



CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

The conclusions of the study could be made as the following:

5.1 Surface Morphology and Chemistry – Hg Adsorption

The adsorption of Hg on the steel coupon surface were examined under SEM analysis and found that various sizes of Hg spherical droplets were observed on the steel coupon surface. The bigger droplets could be greater than 10 μm , whereas the smaller one were less than 1 μm . The adsorption of Hg on the steel coupon surface occur in two different manners including 1) attachment on the surface and 2) falling into cracks, pits and crevices present on the irregular steel coupon surfaces. Distribution of Hg droplets on the steel coupon surface was therefore inconsistent and could largely be the influence of heterogeneous surface characteristic.

The EDS analysis, undertaken soon after reaching the pre-determined adsorption periods, shows that there was no reasonable correlation existed between Hg adsorption periods (15, 30, 45, 60, 75 and 90 days) and average surface Hg concentrations. High variations of surface Hg concentrations were observed in each Hg adsorption periods. However, the EDS results on surface mercury provides an indication that surface Hg concentrations tend to slowly increase from 15 to 60 day before they started to equalize and decrease upon reaching 75 and 90 day, respectively. Based on the results of EDS, the initial surface Hg concentrations could be categorized into three groups including a) low; 15 and 90 day Hg adsorption (% atom-Hg of about 20.45) b) medium; 30, 45 and 60 day Hg adsorption (average % atom-Hg of 23.7 – 25.11) and c) high; 75 day Hg adsorption (% atom-Hg of 33.9). However, the statistical analysis using ANOVA method indicates that surface Hg concentrations of each Hg treatment periods are not significantly different at 95% degree of confident.

The estimation of surface mercury concentrations using XPS-Handheld XRF (HXRF) correlations provided the results as presented in Figure 5-1 below:

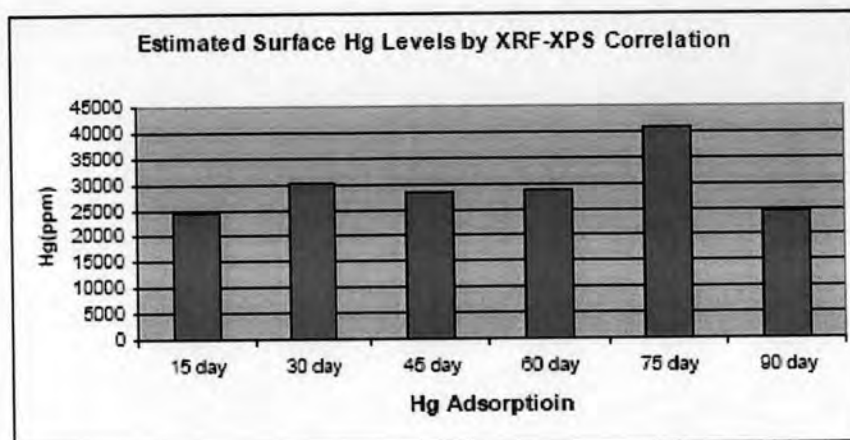


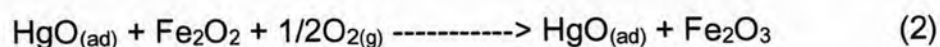
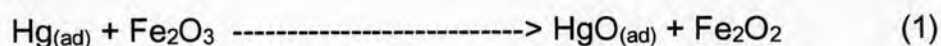
Figure 5-1 Estimated surface Hg concentrations using EDS measurements and XPS-HXRF correlations at different Hg adsorption periods

It is noted here that the calculation of surface Hg using the XPS-HXRF correlations take into account limitations of the correlations which serves as basis of the estimation. The figure shows that surface Hg concentrations from 15 to 90 day Hg treatments range 25,000 to 40,000 ppm of the minimum to the maximum concentrations, respectively.

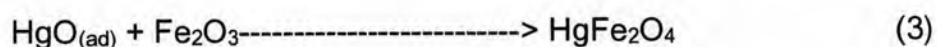
The XRD and XPS analyses (undertaken no later than one and two week respectively after the EDS analysis) showed that Hg was found in HgO form beside its original elemental Hg (zero valence) form; observed under SEM right after Hg adsorption. The reactions of surface Hg oxidation were investigated and found that oxidation of Hg by Oxygen present in the air or on the metal surface could not thermodynamically possible. Hg could be oxidized by Oxygen to HgO only by heating Hg up to 350 °C.

