



Decontamination of Mercury Contaminated Steel (API 5L-X52) Using Iodine and Iodide Lixiviant

Narongsak Chaiyasit

Interdisciplinary Environmental Science, Chulalongkorn University
Phayathai, Bangkok, 10300, Thailand

Tel: 66-89-204-8199 E-mail: thomas_2106@yahoo.com

Charnwit Kositanont (Corresponding author)

Interdisciplinary Environmental Science, Chulalongkorn University
Phayathai, Bangkok, 10300, Thailand

Tel: 66-2-218-7667 E-mail: charnwit@sc.chula.ac.th

Sheila Yeh, Darrell Gallup & Lyman Young

Chevron Energy Technology Company
100 Chevron Way, Richmond, CA, 94802, USA

Tel: 1-510-242-4037

E-mail: swyeh@chevron.com, Dgallup@chevron.com, layo@chevron.com

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Abstract

Investigations assessed the surface chemistry, morphology and depth profile of Hg for gas processing pipe steel coupons of API 5L-X52 after adsorption with elemental Hg at 25 °C in the presence of air. We investigated the effect of Hg adsorption periods and surface Hg levels as well as characterizations of Hg depth profiles. We observed no reasonable correlation between surface Hg levels and Hg adsorption periods. Forms of Hg found on the top surface and in the depth profile were in oxide and elemental forms, respectively. However, most of the Hg present was superficial and did not penetrate below the surface significantly. The lowest concentration lixiviant, with 0.2 Molar iodine and 2.0 Molar potassium iodide, worked well with all ranges of Hg contamination observed, with the final surface Hg levels of less than 0.1 atom% by XPS analysis, for a relative percentage of Hg removal about 99%.

Keywords: Mercury, Adsorption, Depth profile, Decontamination

1. Introduction

Mercury is a naturally occurring element found in geologic hydrocarbons in the Gulf of Thailand. The first observations of mercury in Thai offshore oil and gas operations appeared in the late 1980s (McDaniel, et al., 1998). The mercury-laden hydrocarbons, upon contact with steel, for example, that of petroleum pipeline and separation processes, cause mercury deposition on the metal surfaces. A study conducted at a North German gas field located in the Rotliegend to assess mercury in steel equipment used for natural gas production revealed that mercury of less than 1 and more than 80 mg/kg was found in their tubing and pipe (Zettlizer and Kleinitz, 1997). As a result, the potential for mercury deposits on steel must be considered when classifying production and processing equipment for decommissioning and disposal.

A study, conducted to identify mercury decontamination techniques on porous surfaces, showed that chemical cleaning

methods involving iodine, as oxidizing, and iodide, as complexing agents (so called iodine/iodide lixiviant), could remove up to 90% of elemental mercury (Ebadian, 2001). However, the former study used relatively lower surface mercury concentrations, and further made no assessment regarding its effectiveness for mercury below the surface.

This study assesses mercury levels both on the surface and in the depth profile, and further identifies an optimum iodine concentration for use in the decontamination by the iodine/iodide lixiviant method. Reproducing in the laboratory a high pressure environment to match that of the subsea pipeline would be possible, but very difficult. However, because of the relatively high incompressibility of liquid mercury, the interaction between mercury and steel is not expected to be a strong function of pressure. Therefore, the study was performed at ambient pressure. Ambient temperature (25°C) is a reasonable match to the temperatures of the subsea pipeline.

2. Materials and Methods

2.1 Steel Coupons

The steel coupons used in the experiment measured 2 x 2 x 1.27 cm (width x length x depth), and we prepared them from virgin subsea petroleum pipe with an American Petroleum Institute (API) specification of 5L-X52. We protected five of the surfaces of the cubes with a coating of silicone, excluding the internal concave surface. Table 1 presents the chemical composition of the coupon steel (Hernandez-Rodriguez et al., 2007).

2.2 Mercury Adsorption

We cleaned the uncoated surface with a liquid detergent and placed the coupons in 250 ml sealed bottles, each containing 0.5 kg of elemental mercury with air in the headspace. For each coupon, we immersed the uncoated surface directly into the liquid elemental mercury, and mercury adsorption continued under a controlled temperature of 25°C inside an incubator for one of six (6) different pre-determined adsorption periods (15, 30, 45, 60, 75 and 90 days).

