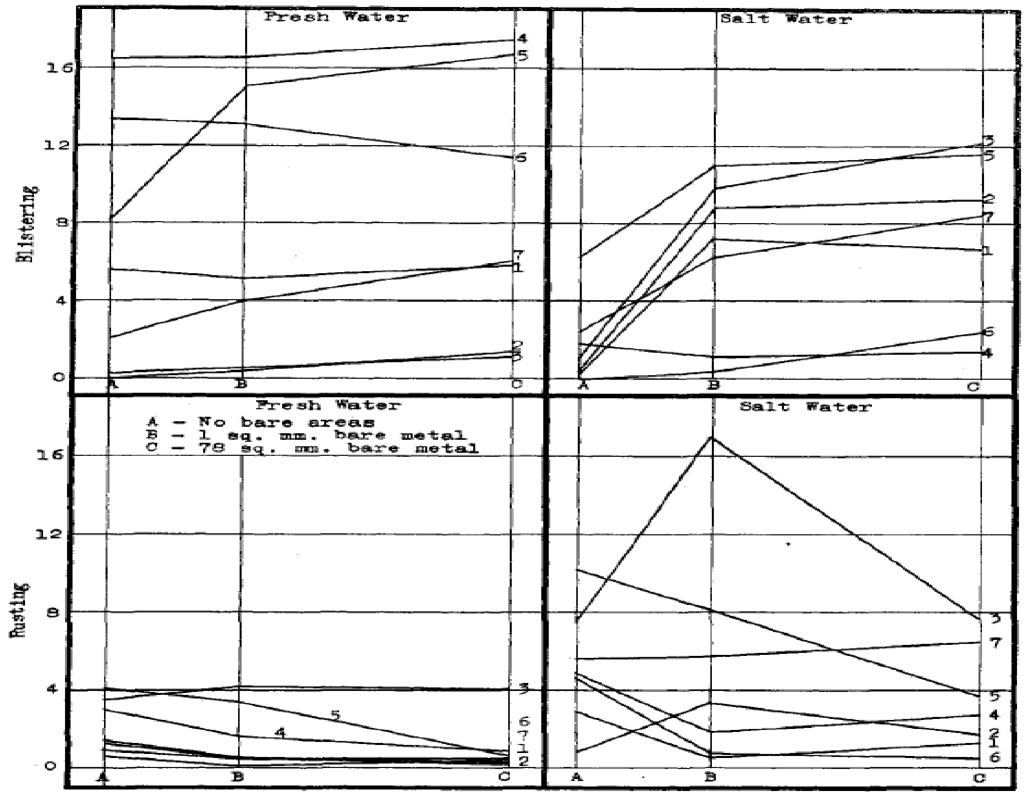


Figure 2.6: Effect of Bare Area on Blistering and Rusting

2.3.3: Coatings for Underwater and Wet Surface Application

Epoxy resin based paints were used in these experiments. This type of paint generally offers very good corrosion protective properties and widely used in harsh environment. Epoxy resins having epoxy equivalent weights 200 (liquid epoxy resin), 500, 900 and 2000 (solid) were taken for this study. Among them, liquid epoxy resin was found to be the best choice as binder.

For this underwater paint system, ketimine is used as a curing agent, which is the condensation product of amines and ketones. Additive was then added to this paint to evaluate its adhesion properties. Only paints system with excellent adhesion properties were selected to be used in the nest experiment which is immersion test. The paint systems are:

Table 2.1: Paint systems

Paint System	**Epoxy Resin Type**	**Ketimine**		**Additives**
		Ketone	Amine	
A	Liquid resin	Methyl ethyl	n-benzyl dimethyl	Propylene glycol and bisphenol-A
B	Liquid resin	Methyl ethyl	n-benzyl dimethyl	Propylene glycol, bisphenol-A and castor oil
C	Liquid resin	Cyclo-hexanone	n-benzyl dimethyl	Propylene glycol and bisphenol-A

Mild steel panels of size 5cm x 7.5 cm coated with this paints system were immersed in 3 per cent NaCl solution and the changes were observes periodically. This test showed that coating system B is the best candidate since very few rust spots visible after 216 hours of immersion. System A have very few spots visible after 144 hours of immersion while system C is the worst candidate since of showed rust spots only after 120 hours of immersion [16].

2.3.4: Electrochemical Impedance Spectroscopy: Testing Coating for Rapid Immersion Service

Objective of this test is to evaluate two high built epoxy linings for rapid water immersion with temperature ranging from 25^{o}C to 40^{o}C. The performance of a two-coat application of a low temperature-cure 80% volume solids modified phenalkamine epoxy was compared with a one-coat application of a 100% volume solids polyamide epoxy. Each system was immersed in distilled and deionized water after only a 24 to 28 hour curing time.

EIS measurement revealed significant nonvisual differences in the performance of rapid immersion grade coatings as they cured under water. The only onset under film corrosion processes beneath the 100% solid polyamide epoxy coating was readily detected using EIS. In contrast, a modified phenalkamine epoxy achieved full cure under water just as if it had cured under normal ambient conditions [17].

2.3.5: Electrochemical Impedance Spectroscopy of Epoxy-Coated Steel Exposed to Dead Sea Water

Electrochemical impedance tests were applied to steel specimens which were coated by 200 micron epoxy and tested after immersion in Dead Sea Water for different periods at room temperature and at 50^{o}C. EIS were carried out by using Autolab PGSTAT 30 provided with frequency response analyzer, FRA2 in the range of 1Hz to 1kHz. Data were collected for specimens immersed in solution for 133 day at room temperature and at 50^{o}C.

Results taken from Nyquist and Bode plots and as were analyzed by means of software provided with the instrument. Results were presented as the values of capacitance and resistance (Cdl and Rct). Results show that degradation of the coating occurred after immersion in the test solution and were more severe at high temperature. Specimens were examined under scanning electron microscope, and micrographs showed clear rupture and degradation in epoxy coating [18].