It is also indicated by using Gibbs formation energy of Hg to HgO that Hg is seldom oxidized by O to become HgO with Gibbs formation energy of -59 kJ/mole (Motohiro, 2003).

However, it was found that lattice oxygen of partial oxides could serve as an oxidant of Hg. From the results of XPS surface analysis, it revealed that metal oxide that served in Hg oxidation was possibly Fe_2O_3 , which is present on the surface from the beginning as the metal oxide deposit. The reactions of Hg oxidation by Fe_2O_3 can be written as the following:



The above reactions could be continued to equation (3) as shown below:



However, the final products of this reaction were not found based on the results of the XPS surface analytical techniques employed in the experiments.

The XPS analysis shows that Hg treatment time was also not correlated with average Hg concentrations on the steel coupon surface. The Hg surface concentrations by XPS increased from 14 to 45 days Hg adsorption, before it decreased and increased again in 60 and after 75 days of Hg adsorption, respectively.

The XPS analysis also revealed that Hg present on the surface was in HgO forms with % atom-Hg by XPS ranging 0.03 to 0.96 from the minimum to maximum, respectively.

The estimations of HgO surface concentrations using XPS-HXRF correlations are presented in Figure 5-2 below:

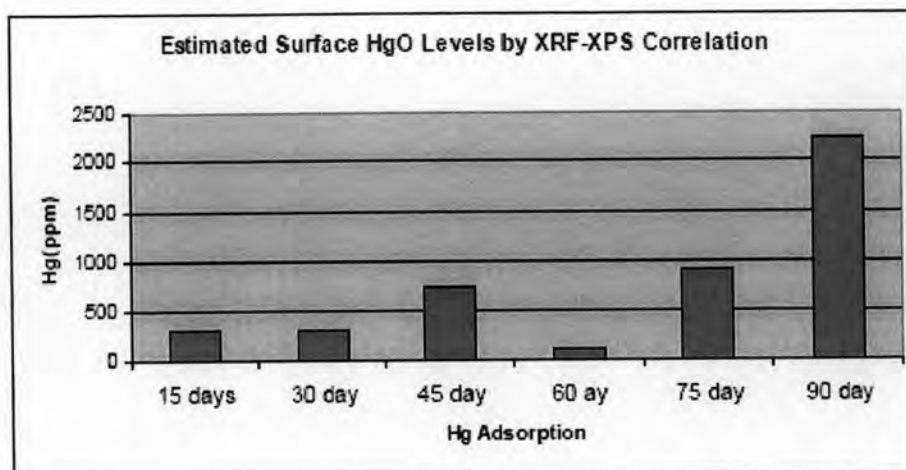


Figure 5-2 Calculated surface Hg concentrations by XPS measurements and XRF-XPS correlations of different Hg treatment samples

Figure 5-2 shows that the estimated surface HgO concentrations range < 500 to about 2000 ppm. The relative benchmarking between initial surface Hg levels by EDS (analyzed soon after reaching pre-determined Hg treatment periods) and XPS (analyzed no later than two weeks after Hg adsorption) revealed considerable quantitative gaps. The benchmarking of surface Hg concentrations between EDS and XPS takes into account the different sampling depth of both techniques. The XPS is a surface-sensitive method whose sampling depth is limited by the finite mean free path of the photoelectrons. In contrast, EDS measures at the greater area and depth. Due to this difference, XPS will sample only the skin measuring a higher Hg concentration understanding that Hg is more consolidated on the surface (Morris, 2002).

These differences indicated losses of Hg through volatilization, which could happen between the time of sampling and laboratory analysis. It also indicated that the rate of Hg volatilization can be much higher than the rate of Hg oxidation and Hg depth penetration. Therefore either the shipment of Hg contaminated steel coupon for laboratory analysis should be undertaken either as soon as possible to ensure reliable Hg analytical results or in-situ measurement technique should be considered.

Mercury oxide also poses potential environmental and health impacts. Zalavutdinov in 2001 reported formation of HgO on the surface of martensitic and austenitic steels after exposure in elemental Hg up to 5000 hours. It was reported that after formation of HgO, it could be peeled-off in the form of HgO scales. The HgO scales could be very fine particulate and become fugitive and dispersed into the surrounding environment. Without proper control and mitigation measures, it could potentially deposit in human and environment and poses potential health and environmental risks.

