



# **Mercury Management and Chemical Decontamination White Paper 2010**

**Mercury in Hydrocarbon  
Process Streams:  
Worker Exposure,  
Process Risk, Sampling  
and Analysis Methods,  
and Chemical Solutions**

## Introduction

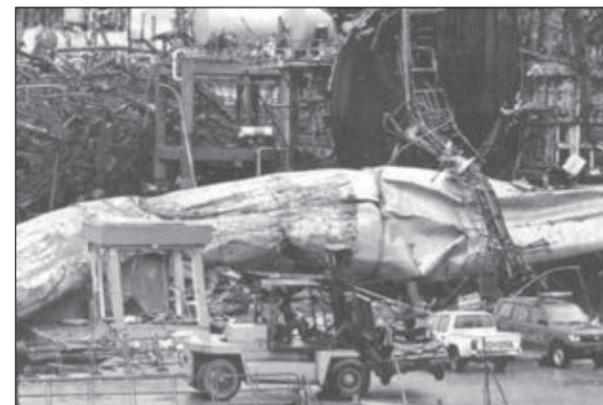
Mercury is found in trace quantities in all forms of hydrocarbons including petroleum and natural gas. Even in trace concentrations mercury presents complicated toxicological, ecological, and hydrocarbon processing risks. Mercury is a neurotoxin and persists in the environment for long periods but it is the unique properties of mercury to poison catalyst and damage aluminum processing equipment that are of significant importance to the hydrocarbon processing industry. Energy companies engaged in production and processing of natural gas and natural gas liquids should understand the risks, and liabilities associated with produced mercury. As part of understanding these risks companies should implement a comprehensive mercury management program that measures mercury in hydrocarbon process streams, identifies worker exposure risks, and mitigates processing risks.

In an effort to mitigate risks associated with production and processing of natural gas containing mercury, Measurement and Monitoring Solutions (MM<sup>S</sup>) has established a research and development program focused on mercury sampling and analysis technology and chemical decontamination. This white paper presents data from two separate analytical and chemical bench tests, designed to first measure baseline mercury mass and concentrations and then quantify the subsequent reductions from chemical processes as measured primarily by atomic fluorescence spectrometry.

## Mercury in Natural Gas and Processing Risks

Mercury is a trace constituent of oil and gas throughout the world but quite prevalent in Asia, parts of Russia, the North Sea, and South America. Natural gas originates in geologic formations associated with ancient basins where transformation has chemically changed ancient organic material into usable hydrocarbons primarily methane, ethane, propane, and butanes. The origin of mercury in natural gas is not fully understood but is hypothesized to be associated with volcanic source rock deposited in ancient basins and through volcanism from magma causing mercury to rise from the mantle.

Mercury exists in several chemical species in natural gas predominately in the elemental or inorganic mercuric form but can also exist in organic, complexed, or other suspended forms. The concentrations of mercury in natural gas, and natural gas condensate vary throughout the world supply but typically range from 1 to 200 micrograms per standard cubic meter ( $\mu\text{g}/\text{scm}$ ) in natural gas. Some fields in Asia exhibit mercury in gas concentrations that exceed  $500 \mu\text{g}/\text{scm}$ . Until recently little data was available regarding mercury concentrations in natural gas in the USA supply; however, several areas including Deep Shelf Gas (>15,000 feet) along



### Skikda, Algeria

In 2004, an explosion caused by an aluminum heat exchanger failure, destroyed three LNG compression trains. The failure was the result of liquid metal embrittlement caused by mercury in the natural gas stream.

Source: SPG Media Limited, a subsidiary of SPG Media Group PLC

the Texas and Louisiana Gulf Coasts and other producing fields located in the western USA and mid-continent have tested positive for mercury at concentrations requiring consideration and mitigation for environmental, worker exposure, and processing risks.

High mercury concentrations were recently measured in one natural gas well that tapped Deep Shelf Gas in the Gulf of Mexico (GOM). Concentrations exceeded  $500 \mu\text{g}/\text{scm}$ . While it is not known presently if high mercury levels will be associated with deeper GOM drilling, the alarm bell has sounded. Increased scrutiny of mercury in deeper wells is certainly warranted, and proactive plans for dealing with the ramifications of mercury in production should be considered early in the field development scheme.

Failure to remove mercury from produced gas streams carries significant liability if gathering, pipeline, and downstream processing facilities become contaminated.