2.3.6: Using EIS to Better Understanding Tank Lining Performance in Laboratory and field Evaluation

The impedance of four commercial epoxy tank linings was measured as the coatings were subjected to a series of conditions simulating laboratory testing or industrial service. Based on the coatings and conditions used within this study, the results based on EIS measurement showed:

- The uptake of water and the change in the permeability of the coatings was consistent with key aspects of the coating's formulation chemistry.
- Significant physical and chemical changes occur in the coatings under test or field conditions at elevated temperature and pressure. Many of these changes reverse at varying rates when the coatings are returned to ambient temperature and pressure. Irreversible changes can be the result of coating deterioration and loss of performance [19].

CHAPTER 3

METHODOLOGY

3.1: Laboratory Tests

Two sets of laboratory tests were conducted to meet the objective of this project. The tests were water immersion test and Electrochemical Impedance Spectroscopy (EIS). The DFT of the coating, dimension of the specimen and coating surface preparation were specified for both tests are listed in Table 2 below.

Table 3.1: Laboratory Test

TEST TYPE	**OBJECTIVES**	**DFT (mm)**	**DIMENSION (mm)**	**SURFACE TREATMENT**
Water immersion (ASTM D870)	To test water resistance of coating	1.0	100 x 100 x 0.63	Sa 2.5
		2.0		
		2.5		
		3.0		
Electrochemical Impedance Spectroscopy (EIS)	To determine degradation mechanism in the substrate	2.0	15 x 15 x 0.63	Sa 2.5

The surface to be coated must be completely dry and free from burrs, weld spatter, flux, rust, loose scale, dirt, grease, oil and other foreign matter before any paint is applied for optimum paint coating performance. In this project, the surface preparation method used was blast cleaning using garnet. The specimens were blasted until Sa2.5 standard was reach according to specification by ISO 8501-1.

Polyurea coating was then applied within four hours after the specimens were blasted by spay application. The specimens were allowed to fully cure and dry for 24 hours. The coated carbon steels were received from the coating vendor in large dimension. The specimens were then cut according to the desired dimension before these two laboratory tests can be conducted. Figure below shows general process flow of these tests.

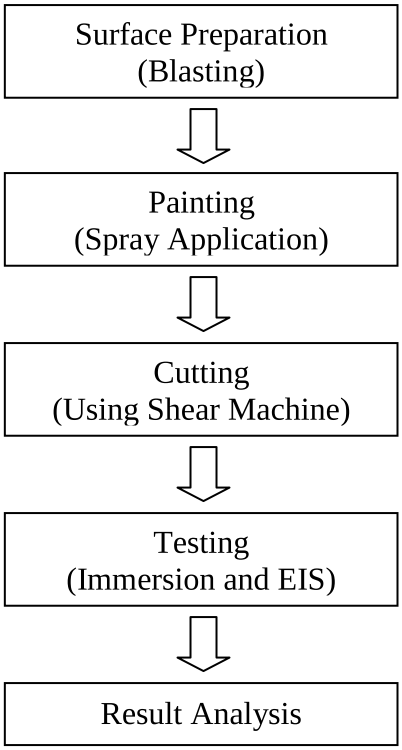


Figure 3.1: Tests General Process Flow

3.1.1: Water immersion test

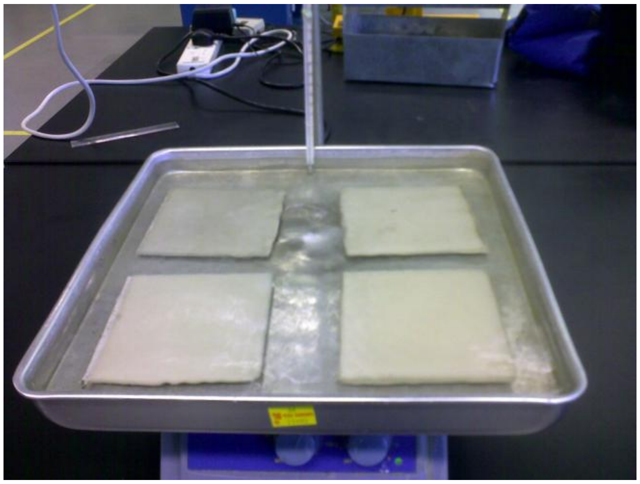


Figure 3.2: Water Immersion Experimental Setup

a) Apparatus:

1. 30cm x 30cm container to place the specimens.
2. Stirrer: For circulation of the water and equal distribution of heat.

3. Supports for the test specimens: Constructed of a non-conductive materials to hold the specimens 30mm apart and 30 mm from the bottom and sidewalks of the tank.
4. Thermometer: To record the degree of hotness or coldness of the water inside the container.
5. Hot Plate: To heat up water inside the container.
6. 10cm x 10cm polyurea coated Carbon Steel with different DFT.

b) Procedure:

1. The container is filled with water to a depth where the test specimens are fully immersed.

2. The water is heated to the desired temperature which is 70ºC with the circulating system in operation. The temperature will be maintained throughout the test.

3. The water is replaced if it became cloudy or colored. Water is added to maintain original water level if needed.

4. The test is conducted for 42 days.

5. The specimens is wiped and it will be rated in change in color, blistering, rusting, loss of adhesion and softening. The specimens were evaluated in no less than 5 min and no more than 10 min after removal from test as the effect from water exposure can change within a short time [20].

The specimens were examined under scanning electron microscope to identify any changes in the microstructure of the coating. An immersed sample with 2mm DFT was used and its microstructure image were compared with 2mm DFT coated specimen which not been immersed. The underlying metal of these two specimens were examined under scanning electron microscope as well to detect any presence of corrosion under insulation.

3.1.2: Elctrochemical Impedance Spectroscopy

a) Apparatus

1. Glass cell to place the specimens.
2. Thermometer: To record the degree of hotness or coldness of the water inside the container.
3. Hot Plate: To heat up water inside the glass cell.
4. 1.5cm x 1.5cm mounted polyurea coated Carbon Steel with 2mm DFT and uncoated mounted carbon steel.

b) Procedures:

1. The 1.5cm specimens were mounted using resin and hardener in 5:1 ratio.
2. The specimens were allowed to cure for 24 hours.