Therefore upon decommissioning of the subsea pipeline with Hg, air can be supplied inside the pipeline to facilitate Hg volatilization. The generated exhaust air can be directed to a filter unit containing metal oxide catalyst normally used in petroleum industry to remove Hg prior to discharge into the atmosphere. The remained HgO deposit on the pipeline surface can be finally removed by using the lixiviant, but at much lower concentrations. This makes the application of the technique for in-situ Hg decontamination more feasible.

5.2 Hg Depth Profiling – Adsorption

The XPS analysis was undertaken with 15, 30, 45, 60, 75 and 90 day Hg treatments, respectively. The XPS analysis showed that Hg found on the surface was in HgO form as discussed above (with XPS binding energy of 100.6 eV); however, thereafter a brief etche to only 6 nm from the topmost surface, Hg was found in its elemental state (with zero valence).

The change of Hg oxidation states could be due to ion-gun induced reduction employed in the etching process. In order to verify this, XPS depth profile analysis was, therefore, carried out with HgO. The results showed that there was no evidence to suggest decreases in O content with etching of HgO. The calculation of Hg/O ratio remained close to 1.0 throughout the course of the depth profile. Based on the results, it could be ascertained that

observation of HgO at the surface, and metallic Hg at the smallest depth was not an experiment anomaly, but a reliable experimental observation.

Reviewing the XPS spectrum at Fe2p region found that the at higher Hg adsorption periods, the thicker oxide layers found growing in the depth profile. Reference to the published XPS binding energies, it was found that the binding energies of the growing oxide layer matched with those of Fe₂O₃. A plot of oxide thickness versus Hg treatment periods suggested longer the Hg contact time, the thicker Fe-oxide layer is observed.

Two possibilities for the observation of the elemental Hg in the depth profile can be occurred including:

a) Deposition of elemental Hg through the mechanisms 1) penetration of Hg into surface deposit such as rust layers, scales or salt precipitates. 2) Mercury deposit at previously damaged sites of the steel component 3) mercury in pore in the steel, which communicate with the surface by way of channels 4) Hg in grain boundary zone such a a result of transcrystalline diffusion (Zeittlitzer, 1997); and

b) By the reaction below:



The feasibility of the reaction was ascertained using Gibb' s formation energy of which the deltaG of -135 kcal was reported indicating the reaction goes to the right.

It was also reported that reduction of heavy metal (Hg), a toxic oxyanion (arsenate ion) and a chlorinated solvent (TCE) thus appear to be driven by the high reactivity of adsorbed Fe(II). Kinetic measurements at the nanomolar level of elemental Hg formed upon reduction of Hg(II) by Fe(II) in presence on the phlogopite particles provide further convincing evidence for reduction of Hg(II) coupled to oxidation of Fe(II) adsorbed. And indicate that sorption of Fe(II) to mineral surfaces enhances the reduction rate of Hg(II) species (Charlet, 2002).

The XPS depth profile analysis also showed that Hg was more concentrated on the top surface at the depth of 10-20 nm of the steel coupon in all Hg treatments. The Hg depth profile showed that Hg decreased drastically from the top surface to the depth of 10-20 nm from the topmost surface before it reached a plateau after the depth of approximately 50 nm from the topmost surface in all Hg treatments. The minimum to maximum Hg levels after reaching the plateau ranged from 0 to 0.1% atom-Hg by XPS. The estimations of % atom-Hg by XPS against HXRF-XPS correlations showed that the maximum Hg levels in the depth profile could be about 120 ppm.

5.3 Hg Adsorption – Conceptual Model

Based on the findings and results from the Hg adsorption experiments above, the conceptual model of major phenomena that occur on the surface of Hg can be developed and presented in Figure 5-3 below:

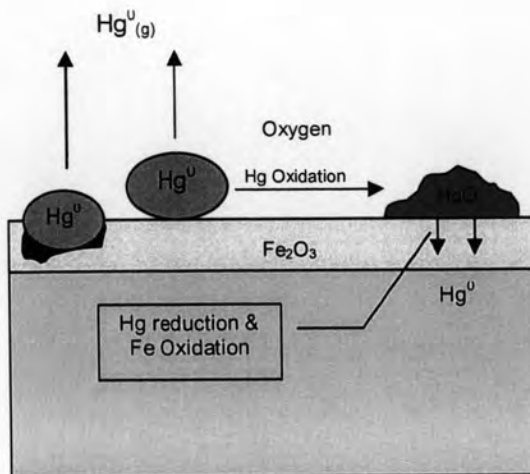


Figure 5-3 Conceptual model of Hg adsorption on the steel coupon surface

Figure 5-3 showed that after Hg adsorbed on the steel surface, three major phenomena occurred including:

- Hg oxidation; occurred on the top surface with the involvement of $O_{(g)}$ and Fe_2O_3 that oxidize Hg to HgO;
- Evaporation; occurred potentially with both Hg adsorbed on the surface which cause significant Hg losses from the system;
- Hg reduction; occurred in the depth profile where HgO is reduced to Hg coupling with Fe oxidation to Fe_2O_3 .