The appearance of mercury at downstream processing facilities can be delayed by months or years due to scavenging of elemental mercury by steel pipeline surfaces. However, over time the mercury concentration measured at the plant inlet will rise to close to the wellhead level. Plants contaminated by mercury in processed gas experience

elevated concentrations in sludge in equipment, in glycol dehydration systems, in sour gas removal systems and wastewater. As with pipelines mercury reacts with and incorporates into steel surfaces such that elemental mercury vapor is emitted to the work environment when vessels are opened for inspection and maintenance. Mercury vapor is toxic to workers and stringent safety precautions must be employed to protect workers in gas plants contaminated by mercury.

Cryogenic processing plants are subject to increased risks from processing natural gas with trace components of mercury, as condensation of elemental mercury can cause Liquid Metal Embrittlement (LME), and Amalgam Corrosion (AMC) on surfaces of Aluminum Heat Exchangers (AHX) under certain conditions causing an immediate and catastrophic pressure loss. The processes and conditions that lead to LME and AMC are well defined and discussed in detail in *Risk Analysis for Operation of Aluminum Heat Exchangers Contaminated by Mercury* (MTS, Wilhelm, AIChE, April 2008).

A number of mercury-related failures of aluminum equipment have occurred over the years; some recently in spite of the advancement in understanding of mechanisms and availability of systems to prevent contamination. A heat exchanger failed in North Africa in 2004 resulting in a large explosion and fire with associated fatalities.

## Mercury Sampling and Analysis

Measuring elemental mercury concentration in natural gas at low concentration is a technical challenge for a variety of reasons. First and foremost is the difficulty to obtain representative gas samples due to the fact that mercury is scavenged by the sampling system. Valves, tubing, and regulators, etc. can remove mercury from the stream being sampled, even if constructed by otherwise inert materials. The sampling system can be conditioned by flowing gas for long periods (hours, days or weeks depending on concentration) but this approach is a practical handicap. Teflon™ or silica coated internals lessen the time of equilibration substantially. The methods employed by the gas industry have evolved overtime to overcome the difficulties associated with adsorption of mercury. The trend has been to large sample volumes obtained with special materials at elevated temperature.

International Standards Organization (ISO) 6978-3 (Natural Gas - Determination of Mercury) was selected as the analytical method for determining baseline and post verification mercury concentrations for this research. The ISO 6978-3 method consists of collecting mercury on a gold trap (quartz sample trap with gilded silica bead sample bed) followed by thermal desorption of the mercury into a cold vapor atomic fluorescence spectrometer (CVAFS) for detection and quantification. The measured mercury mass is then integrated with laboratory bench data primarily sample volume to calculate a total mercury concentration. A Tekran™ Model 2600 CVAFS was used for mercury analysis and was calibrated with saturated mercury vapor phase injections using a Tekran™ Model 2505 mercury vapor calibration unit.

A MAK II™ Mercury Sampling System designed and manufactured by MM<sup>s</sup> was used for the collection of mercury samples for chemical analysis. The MAK II™ Mercury Sampling System design provides a very reliable and precise mercury sampling system and exceeds the requirements for mercury sampling equipment specified in the most recent versions of ASTM, ISO, and EPA standard methods for sampling and analysis of mercury.

## Chemical Decontamination Solutions

Two sets of laboratory equipment were employed to test the effectiveness of chemicals designed to remove mercury from metal surfaces as might be found in contaminated process equipment.

The first test apparatus was constructed using a 2-inch flange assembly from a mercury contaminated pipeline system characterized to contain between 2 and 10 grams per square meter mercury. The test flange had been in service for several years handling a natural gas stream with mercury concentrations around 30 to 100 µg/scm.

The second test apparatus was constructed using Sulfinert™ coated mercury sampling equipment which included: a) PIP insertion probe (Model 702); b) 30-linear feet of ¼-inch stainless steel heat traced gas sampling tubing; and c) the first 3 sample trains to a MAK II™ Mercury Sampling System heater unit all of which were previously in service on a mercury contaminated pipeline system with mercury concentrations greater than 100 µg/scm.

Chemical cleaning of mercury contaminated carbon steel process systems present unique challenges since process system chemistry and equipment mercury loading are different for each system. It is hypothesized that mercury can penetrate pipeline carbon steel and complex in and near the steel grain boundary. Mercury in the form of HgS can also be present overlying corrosion scale (iron oxide) in a non-uniform layer. Residual liquid hydrocarbons (gas condensate) on pipeline and equipment surfaces can hold up to 2 ppm soluble mercury, and due to pressure and temperature changes in process systems, elemental mercury can be present in liquid form collecting in low points throughout a system.