3. The mounted specimens were then grinded to remove the resin the cover the surface of that need to be tested. This process is conducted using grinding machine with 400, 800, and 1000 grit sand paper.

4. The specimens were immersed in tap water at $70^{o}C$ for 7 days.

5. The Autolab instrument is connected to the specimen and the following frequency was subjected:

    - 0.1 to 100000 for uncoated specimen

    - 0.1 to 1000000 for coated specimen

6. After the instrument has completed the measurement, the fitting process was conducted in order to identify the equivalent electrical circuit.

7. Value of solution resistance, Rs, pore resistance, Rp and capacitance, Cdl were recorded.

CHAPTER 4

RESULTS AND DISCUSSION

4.1: Water Immersion Test

A few rust spot were observed from all of the specimens after 48 hours of water immersion test was started. More rust spots were formed along the uncoated edges as shown in Figure 4.1 below after 42 days of immersion.

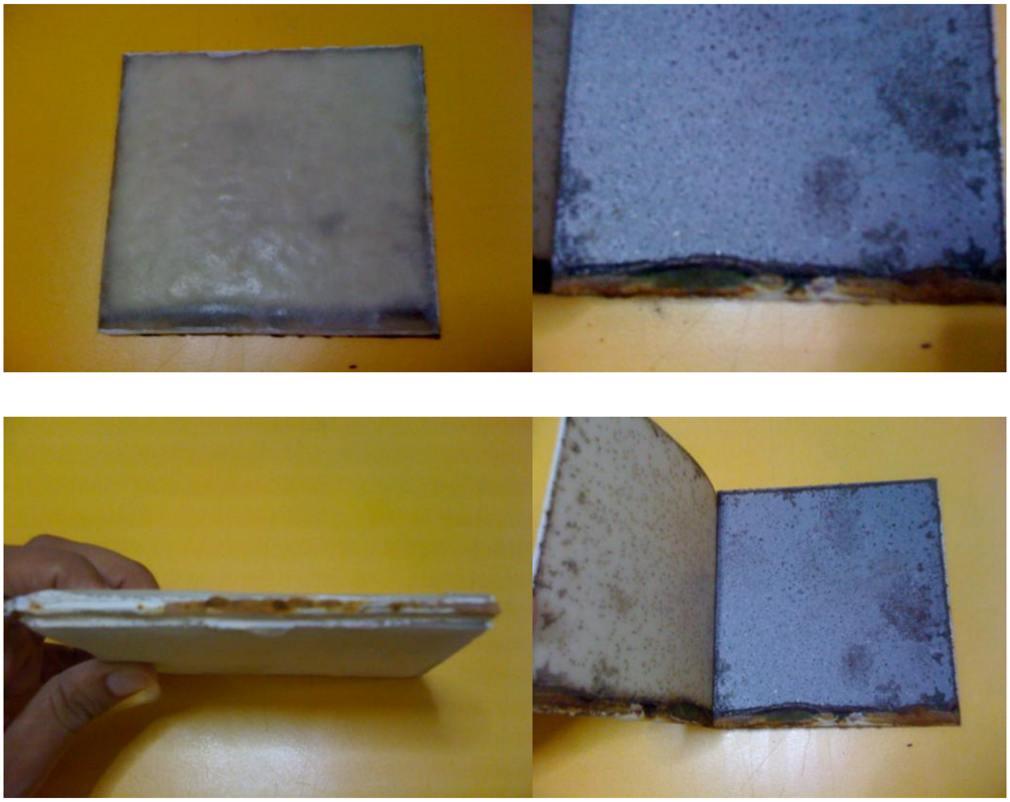


Figure 4.1: Rusting at the Edge of the Specimen

After one (1) week of immersion, change of colour was observed. Further continuation of the test result in softening of the coating layer. Table 4.1 below summarizes the coating defect after 42 days. The defects were determined based on the ASTM D 870.

Table 4.1: Result of water immersion test

DFT (mm)	**Rusting**	**Blistering**	**Loss of adhesion**	**Change in colour**	**Softening**
1.0	YES	NO	YES	YES	YES
2.0	YES	NO	NO	YES	YES
2.5	YES	NO	NO	YES	YES
3.0	YES	NO	NO	YES	YES

Coating colour varies from the original state after being exposed to operation conditions. Colour change indicates a poor colour retention ability of the coating system. However, change in colour cannot be observed clearly since the original colour of the coating is grayish in colour. This defect can be proved by looking at the quality and cloudy colour of the water inside the container when the water is replaced.

Polymeric material experience deterioration by means of environmental interactions. When polymers are exposed to liquids, the main forms of degradation are swelling and dissolution. With swellings, the liquid or solute diffuses into and is absorbed within the polymer. Thus more solute molecules fit into and occupy positions among the polymer molecules. Thus, the macromolecules are forced apart such that the specimen expand or swells. Furthermore, this increase in chain separation results in a reduction of the secondary intermolecular bonding forces. As a consequence, the material becomes softer.

Swelling may be considered to be a partial dissolution process in which there is only limited solubility of the polymer in the solvent. Dissolutions, which occur when the polymer is completely soluble, may be thought of as just a continuation of swelling.

Polymer may also experience degradation by a process termed scission – the severance or rupture of molecular chain bonds. This cause a separation of chain segments at the point of scission and a reduction in the molecular weight. Bond rupture may result from exposure to radiation, heat and chemical reaction

The thermal degradation corresponds to the scission of molecular chains at elevated temperatures. As a consequence, some polymers undergo chemical reactions in which gaseous species are produced. These reactions are evidenced by a weight loss of material. A polymer’s thermal stability is a measure of its resilience to this decomposition. Thermal stability is related primarily to the magnitude of the bonding energies between the various atomic constituents of the polymer. Higher bonding energies result in more thermally stable materials [21].