2.3 Mercury Decontamination

Upon reaching the pre-determined mercury contamination periods, we retrieved the Hg contaminated steel coupons and removed the silicone coating. Then, we placed coupons into 100 ml tight lid laboratory bottles containing 30 ml of iodine and potassium iodide lixiviant with varied iodine concentrations of 0, 0.2, 0.4, 0.6, 0.8 and 1.0 Molar and constant potassium iodide concentration at 2.0 Molar, respectively. The decontamination proceeded in the dark, in a closed cabinet, to prevent loss of iodine due to the sunlight. Upon reaching 24 hours of decontamination we removed the steel coupons from the bottles, rinsed each thoroughly with doubly-distilled water, and placed each in a separate, tightly sealed wide-mouthed High Density Polyethylene (HDPE) bottle for subsequent analysis.

2.4 Metal Coupon Analysis

At the end of each mercury adsorption and decontamination experiment, we analyzed the steel coupons for surface morphology and chemistry using the JEOL JSM-5300 Scanning Electron Microscope with Energy Dispersive X-Ray (EDX) fluorescence spectrophotometer. We measured surface elements and compounds, including the compositional depth profiles, using the Phi Quantera Scanning X-ray Microprobe X-ray Photoelectron Spectrometer (XPS), within two weeks after completion of the adsorption and decontamination experiments. For the XPS analysis, sets of four coupons were mounted on a sample platen using standard high vacuum techniques. 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 at least one of the several areas, we additionally obtained depth profiles. In the depth profiles, we acquired data for the same spectral regions, and etched the surface with a SiO₂-calibrated rastered Ar-ion beam operated with azimuthal sample rotation. We used standard XPS data handling techniques to obtain the surface compositional and chemical data, as well as the depth profile characterizations.

3. Results and Discussion

3.1 Surface Morphology and Chemistry after Adsorption of Elemental Mercury (Hg⁰)

Illustrations from SEM, as shown in Fig. 1, revealed mercury as spherical droplets of various sizes on the coupon surface. The larger droplets could be greater than 10 μm in diameter, whereas the smaller ones could be less than 1 μm. Surface distribution of the Hg droplets was irregular with respect to both adsorption site and droplet size.

Fig. 2 presents the results of surface Hg analysis using EDX at the end of each Hg⁰ adsorption period, and shows that the surface Hg levels range from less than 5 to 45 atom%. However, analysis of surface Hg levels using XPS analysis two weeks after the end of each Hg⁰ adsorption period showed much lower surface Hg concentrations, ranging from less than 0.5 to about 3.0 atom%. We found no reasonable correlation between the surface Hg levels and the adsorption periods for either of the surface analysis techniques used. Fig. 3 shows surface Hg levels at the end of each Hg adsorption period by XPS analysis.

The XPS chemical state analysis, with Hg 4f_{7/2} at 100.7 eV and Hg 4f_{5/2} at 104.7 eV, revealed the presence of Hg oxide on the steel coupon surface (Motohiro et al., 2003, Kleiman et al., 1982 and Humbert, 1986). The results of the

above suggest that at the end of the Hg^0 adsorption period, Hg was predominantly found in its elemental form. After two weeks, however, significant levels of the surface Hg vaporized due to the high Hg^0 vapor pressure, and leaving behind the less volatile Hg oxide on the coupon surface.

3.2 Depth Profiling and Chemistry after Adsorption of Elemental Mercury (Hg^0)

The XPS spectra showed that after etching the steel to only 6 nm from the topmost surface, the binding energies of Hg 4f7/2 and Hg 4f5/2 were shifted to 99.6 and 104.0 eV, respectively, indicating subsurface Hg was in the zero valence state of elemental mercury in contrast to the oxide state found on the topmost surface (Motohiro et al., 2003, Kleiman et al., 1982 and Humbert, 1986). A control depth profile experiment on HgO showed no beam-induced reduction.