Mercury decontamination of Sulfinert™ sampling and analysis equipment and components is complicated but slightly less challenging since the silica coating process is designed to minimize the chemical effects of mercury on metallic surfaces. As with chemistry selected for carbon steel surfaces, special considerations are required for decontaminating Sulfinert™ coated systems. Chemistry used to decontaminate silica coated systems must be protective of the Sulfinert™ coating.

There are many reasons to implement chemical cleaning of mercury contaminated process equipment and each will have different considerations when selecting a remedial action criterion. A key factor in designing a chemical cleaning program for any mercury contaminated systems is selecting a remedial action criterion that is reasonably obtainable and protective of process risks, worker exposure, and the environment. Several methods of verification of chemical cleaning include measuring defused mercury in gas, wipe sampling to measure residual surface concentrations, and thermal desorption testing of coupons.

### DECONTAMINATION CHEMISTRY

A variety of chemical solutions exist for decontaminating mercury contaminated process systems including oxidizing agents like hydrogen peroxide, sulfuric acid, and nitric acid, iodine and iodide. Reactive chemistries react with mercury to form water soluble (ionic mercury halides) or insoluble mercury (HgS) or otherwise combine with metal ions. Chemistries selected for this research include: 1) Hydrocarbon removal phase - MMS100, and 2) Mercury reactive removal phase - MMS200. MMS100 is a proprietary surfactant blend that forms a microemulsion with hydrocarbons and MMS200 is a surfactant/chelant blend that reacts with mercury to form inorganic soluble mercury salts.

## OBJECTIVES AND ANALYTICAL APPROACH

The objective of this research was to evaluate the effectiveness of selected chemistry applied to two separate mercury contaminated systems each with different surface and exposure characteristics. Verification of decontamination was performed using several analytical methods but primarily atomic fluorescence spectrometry due to its excellent sensitivity. Post verification chemical and wipe samples were analyzed using EPA Method 7470A/7471A.

## PROCEDURE

The chemical cleaning procedure consisted of circulating selected chemistries for pre-determined residence times at various temperatures. Virgin chemical samples were collected and analyzed for mercury for each chemical phase as part of the procedure. All virgin chemical samples were non-detect for mercury. The following sections describe the procedures for each test apparatus and details of each test are depicted in Figure 1, and Figure 2.

### TEST APPARATUS I (2-Inch Test Flange Assembly)

A new carbon steel 2-inch flange and associated appurtenances were constructed to form an air-tight closed-loop system by mating both flange surfaces. The contaminated 2-inch test flange had a pre-drilled ½-inch threaded hole through the middle as part of prior service on the pipeline system. System components were constructed of carbon steel (2-inch flanges and fittings), stainless steel (purified air and chemical connections), ½-inch braided chemical hose (chemical circulation), and Teflon tubing (purified air supply and sampling train).

The system was allowed to condition at 18°C flowing 500 milliliters per minute for 2 hours prior to collecting baseline mercury mass concentration data. Once the mercury in gas baseline mass and concentrations were calculated the flange assembly was separated in order to collect a baseline surface concentration from the test flange as measured by a wipe sample. After the baseline wipe sample was collected the flange assembly was reassembled and pressure tested prior to initiating chemical circulation.

A 20:1 solution of MMS100 was mixed in 2,950 milliliters of water and circulated at 14°C for 10 minutes at 3,000 milliliters per minute. A 5 minute purified air purge at 20 psi was used to return the chemical cleaning solutions to dedicated 5 liter chemical vessels with iodized carbon vents. Post treatment verification mercury-in-gas phase and surface concentrations were sampled and analyzed as previously described and

a post treatment verification chemical cleaning solution sample was collected for laboratory analysis. The reactive chemical circulation phase was performed using a 1:1 solution of MMS200 mixed in 1,500 milliliters of water and circulated at 15°C for 60 minutes at 3,000 milliliters per minute followed by a 5 minute purified air purge at 20 psi. Post treatment verification sampling and analysis were performed for all three matrices as previously described.