Uncoated area of the specimens expose the carbon steel directly to the environment and react with water to achieve stability. This reaction result in the formation of rust**.** Rusting of iron consists of the formation of hydrated oxide, $Fe(OH)_3$, FeO(OH), or even

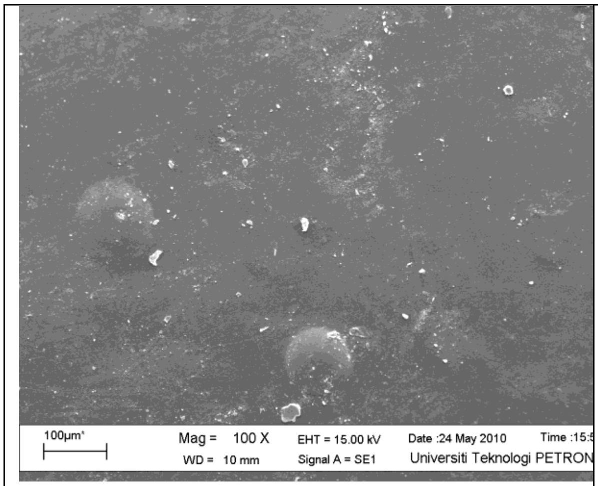
$Fe_2O_3.H_2O$. It is an electrochemical process which requires the presence of water, oxygen and an electrolyte. In the absence of any one of these rusting does not occur to any significant extent. In air, a relative humidity of over 50% provides the necessary amount of water and at 80% or above corrosion of bare steel is worse [22].

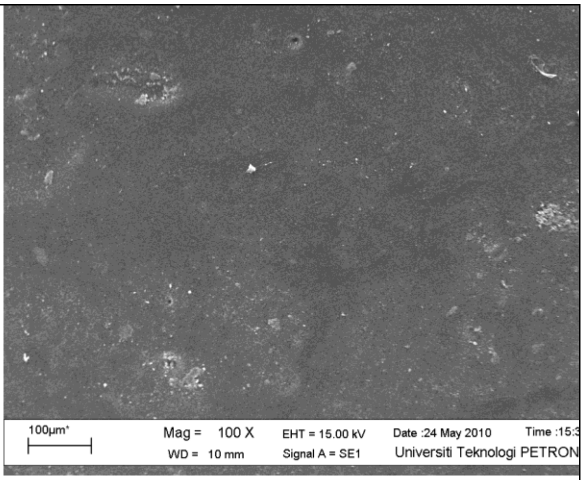
From the above figure, rusting was obviously notified at the area that is directly contact with the water. Substrate under the coating is clear from any rusting formation. Even though water molecules have penetrated into the coating pore, it do not be able to touch the substrate due to high DFT of this coating. Therefore, the underlying substrate is still protected.

For specimen with 1.00 mm DFT, rusting formation result in loss of adhesion of the coating layer. The coating layer can easily tear off from the substrate. Poor adhesion is the result of improper bonding or wetting of the paint film to the surface onto which the coating is being applied. For specimens with 2.00 mm, 2.50 mm and 3.00 mm adhesion the coating layer are hard to be removed from the substrate and thus indicate that polyurea poses greater adhesion property as the DFT increase. With higher DFT, longer time is required for water molecule to be in contact with the substrate. Therefore, corrosion process is delayed.

The ability of polyurea coating to remain stick to the substrate in water immersion at 60^oC shows that is has a superior property. However, polyurea cannot stand on its strength only. Without proper surface preparation and adequate amount of mixture to produce polyurea during the spray application, coating defect can easily be developed no matter how powerful the coating system is claim to be.

A coated specimen with 2mm DFT was examined under scanning electron microscope (SEM) to identify any change in the coating microstructure. An unimmersed coated specimen with 2mm DFT was also examined so that the image can be compared. Apart from that, the microstructures of the underlying metal were also examined. Figure 4.2 – 4.3 show the images of the microstructure at magnification of 100, 500 and 1000. From the image in Figure 4.2 swelling can be observed from the coating surface. However, no swelling is observed from the uncoated specimen.