The Hg concentration depth profiles showed that most Hg was present within the short depth of only about 10 nm from the topmost surface. The levels of Hg in the depth profile were low, mostly below 0.1 atom%. Therefore, Hg is present on the surface only and does not penetrate significantly into the depth. A previous study of field samples of gas processing pipe collected in a gas field of Northern Germany also with naturally-occurring mercury reported a similar finding. This previous study indicated that mercury is only adsorbed on the steel surface and did not penetrate into the depth (Zettlitzer and Kleinitz, 1997). Figs. 4 through 6 show Hg levels in the depth profile at the end of 30, 75 and 90 day of Hg^0 adsorption, respectively. Note that Hg levels in these figures are multiplied by 50 to better match the scale of other elements' concentrations.

3.3 Surface Morphology of the Steel Coupons after Mercury Decontamination

Surface morphology of steel coupons after the mercury decontamination of 30, 75 and 90 days of Hg^0 adsorption is shown in Figs. 8 through 10, respectively. The post-decontamination surface morphology showed no droplets of elemental mercury. We also found that with higher iodine concentrations, more surface corrosion occurred. These observations are consistent with iodine as an oxidizing agent that not only oxidized Hg present on the top surface, but also corroded the steel surface allowing contact with any small amount of Hg below the surface. Therefore further investigation of Hg in the depth profile after the decontamination is deemed unnecessary.

3.4 Surface Chemistry of the Steel Coupon after Mercury Decontamination

The XPS analysis of the surface mercury after the mercury decontamination of 30, 75 and 90 day Hg^0 adsorption, respectively, using various concentrations of iodine (0-1.0 Molar) and at a constant concentration of potassium iodide (2.0 Molar) showed that there was no major difference in the resulting surface Hg level due to different iodine concentrations, including the control experiment without iodine (0 Molar). This finding can be due to the oxide form of mercury found on the surface which reportedly could be peeled off as a metal oxide scale leaving just a thin oxide film (Zalavutdinov, 2001). Therefore, removal of the oxide form of Hg could be potentially due to the peeling off process. However, since the peeled off mercury oxide scale might have been obscuring minute levels of Hg^0 present in the coupon's subsurface, iodine and potassium iodide are still required to stabilize all possible mercury for further handling and final disposal. Other surface cleaning techniques, such as surface brushing or polishing, could make toxic mercury oxide become airborne. Once airborne, the contaminant would pose higher potential exposure risks to both humans and the environment from any emissions. A previous investigation showed that the iodine and iodide lixiviant mobilized mercury in solid wastes whether in the form of oxides, sulfides, or elemental through the oxidation and complex-forming reactions (Ebadian et al, 2001).

The EDX analysis of the coupon surfaces after the decontamination of 30, 75 and 90 day Hg^0 adsorption showed no mercury present. Note that the detection limit of the employed EDX is less than 1 atom% Hg. However, the XPS analysis, with its lower surface detection limit, revealed the maximum levels of mercury on the coupon surfaces after the decontamination of 30, 75 and 90 day Hg^0 adsorption of 0.1, 0.19 and 0.14 % atom, respectively, at various iodine concentrations. We present these data in Figs. 10 through 12.

3.5 Mercury Removal and Iodine Concentrations

Fig. 13 plots the percentage of Hg removed by the decontamination of 30, 75 and 90 day Hg^0 adsorption coupons using various concentrations of iodine between 0 and 1.0 Molar with a constant concentration of potassium iodide (2.0 Molar). These data demonstrate that there was no significant difference, in terms of surface Hg removal, among the various concentrations of iodine used, including with no iodine. As mentioned earlier, iodine is required to oxidize elemental mercury present on or just below the surface. As a result, we find 0.2 Molar iodine is the lowest iodine concentration that should be used. Taking into account the surface Hg levels by the EDX analysis of about 40 atom% generally found in 30, 75 and 90 day Hg^0 adsorption samples and those of the same set after the decontamination with the maximum Hg levels of 0.1 atom% Hg by XPS, the relative percentage of Hg removal using iodine/iodide of 0.2/2.0 Molar is, therefore, more than 99%.

