CHAPTER III
METHODOLOGY

3.1 Materials and Chemicals

3.1.1 Steel Coupons

The steel coupons were prepared from a new offshore petroleum subsea pipeline with the specifications of API 5L-X52. The pipeline was cold cut into coupons with the dimensions of 2 x 2 x 1.27 cm (WxLxD). The general metal compositions of the pipeline are presented in Table 4-2.

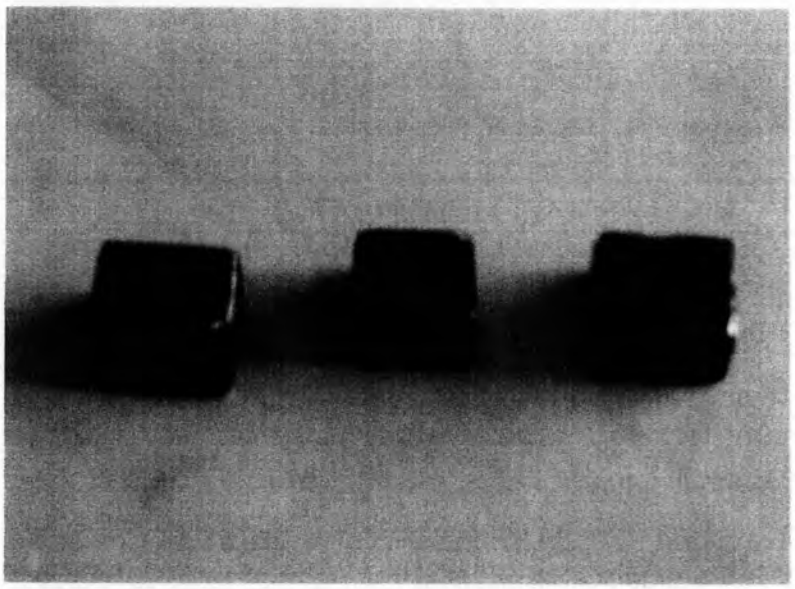

Figure 3-1 Steel coupon samples used in the study

3.1.2 Elemental Mercury

The elemental mercury was obtained from a local manufacturer with purity of 99.95% by weight. The elemental mercury was supplied in ½ kg glass container with tight seal.

3.1.3 Iodine (I_2) and Potassium Iodide (KI) Mixture

Iodine and Potassium Iodide (certified ACS Grade) with pre-determined weights in accordance with the required concentration mixture were placed in 1 liter volumetric flasks and diluted to the mark with doubled distilled water. However, the concentration of KI was kept constant throughout the study at 2.0 Molar, prepared by dissolving 332 g of KI in 1 liter of doubled distilled water. The weights of I_2 required to satisfying its varied concentrations employed in the study are presented in Table 3-1 below. The solution is well stirred until completely dissolved. The solution was stored in a 500 ml glass bottle covered with aluminum foil.

Table 3-1 Weight of Iodine (g) Used at each Varied Concentration

Iodine Concentration (Molar)	Iodine Weight (g)
0.2	254.0
0.4	203.2
0.6	152.4
0.8	101.6
1.0	50.8

3.2 Laboratory Analysis

3.2.1 Scanning Electron Microscope (SEM)

SEM analysis was carried out using a JSL 5300 Series with Energy Dispersive X-ray Fluorescence (SEM-EDX). SEM scanning was carried out with blanks, Hg-contaminated and decontaminated samples. For Hg decontamination and decontamination samples, the analysis was undertaken on the following day upon reaching pre-determined Hg adsorption periods and completion of the Hg decontamination process, respectively.

During the analysis, three samples were mounted on the platform for each batch of the analysis. The observations of the surface morphology were carried out under X200, X2000 and X5000 magnification, respectively, at three different locations or spots across the surface on each coupon. The SEM illustrations of each observed spot and each magnification were printed out and recorded for further result interpretation.

3.2.2 Energy Dispersive X-ray Fluorescence (EDS)

EDS was carried out using a JSL 5300 series, attached to the SEM. EDS scans were carried out in conjunction with SEM observations on blanks, Hg contaminated and decontaminated samples to identify surface elemental composition. Likewise for SEM analyses, they were undertaken on the following day upon reaching pre-determined Hg adsorption periods and upon completion of Hg decontamination process, respectively. The EDS full scan was carried out on the area which could be observed by SEM under X2000 magnification. Three different locations across coupon surface were analyzed of which the results were recorded for further interpretation and analysis.

3.2.3 X-ray Diffractometry (XRD)

XRD analysis was carried out using D8 Advance X-ray Diffractometer. The analysis was used to characterize crystalline chemical compounds present on the surface of the coupons of Hg contaminated and decontaminated samples. The XRD scan on the whole surface of the steel coupon of which the results were recorded for further interpretation and analysis. The XRD analysis for both Hg contamination and decontaminated was undertaken no later than a week after the samples reached pre-determined adsorption periods and upon completion of Hg decontamination experiment, respectively.

3.2.4 X-ray Photoelectron Spectroscopy

XPS characterizations of selected coupons were carried out using a Phi Quantera Scanning X-ray Microprobe. XPS analysis was undertaken for Hg contamination and decontamination no later than two weeks after they reached pre-determined contamination periods and upon completion of Hg decontamination experiments, respectively. Sets of four coupons could be mounted onto sample platens using standard high vacuum techniques.