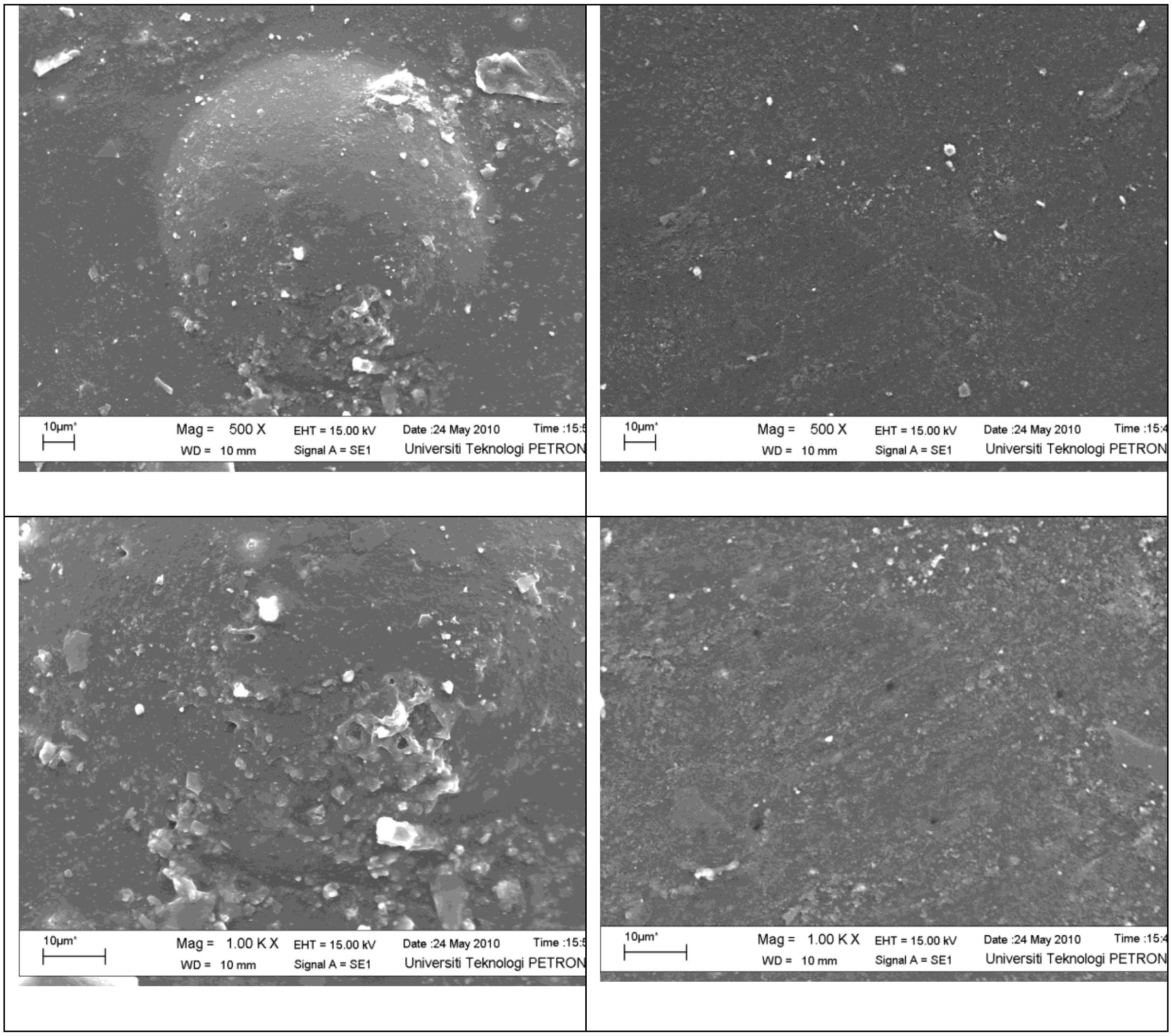
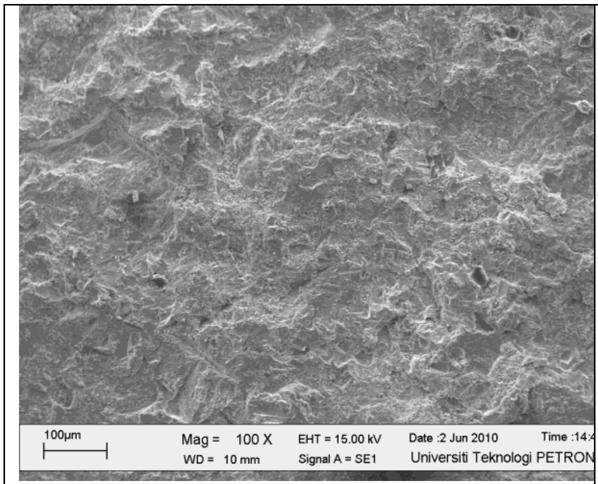
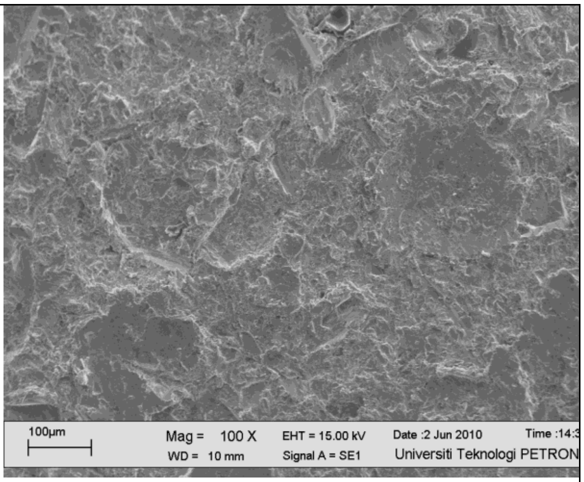
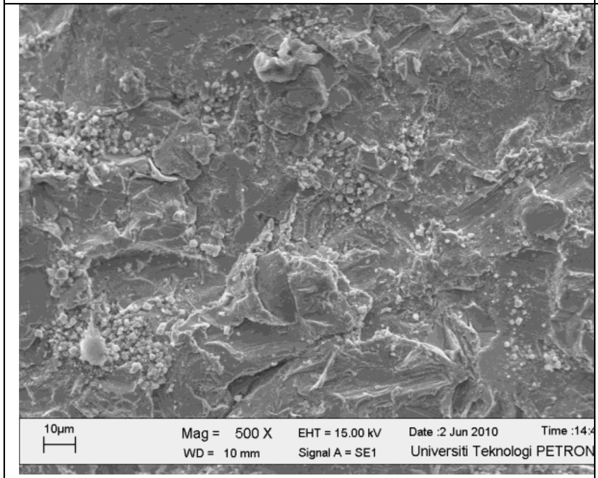
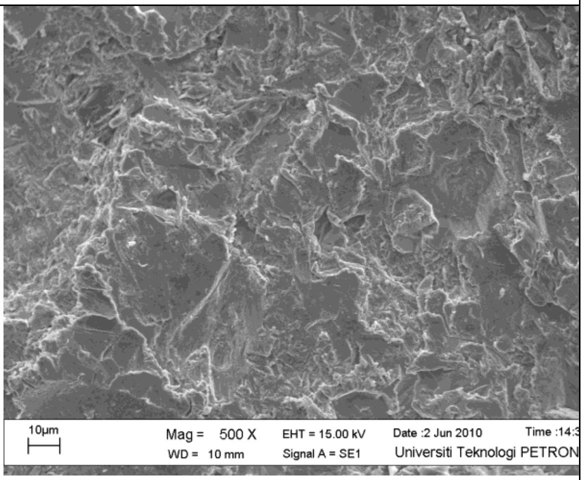