4. Conclusion

We observed mercury as spherical droplets of Hg^0 attached on the steel coupon surface at the end of each adsorption

period, and found the Hg concentration ranged from less than 5 to about 45 atom% by EDX analysis. Examination of the steel coupon surfaces using XPS analysis two weeks later found Hg in the oxide form with surface concentrations ranging from less than 0.5 to about 3.0 atom% of Hg. These differences suggest loss of Hg through vaporization due to high Hg⁰ vapor pressure, leaving much lower Hg levels on the coupon surface, and only in the oxide form. This knowledge is critical in the planning process to prevent and control Hg vapor as well as HgO particulates during any decontamination activity. XPS depth profile analysis further showed that Hg was present predominantly on the topmost surface to only about 10 nm depth. Insignificant concentrations of less than 0.1 atom% Hg by XPS analysis were observed and persistent throughout the depth profile regardless of the Hg⁰ adsorption periods investigated. These data indicate that Hg, under the applied conditions, was present only on the top surface and did not penetrate significantly into the depth. The decontamination of Hg using iodine and potassium iodide lixiviant showed that there was no significant difference in the surface Hg concentrations after the decontamination with various iodine concentrations applied, including even the treatment with no iodine. However, since iodine would be needed to oxidize elemental Hg, we recommend a minimum concentration of 0.2 Molar iodine to remove all mercury forms. Other means of surface cleaning such as surface polishing could make toxic mercury and mercury oxide airborne and would pose significantly greater environmental and health risks. With 0.2 Molar iodine, we observed substantial decontamination, with mercury removal rates of 99%.

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Table 1. Composition in weight- and atom-% (by EDX) of the surface of the API 5L-X52 steel coupons.

| Element | Weight-% | Atom-% |
|----------------|-----------|-----------|
| Iron (Fe) | 75.2±10.4 | 45.5±14.4 |
| Manganese (Mn) | 0.9± 0.1 | 0.5± 0.2 |
| Carbon (C) | 11.4± 4.2 | 29.9± 5.8 |
| Oxygen (O) | 12.6± 6.4 | 24.2± 9.1 |

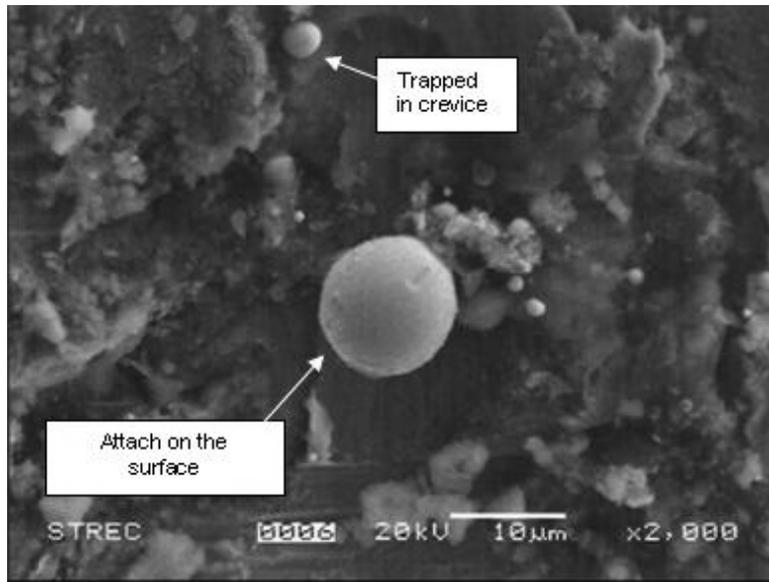


Figure 1. Spherical Hg^0 droplets are present on the metal coupon surface following adsorption

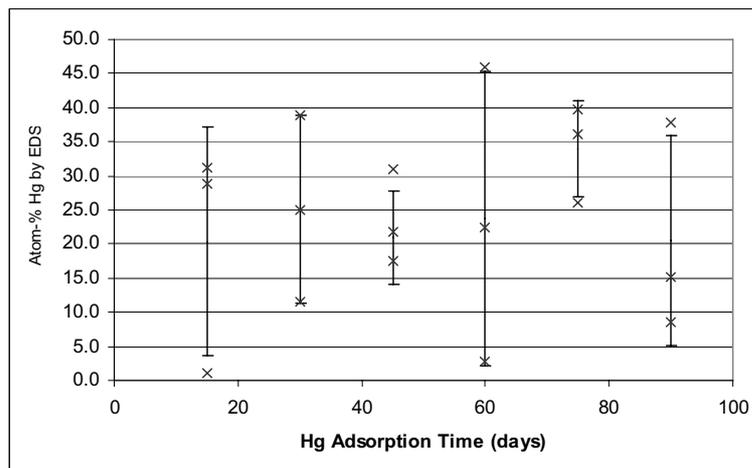


Figure 2. Surface Hg concentrations at the end of each Hg adsorption period using EDX analysis