5.4 Surface Morphology and Chemistry – Hg Decontamination

Examination of all Hg decontaminated coupon surfaces under SEM revealed that there were no droplets of elemental Hg found, regardless of concentrations of I_2 used and also Hg adsorption periods. This includes the control experimental of without I_2 . The SEM results showed that at the higher I_2 concentrations, the more corrosion could be observed in all Hg adsorption treatments.

Without the XPS analysis results, the findings of no Hg on the decontaminated coupon surface were ascertained by the EDS analysis which showed that none of surface Hg was detected in all Hg decontaminated samples including those without I₂. It is noted here that the detection limit of the EDS is > 1.0% atom-Hg.

The XRD analysis of the Hg decontaminated samples showed that after decontamination, HgO could still be detected on the surfaces of almost all decontaminated samples, except for 30 and 90 day Hg adsorptions with high I₂ concentration e.g. > 0.6 M. This could be due to low initial Hg concentrations on these treatment samples and also excessive iodine concentrations that could possibly oxidize all Hg.

The XPS surface Hg analysis was undertaken with the selected sets of Hg adsorption in combination with I₂ concentrations. The surface Hg levels include 90-day Hg treatment (low), 30-day Hg treatment (moderate) and 75-day Hg treatment (high) and I₂ concentrations of without iodine, 0.2, 0.6 and 1.0 M, respectively.

The statistical analysis on the surface Hg levels, analyzed by XPS, after decontamination revealed the following:

- For 30 and 90 day Hg treatments, surface Hg levels after decontamination are not significantly different in all I₂ treatment with 95% degree of confident; and
- For 75-day Hg treatment, surface Hg levels after decontamination are significantly different in each of I₂ treatment.

The estimated average surface Hg levels analyzed by XPS using XRF-XPS correlation based on the results of XPS analysis after the decontamination are presented in Figure 5-4 below:

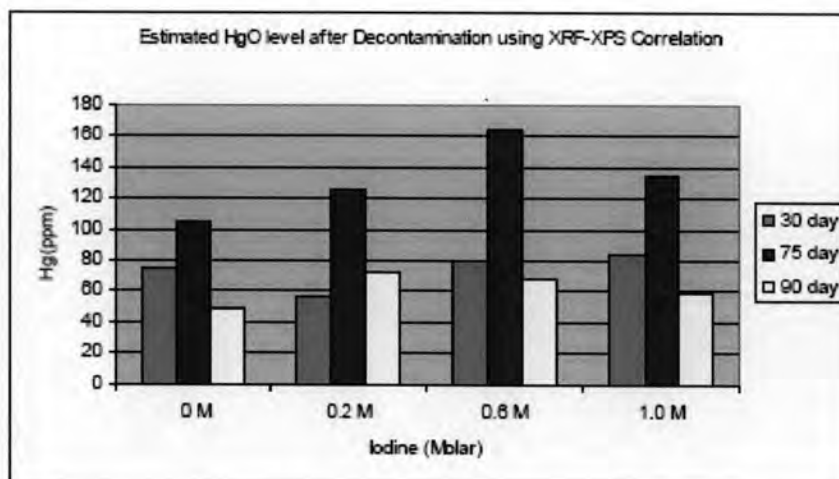


Figure 5-4 Surface HgO Levels estimated using XRF-XPS correlation based on XPS analytical after the decontamination

Figure 5-4 shows that at I_2 treatment of 0 and 0.2 M, there were no major differences in residual surface Hg concentrations in all Hg treatment periods of which the surface Hg concentrations were reduced to approximately less than 120 ppm. However, it is hard to conclude at this stage that the treatment without iodine is recommended to effectively decontaminate Hg on the steel surface, because washed-off Hg droplet still requires I_2 to stabilize it and effectiveness in Hg removal in the depth profile has yet to be determined.