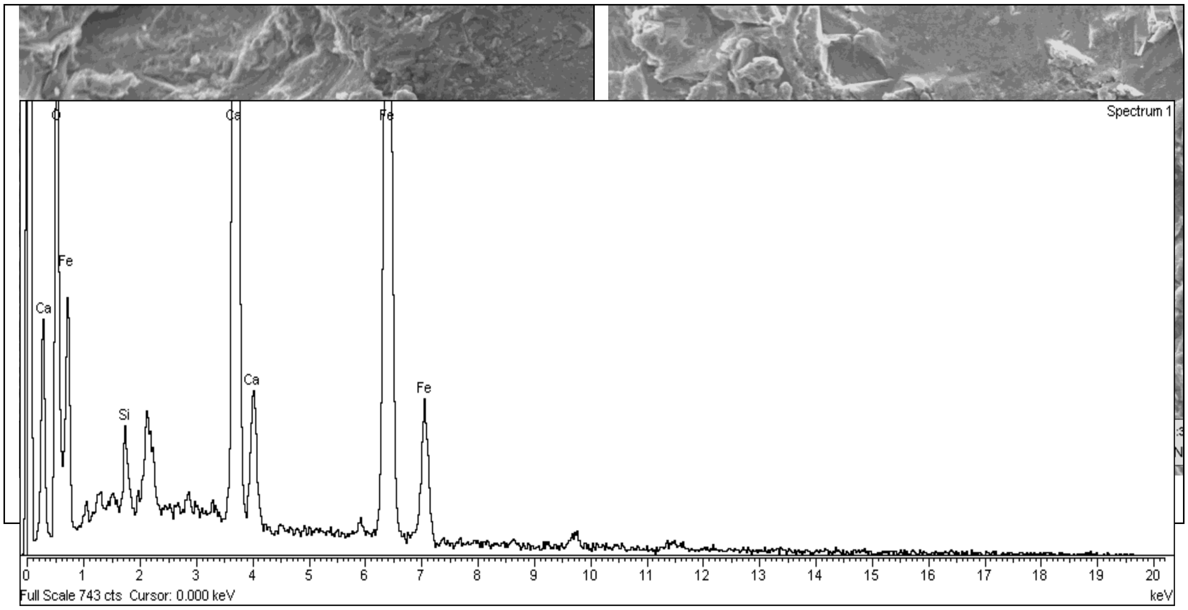
Figure 4.2: Coating Images for Immersed Specimen (Left Hand Side) and Unimmersed Specimen (Right Hand Side)


100µm
Mag = 100 X
WD = 10 mm
EHT = 15.00 kV
Signal A = SE1
Date :2 Jun 2010
Time :14:
Universiti Teknologi PETRON


100µm
Mag = 100 X
WD = 10 mm
EHT = 15.00 kV
Signal A = SE1
Date :2 Jun 2010
Time :14:3
Universiti Teknologi PETRON


10µm
Mag = 500 X
WD = 10 mm
EHT = 15.00 kV
Signal A = SE1
Date :2 Jun 2010
Time :14:
Universiti Teknologi PETRON


10µm
Mag = 500 X
WD = 10 mm
EHT = 15.00 kV
Signal A = SE1
Date :2 Jun 2010
Time :14:3
Universiti Teknologi PETRON



and Unimmersed Specimen (Right Hand Side)

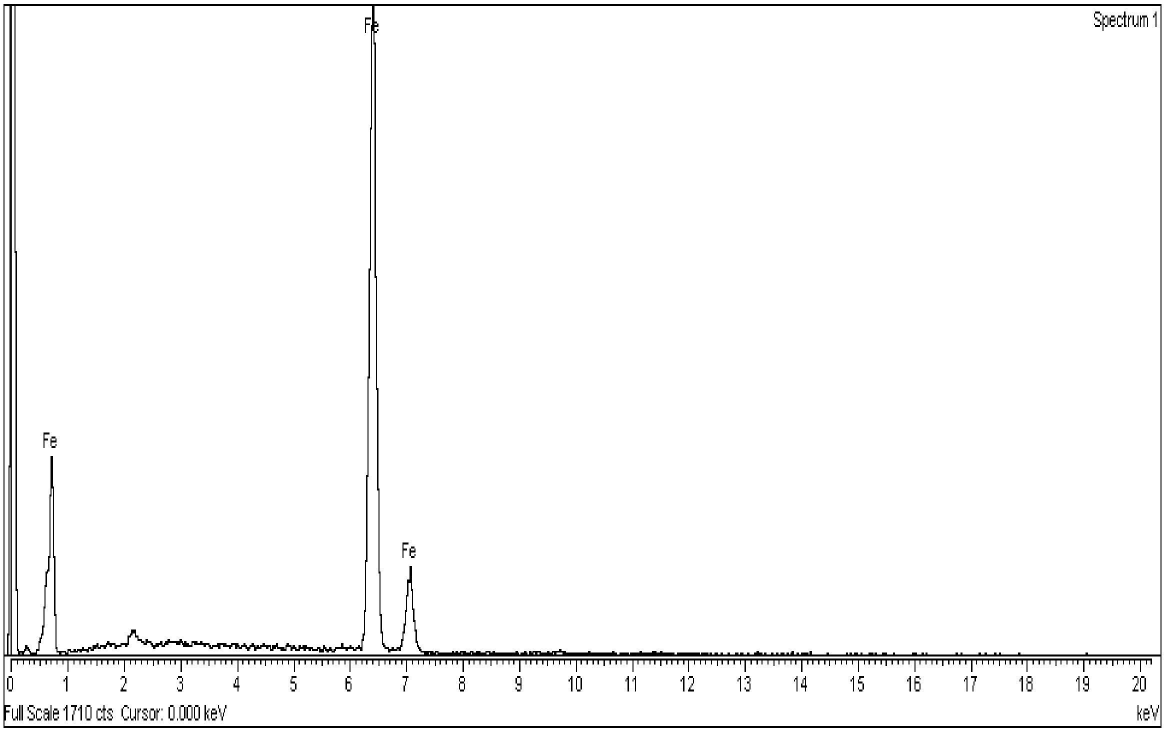


Figure 4.4: EDX Spectrum for Underlying Specimen for Immersed Sample

Figure 4.5: EDX Spectrum for Underlying Specimen for Unimmersed Sample

Below are some limitations associated with this experiment which may affect the result:

1. Temperature range is between 45ºC to 65ºC. The operating temperature is 70ºC. It is quite difficult to achieve the temperature because the heat transfer efficiency of the system is low due to two (2) main factors.