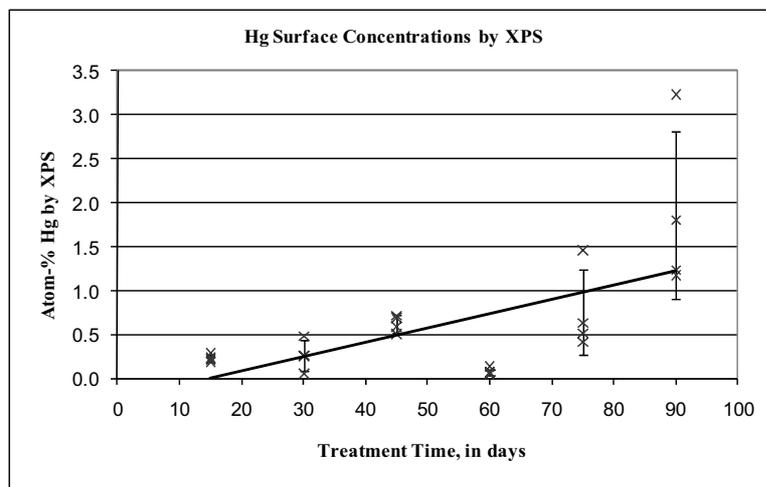


Figure 3. Surface Hg levels by XPS analysis at the end of each Hg^0 adsorption period