5.5 Depth Profiling – Hg Decontamination

The XPS depth profiling was undertaken in selected decontamination treatment including 30, 75 and 90-day of Hg adsorption in combination with I_2 treatment of 0, 0.2, 0.6 and 1.0, respectively.

Based on the XPS Hg depth profile, it shows that at low initial surface Hg levels (e.g. 90 day Hg adsorption), Hg decreased rapidly from the surface to the depth of about 50 nm in all I_2 treatment with estimated surface Hg levels (by XPS-HXRF correlation) of well below 60 mg/kg prior to they stay persistent through out the course of the depth profile.

However, for higher initial surface Hg levels (e.g. 30 and 75 day Hg treatment), Hg decreases rapidly from the top surface to the depth about 50 nm and stays persistent through out the course of the depth profile in all I₂ treatment, except those without I₂ where Hg in the depth profile increased instead of decreased.

The results above suggest that without I₂ in the decontamination solution, Hg in the depth profile especially with high initial surface Hg level; could not be reduced. This may be due to the I₂ effect that cause corrosion of metal surface and also dissolved Hg stay in the depth profile as discussed earlier in Section 4.3.1.

5.6 Optimal I₂ Concentrations

Based on the results above, I₂ concentration of 0.2 M is, therefore, chosen as the optimal concentration for decontamination given with the rational as the following:

- It is the lowest concentration of I₂ investigated in the study;
- It provides a minimum corrosion impact on the steel coupon surface as supported by SEM observations;
- It works well with all ranges of surface Hg levels found in the experiment (20.45 to 33.9 % atom-Hg by XPS or 25,000 to 40,000 ppm Hg on XPS-HXRF correlation estimates);
- It can remove Hg from the surface from the above initial surface Hg ranges to the final residual surface concentrations ranging 40 to about 120 ppm Hg (by XPS-HXRF correlation estimates).
- However, these concentrations are present mostly on the topmost surface (about 10-20 nm) which accounted for less than 1% of overall weight of metal coupon. Therefore the overall Hg

concentrations per overall weight of the steel coupon could be more than 100 times less.

- It also contains I_2 to stabilize Hg wash-off in the decontamination solution.

5.7 Hg Measurement Technique

As discussed earlier, shipment of Hg impacted steel coupons for laboratory analysis could cause significant losses of Hg through the volatilization process. The current technology of handheld XRF instrument was therefore investigated. The correlations of Hg reading between handheld XRF and XPS on the same sets of Hg adsorption steel coupons were established, of which the results show that they are quite reasonably correlated ($R^2 = 0.72$). The XRF instrument has advantages over the XPS analysis as the following:

- It is easily portable and can be used for in-situ or field measurement without taking the sample to the laboratory for the analysis;
- Sampling Hg impacted steel coupons e.g. by cold cutting could also cause significant loss of Hg, besides those during the shipment;
- It measures surface Hg under ambient condition, compared to under high vacuum pressure in XPS chamber which also can cause losses of Hg;
- It is sensitivity of Hg to about 20 ppm or relatively compare to about 0.01% atom of XPS.
- It costs about 35,000 US\$ instead of 850,000 US\$ for XPS (as of August, 2008)

Given with these advantages, handheld XRF is therefore recommended to use for measuring of Hg especially in field application.

5.8 Recommendations

Based on the results of the study, the recommendations could be made as the following:

- The effect of lower I_2 concentrations should be further investigated towards removal efficiency of Hg on the surface and in the depth profile.
- The study was undertaken specifically to the steel coupon with specification of API 5L-52X, which is used for servicing petroleum under subsea condition. For the results of the study with other steel specifications, similar investigations should also be undertaken.
- Other decontamination conditions, including concentrations of KI and Hg decontamination treatment times, should be further investigated.
- Surface measurement is a critical topic in this study. However based on the results of the study the analytical or measurement methodology should be those that will minimize losses of Hg through volatilization. Shipment the samples to the laboratory could also cause potential losses of Hg.
- Handheld XRF instrument should be obtained and used to measure initial Hg concentrations upon reaching each pre-determined Hg treatment periods and develop correlation with those of the EDS analysis.
- The current correlation of surface Hg levels between handheld XRD and XPS should be developed with higher Hg concentrations.

- Other models of handheld XRF, currently available commercially should be assessed if they can provide better correlation between its Hg surface readings against those of XPS measurements.