    - There are many metal layers between the hot plate and the water. This will definitely reduce the amount of heat transferred to the water inside the container.

    - The environment temperature is low resulting in more heat from the system is transferred to the environment to achieve equilibrium.

When the water is heated, it will be converted to steam. After a few hours, the water level was decrease and more water need to be added into the container. When the experiment was left overnight at the lab, the temperature must be reduced so that amount of water converted to steam cam be minimized. Therefore, at night the water temperature is 45ºC only.

2. The specimens are not fully coated at the edges. According to the ASTM D 870, the coating system used for water immersion test must be fully coated. This cannot be achieved since we received a large coated plate from the supplier. Then we need to cut the large plate according to our dimension. As a result, all specimens are not coated at the edges. To protect these edges, nail polisher was applied at the exposed area. However, durability of the nail polisher was not equal to polyurea at high temperature. Therefore, we can observe rust spots were formed at the specimens after 48 hours of immersion.
3. The experiment should be conducted continuously. However, it must be stopped during weekend since the laboratory was closed during weekend.

4.2: Electrochemical Impedance Spectroscopy

Electrochemical Impedance Spectroscopy test were carried out by using Autolab provided with frequency response analyzer, FRA to collect the required data. Data were collected by means of Frequency Response Analyzer software developed by Autolab instruments in the form of Nyquist plots as shown in Figure 4.6 and Figure 4.8. Figure 4.7 and 4.9 show the equivalent circuit model that fit the Nyquist Plots.