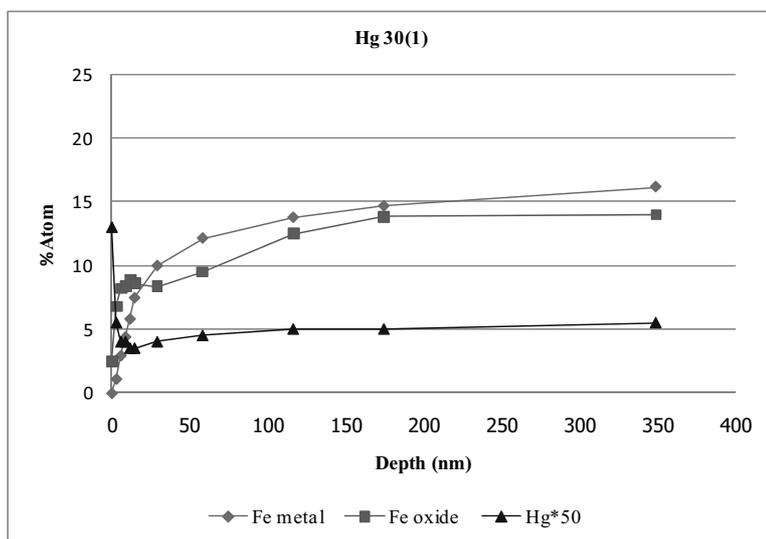


Figure 4. Hg in the depth profile of the 30 day Hg⁰ adsorption coupon

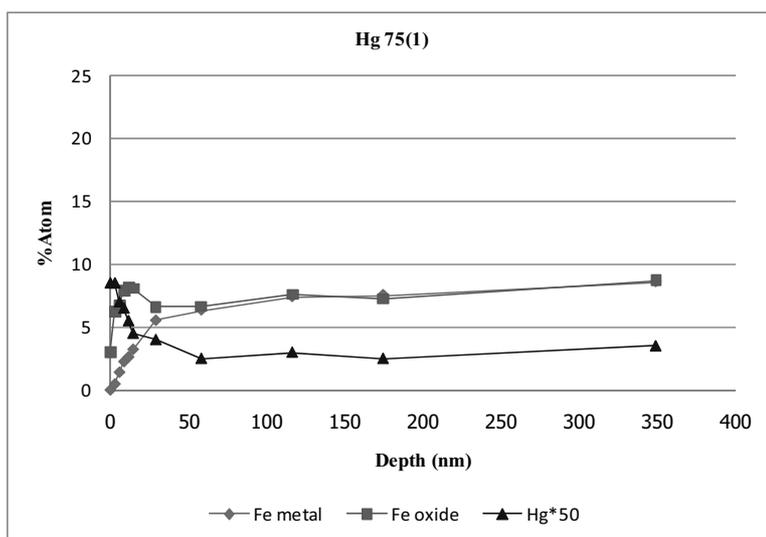


Figure 5. Hg in the depth profile of the 75 day Hg⁰ adsorption coupon

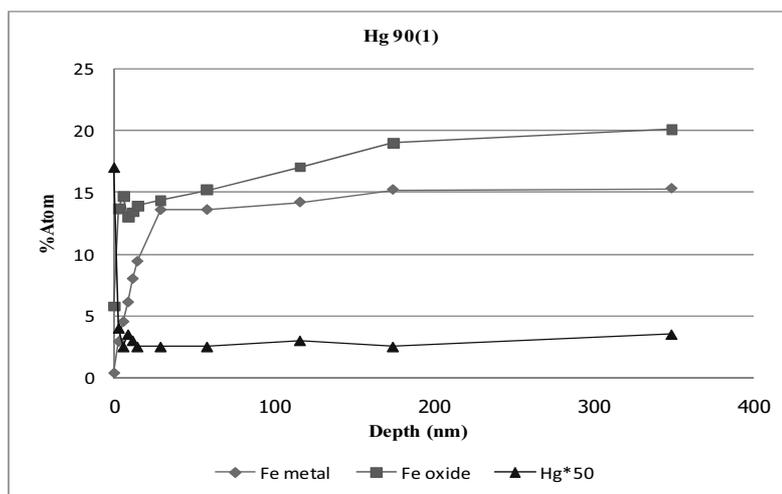


Figure 6. Hg in the depth profile of the 90 day Hg⁰ adsorption coupon

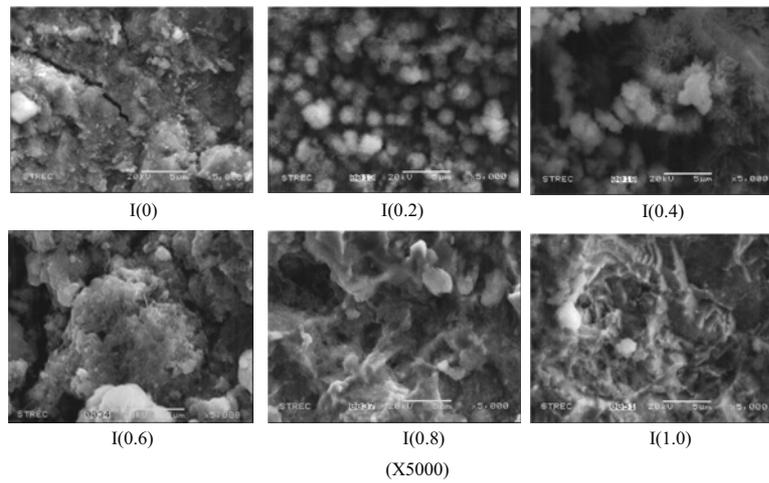


Figure 7. Surface morphology of the 30 day Hg^0 adsorption coupons after lixivient treatment
The concentration of iodine, ranging from 0 Molar to 1.0 Molar, is listed below the corresponding micrograph