### TEST APPARATUS II (Sulfinert™ Mercury Sampling Components)

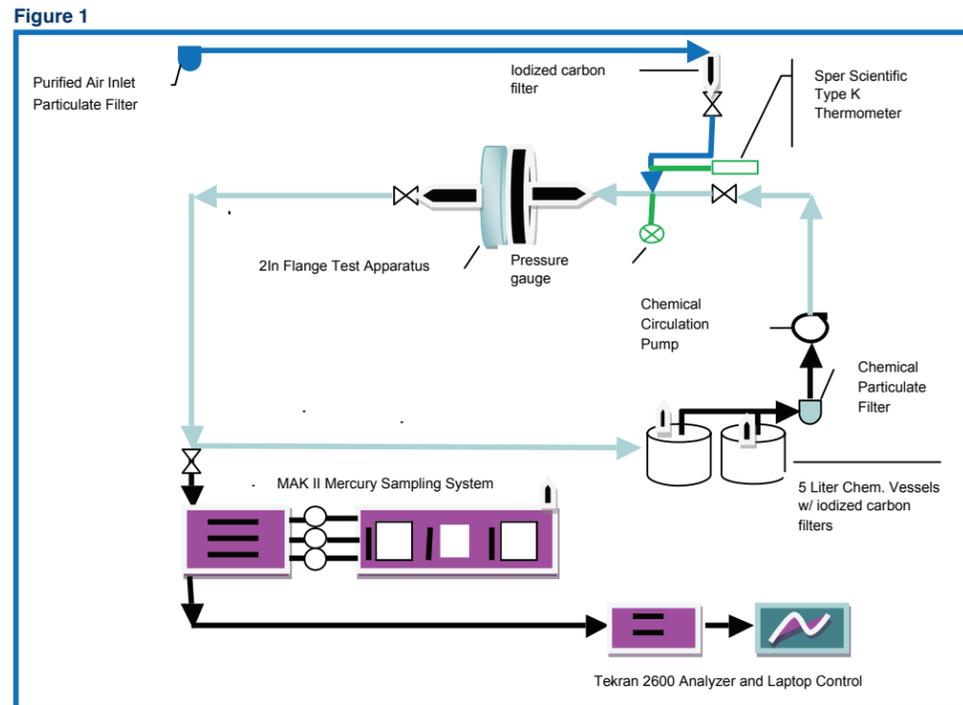
The second test apparatus comprised of three Sulfinert™ mercury gas sampling components and associated carbon steel insertion probe extraction chamber. The carbon steel extraction chamber provided chemical exposure to annulus surfaces from the extracted insertion section of the probe while simultaneously cleaning the interior. All components of this test apparatus were connected to form an air tight closed loop system. System components were constructed of new carbon steel (extraction chamber and fittings), stainless steel (purified air and chemical connections), ½-inch braided chemical hose (chemical circulation), and Teflon™ tubing (purified air supply and sampling train).

The system was allowed to condition at 18°C flowing 500 milliliters per minute for 2 hours prior to collecting baseline mercury mass concentration data. Systems components from this test apparatus did not allow for wipe sampling; however, post treatment verification chemical samples were collected from each chemical phase. After baseline mercury mass and concentrations were calculated the system was pressure tested prior to initiating chemical circulation.

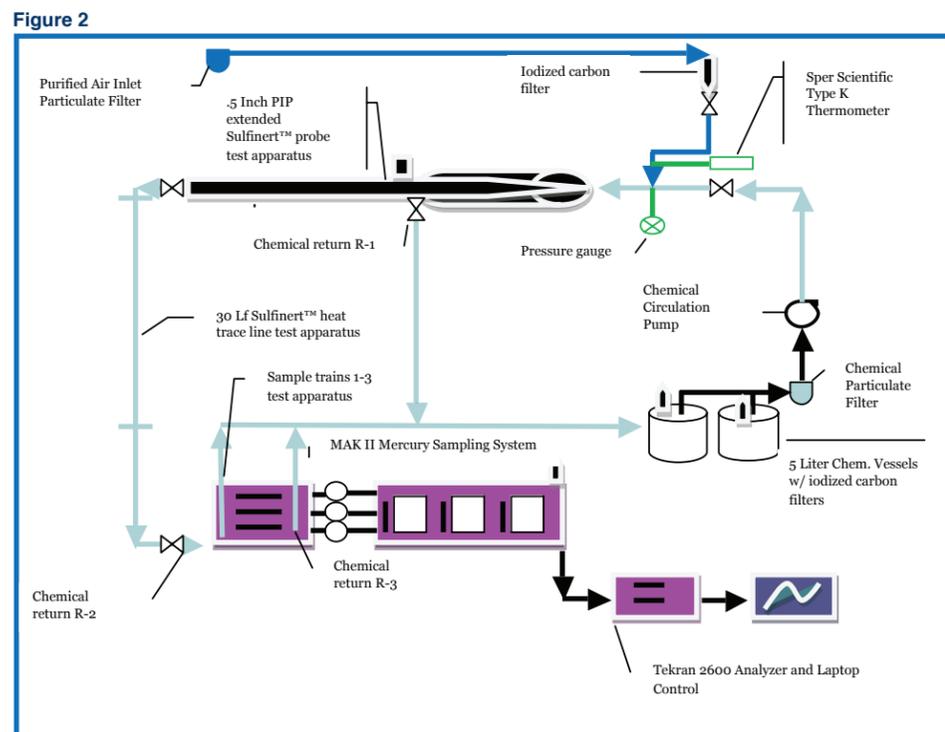
A 20:1 solution of MMS100 was mixed in 2,950 milliliters of water and circulated at 45°C for 40 minutes at 3,000 milliliters per minute (R-1), and around 100 milliliters per minute for R2 and R3 (see Figure 2). A 5 minute purified air purge at 20 psi was used to return the chemical cleaning solution to dedicated 5 liter chemical vessels with iodized carbon vents. Post verification mercury in gas phase concentrations were sampled and analyzed as previously described and a post treatment verification chemical cleaning solution sample was collected for laboratory analysis.