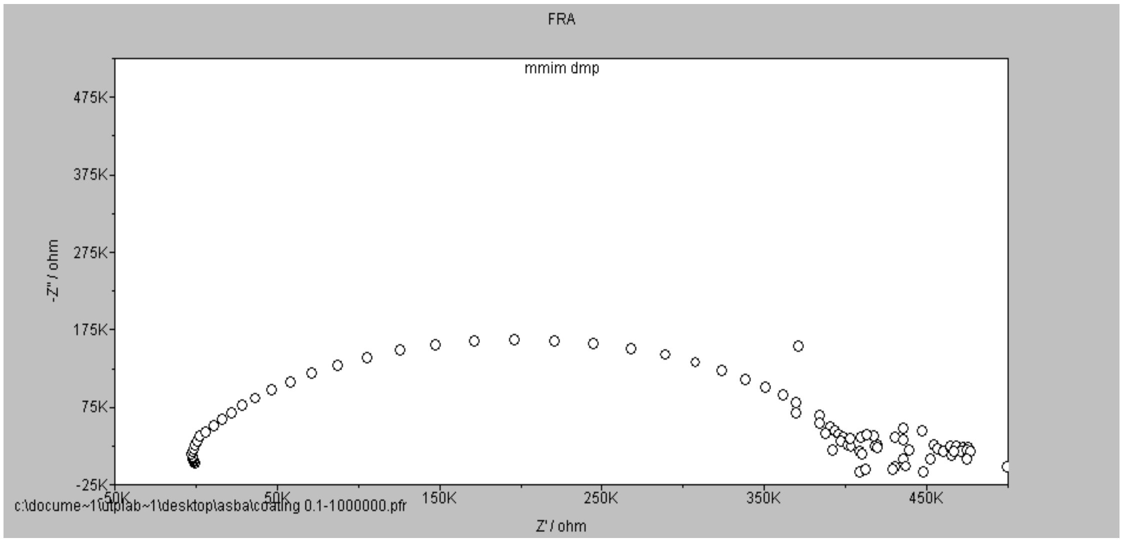


Figure 4.6: Nyquist Plots of 2mm Polyurea Coated Specimen

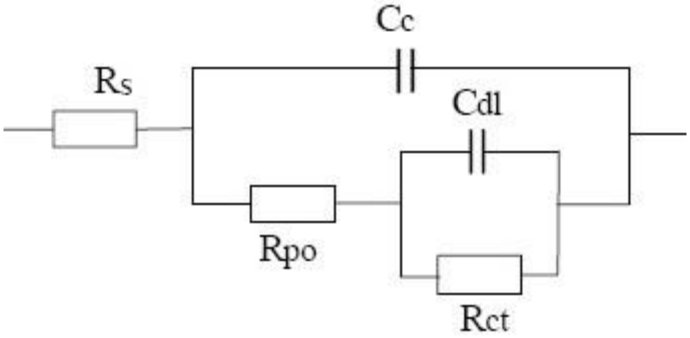


Figure 4.7: Equivalent Circuit Model for Failed Coated

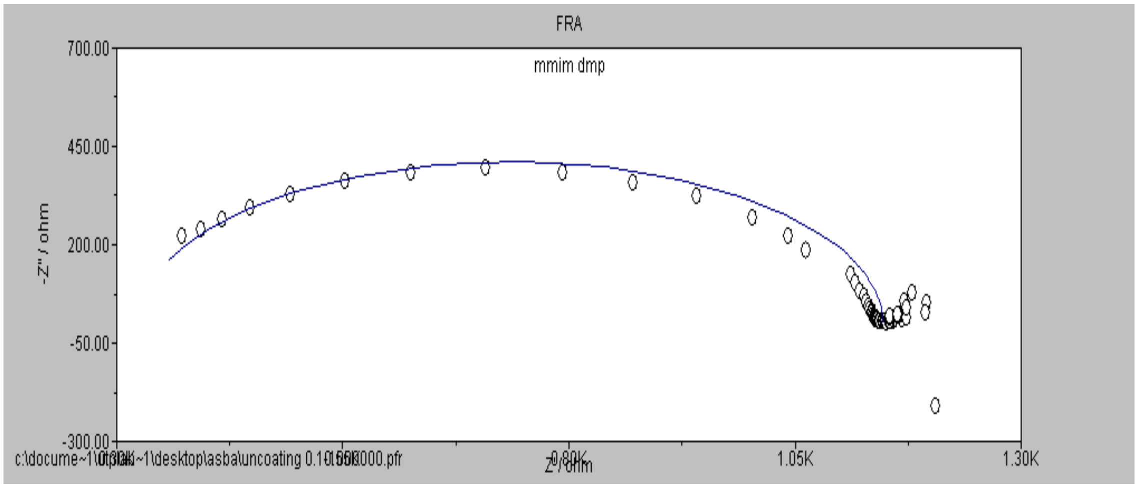


Figure 4.8: Nyquist Plots of Uncoated Specimen

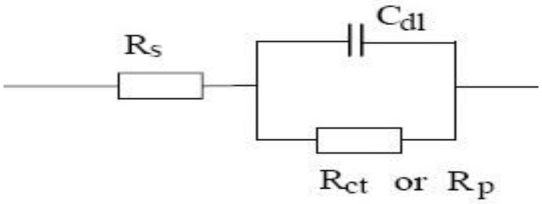


Figure 4.9: Equivalent Circuit Model for Uncoated Metal

When using EIS to test the coating, a data curve is fit to this type of model. The fit returns estimates for the model parameter, such as pore resistance or the double layer capacitance [23]. Table 4.2 below list the values that obtained automatically from the instrument:

Table 4.2: EIS Parameter for Water Immersion Polyurea Coating

EIS Parameter	Uncoated Specimen	Coated Specimen

Rs (Ωcm^2)	2.879 x 10^{2}	2.879 x 10^{2}
Rp (Ωcm^2)	8.513 x 10^{2}	4.432 x 10^{5}
Cdl (F/cm^2)	2.032 x 10^{-9}	4.321 x 10^{-10}

Where:

- Rs = The resistance of the test solution
- Rp = The electrical resistance to current travelling through the pore network in the coating. Higher value indicate higher resistance to penetration of corrosive species
- Cdl = The capacitance produced by the electric double layer at the water / substrate interface. A measureable Cdl value indicate that water is present at the substrate. Higher values of Cdl indicate a greater wetted area of substrate [17].

It was accepted by some researchers [21] that the value of coating resistance, is the best for the measurement of the coating degradation, where can be found from semi-circle diameter of the Nyquist plot. Double semi-circle Nyquist plot indicate the failure of the coating and the interaction between steel surface and solution [18].

The uptake of water in organic coating can be determined directly from capacitance measurements. The dielectric constants of organic coatings are generally small, and hence it is normal for them to be an order magnitude smaller than that of water which has a dielectric constant around 80 at ambient temperatures. For his reason the absorption of a small amount of water can significantly effect the capacitance of the film.

From the immersion of the coating to water the penetration or absorption process begins and lead to increasing value of coating capacitance. This penetration can be through breakdown sites of the coating.

A unique advantage of impedance technique are that data relating to the coatings performance can be obtained in-situ, in a non-destructive manner, leading to a detailed understanding of the probable mechanism of adhesion loss [12].

EIS also facilitate detection of changes in a coating's behavior at a small fraction of the exposure time required for those changes to be detectable by the traditional mechanism or by visual methods [24-26].

CHAPTER 5

CONCLUSION

Performance of polyurea coating for internal section of deaerator which operates under water immersion at high temperature was evaluated and analyzed using water immersion test and electrochemical impedance spectroscopy test. In this project, these two tests were conducted to inspect merely the effect of temperature to the coating performance. No salt or oxygen was added into the solution. From water immersion test, rusting, softening and change of colour of the coating film were observed. In electrochemical impedance spectroscopy test, value of pore resistance and capacitance are valuable parameters used to determine ability of polyurea coating to prevent corrosion in the internal section of deaerator.

Water molecules penetrate into the coating film and the film decomposed at high temperature results in change of coating colour and softening. From these two tests, it can be concluded that polyurea coating can be a suitable candidate to protect internal section of deaerator which operates under water immersion at high temperature. However, a proper surface preparation, coating application and zero initial coating defects are necessary for this coating to have excellent performance and avoid coating failure.

RECOMMENDATION

Below are some recommendations on the idea that can be implemented in order to improve the quality and result of this project as well of for the evaluation of the polyurea coating:

1. Duration to conduct water immersion test (ASTM D870) should be minimum eight (8) month. This will provide sufficient time for coating defect to take place and therefore, more analysis can be conducted to test this new coating system. In this project, the test was only conducted for 42 days due to limited time and delay in starting the tests.

2. If time provided is not adequate to complete the test according to the specified period in the standards, it is recommended to conduct the test at extreme temperature to accelerate the process and time to obtain the result. However, care should be taken when carried out this useful technique as working at high operation temperature can be very dangerous and risky. This method would also require assistance from experience personnel and close monitoring to avoid any incident.

3. This experiment can be repeated using fully coated specimens as according to the ASTM D870. Results obtained from experiment that are hundred percent follows to the standards are more reliable and beneficial.

4. Analysis using electrochemical impedance spectroscopy can be improved by testing all specimens with different DFT. We can achieve better insight of the

polyurea coating performance if the properties are evaluated based on different DFT. The adhesion property of polyurea coating is the most significant parameter to be evaluated under this condition.

5. Conduct the water immersion test and electrochemical impedance spectroscopy test together with other coating system so that result can be compared to better determine which coating system are better under the specified operating environment. Besides that, analysis of the result can also be done based of the different coating composition.

6. Conduct other forms of test to test the ability of polyurea coating to sustain at other extreme condition such as under high intensity UV light and under immersion in acid solution. Many tests should be conducted to evaluate new coating system.

7. Conduct the same immersion test together with other coating system so that the performance of polyurea coating can be determined precisely since another coating can be evaluated for comparison.