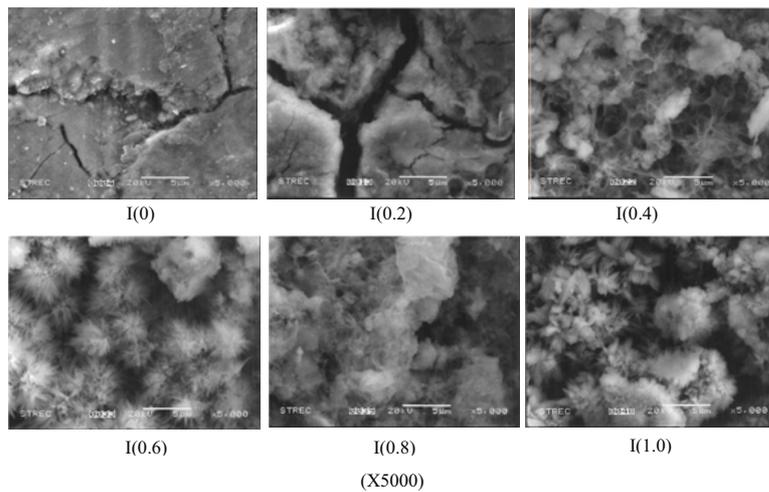


Figure 8. Surface morphology of the 75 day Hg^0 adsorption coupons after lixivient treatment
The concentration of iodine, ranging from 0 Molar to 1.0 Molar, is listed below the corresponding micrograph

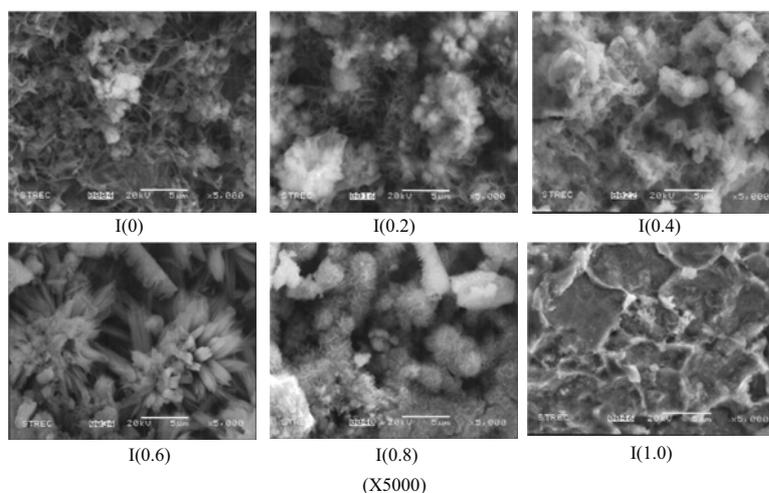
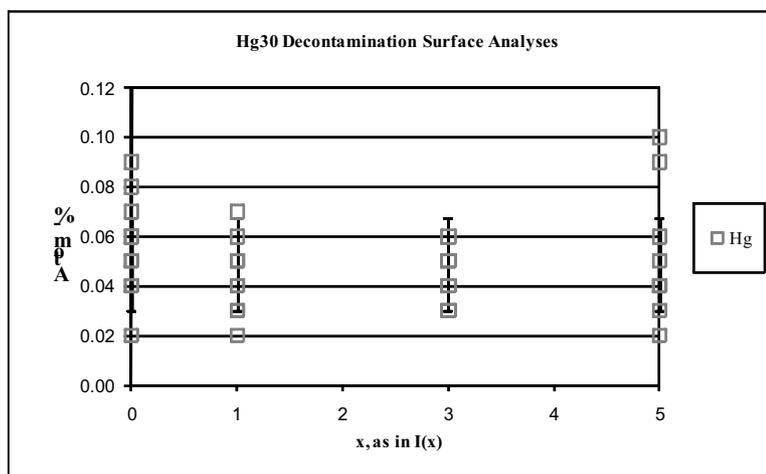
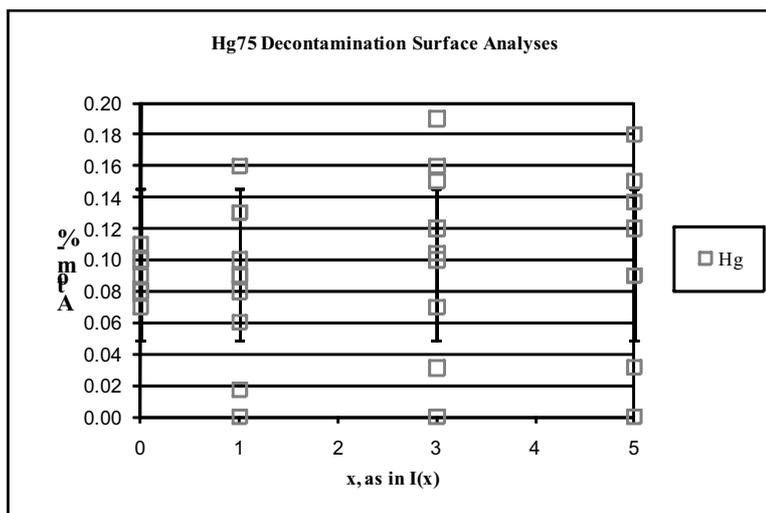