For each coupon, ten areas (each 100 microns by 1.4 mm) were selected for detailed analysis. Detailed analyses consisted of scans of the Fe 2p, Si 2s/Si 2p/Hg 4f, C 1s, and O 1s spectral windows, with data acquisition time of 45 minutes, and the instrument operating at a resolution of about 1.2 eV. For two of the ten areas, depth profiles were additionally obtained. Data were acquired for the same spectral regions, and sample etching was performed using an SiO2-calibrated rastered Ar ion beam operated with azimuthal sample rotation. Surface compositional data, as well as depth profile characterization were obtained by standard data handling techniques.

To simply characterize the thickness of the oxide layer in any of the depth profiles, we calculated the percentage of Fe present as Fe oxide at a given depth relative to the total Fe observed at that depth. We used this measure to comparatively assess oxide thickness, since it is a value that ranges from 100% at the topmost surface for these coupons to essentially 0% (in the limit of a very long etch.).

3.3 Experimental Procedures

3.3.1 Blank Surface and Depth Profile Analysis

Three representatives of blank samples were sampled from each of three batches of blank samples prepared and submitted to the analysis. The analysis conducted with blank samples included SEM, EDS, XRD and XRF upon receipt of the steel coupon samples.

3.3.2 Hg Adsorption

3.3.2.1 Preparation of Hg Contaminated Steel Coupons

Contamination of steel coupon by elemental Hg was undertaken as follows:

1) The steel coupons were surface cleaned to remove oxide and hydrocarbon layers using a wire brush and followed by detergent and doubled rinsed using doubled distilled water and left to open dry.

2) The steel coupons were then five-sided coated using silicone leaving only its internal surface uncoated.

3) Three steel coupons were then placed in 250 ml tightly sealed laboratory glass bottle containing 1/2 kg of elemental mercury. The steel coupons were placed such that the non-coated surface was partly immersed into liquid mercury.

4) Then the sealed bottles were incubated at 25 ^{0}C allowing mercury adsorption reaching the pre-determined adsorption periods including 15, 30, 45, 60, 75 and 90 days respectively.

5) Upon reaching the pre-determined Hg contamination periods, the Hg treated coupons were then removed from the Hg contamination bottles and then submitted for further laboratory analysis.

3.3.3.2 Surface Chemistry and Morphology analysis

Upon reaching each pre-determined Hg adsorption periods, individual Hg treatment samples were submitted to the laboratory for surface analysis including a) SEM – surface morphology b) EDS – surface elemental components c) XRD – surface crystalline compound analysis d) XPS – surface elemental and chemical compound. The details of these analyses are presented in Section 3.2 above.

3.3.3 Hg Decontamination

3.3.3.1 Preparation of Hg contaminated steel coupons

The preparation of Hg contaminated steel coupons samples was undertaken following the same procedure as detailed in Section 3.3.1.1 above.

3.3.3.2 Hg Decontamination

1) Table 3-2 presents the designs of this experiment which have a combination between varied I_2 concentration mixtures (with fixed concentration of KI) and Hg contamination periods.

2) Upon reaching the pre-determined mercury contamination periods, including 15, 30, 45, 60, 75 and 90 days respectively, the Hg contaminated steel coupons were retrieved from each Hg contamination bottle.

3) Silicone coating was removed from the steel coupon before they were placed into 100 ml tight lid laboratory bottles containing 30 ml of I_2/KI lixiviant with their concentrations and mixtures as detailed in Table 3-2 below:

4) The decontamination procedure was undertaken in the dark, in a closed cabinet, to prevent loses of iodine due to the sunlight.

5) Upon reaching 24 hours of decontamination periods the decontaminated steel coupons were removed from the bottles and rinsed thoroughly with doubled distilled water.

6) Afterward, each steel coupon was placed in a wide-mouthed High Density Polyethylene (HDPE) bottles and submitted for laboratory analysis.

Table 3-2 Varied Concentration Mixtures of Iodine and Potassium Iodide

Iodine (Molar)	Potassium Iodide(Molar)	Mercury Contamination Periods (days)
0	2.0	15, 30, 45, 60, 75, 90
0.2	2.0	15, 30, 45, 60, 75, 90
0.4	2.0	15, 30, 45, 60, 75, 90
0.6	2.0	15, 30, 45, 60, 75, 90
0.8	2.0	15, 30, 45, 60, 75, 90
1.0	2.0	15, 30, 45, 60, 75, 90

3.3.3.3 Laboratory Analysis

Upon completion of decontamination, the Hg decontaminated samples were submitted for the laboratory analysis of which the details are presented below:

a) SEM analysis; all decontaminated samples including 15, 30, 45, 60, 75 and 90 day adsorption samples in combination with concentrations of 0, 0.2, 0.4, 0.6, 0.8 and 1.0 M I_2 were all submitted for SEM analysis. The SEM analysis was undertaken on the following day upon completion of the Hg decontamination experiments;

b) EDS analysis; all decontaminated samples including 15, 30, 45, 60, 75 and 90 day adsorption samples in combination with concentrations of 0, 0.2, 0.4, 0.6, 0.8 and 1.0 M I_2 were all submitted for EDS analysis. The EDS analysis was undertaken on the following day upon completion of the Hg decontamination experiments;

c) XRD analysis; all decontaminated samples including 15, 30, 45, 60, 75 and 90 day adsorption samples in combination with concentrations of 0, 0.2, 0.4, 0.6, 0.8 and 1.0 M I_2 were all submitted for XRD analysis. The XRD analysis was undertaken no later than a week after completion of the Hg decontamination experiments; and

d) XPS analysis; selected sets of decontaminated samples were submitted for XPS analysis. These include three categories of high, medium and low initial surface Hg concentrations in combination with selected concentrations of I_2 including 0, 0.2, 0.6 and 1.0 M, respectively. The analysis was undertaken no later than two weeks after completion of the Hg decontamination experiment.