Figure 9. Surface morphology of the 90 day Hg^0 adsorption coupons after lixivient treatment
The concentration of iodine, ranging from 0 Molar to 1.0 Molar, is listed below the corresponding micrograph



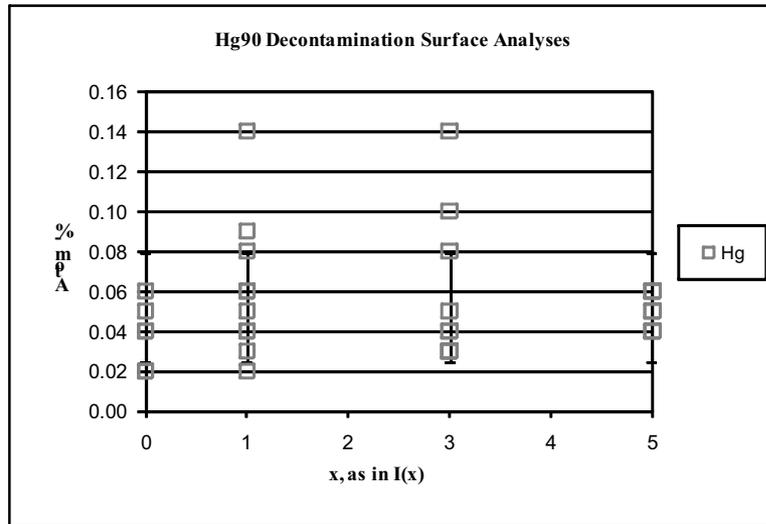
Note I(0) = no iodine, I(1) = 0.2 Molar, I(3) = 0.6 Molar and I(5) = 1.0 Molar

Figure 10. Hg surface concentration by XPS of 30 day Hg adsorption coupons following lixivient treatment with various concentrations of iodine and 2.0 Molar iodide



Note I(0) = no iodine, I(1) = 0.2 Molar, I(3) = 0.6 Molar and I(5) = 1.0 Molar

Figure 11. Hg surface concentration by XPS of 75 day Hg adsorption coupons following lixivient treatment with various concentrations of iodine and 2.0 Molar iodide



Note I(0) = no iodine, I(1) = 0.2 Molar, I(3) = 0.6 Molar and I(5) = 1.0 Molar

Figure 12. Hg surface concentration by XPS of 90 day Hg adsorption coupons following lixiviant treatment with various concentrations of iodine and 2.0 Molar iodide

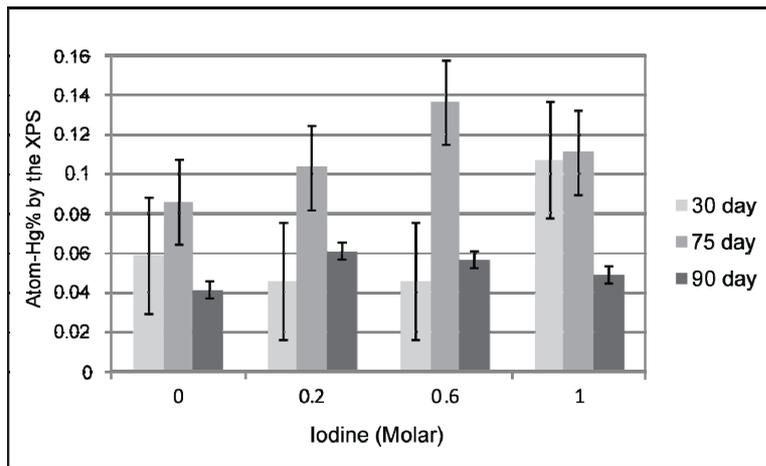


Figure 13. Surface Hg levels in atom% by XPS of steel coupons after the decontamination treatment