The reactive chemical circulation phase was performed using a 1:1 solution of MMS200 combined with 150 milliliters of dilute nitric acid, mixed in 1,500 milliliters of water, and circulated at 45°C for 60 minutes at flow rates specified above followed by a 5 minute purified air purge at 20 psi. Post treatment verification sampling and analysis were performed for all three matrices as previously described.

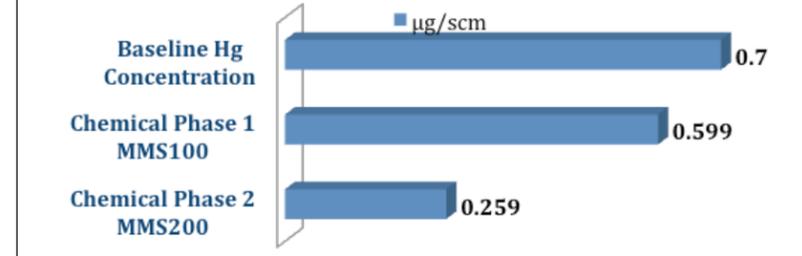
**Figure 1**  
**Test Apparatus I**  
shows a test apparatus, and chemical circulation flow paths, sampling and analysis instrumentation.



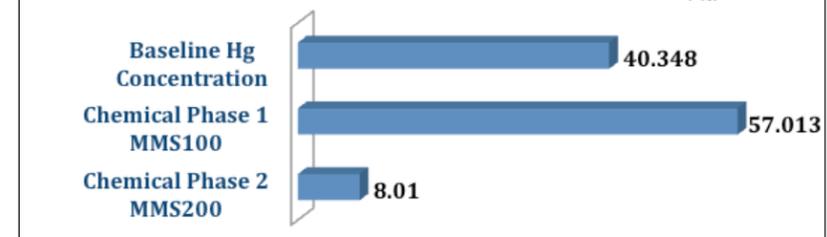
**Figure 2**  
**Test Apparatus II**  
shows an experimental test apparatus, and chemical circulation flow paths, and sampling and analysis instrumentation.



**Graph 1**  
**CVAFS Data Test Apparatus I**



**Graph 2**  
**CVAFS Data Test Apparatus II**



**Graph 3**  
**Mercury Surface Concentrations Test Apparatus I**



| Post Verification Chemical Test Results Summary Table     |             |
|---|-------------|
| Test Apparatus 1<br>2 Inch Flange Assembly                |             |
| Chem. Phase   | Result µg/L |
| MMS100  | 2.4         |
| MMS200  | 1.6         |
| Test Apparatus 2<br>Sulfinert Mercury Sampling Components |             |
| Chem. Phase   | Result µg/L |
| MMS100  | 87          |
| MMS200  | 12          |

**RESULTS**

Results from both bench tests indicate that mercury was successfully removed from each test apparatus. Both test cases (Test Apparatus I and II) show mercury concentration reductions of 71.25% and 85.95% respectively, as measured by atomic fluorescence spectrometry. Respective mercury concentration reductions are illustrated in Graph 1, and Graph 2. Baseline and post verification mercury surface concentrations were measured from Test Apparatus I and resulted in a 37.11% reduction as measured by wipe sampling. Wipe sample result represents a qualitative value based on estimated 38.5 cm<sup>2</sup> sample area normalized to 100 µg/100cm<sup>2</sup>. Surface mercury concentrations and calculated reductions are illustrated in Graph 3. Post verification chemical results are depicted in the summary table to the right.

### CVAFS QA/QC

Tables 1 and 2 provide quality assurance, and quality control data for CVAFS data from both test cases.

| Table 1 QA/QC DATA Test Apparatus I                                    |           |                                   |                  |                  |                    |                                 |                       |                     |                           |
|--|-----------|-----------------------------------|------------------|------------------|--------------------|---------------------------------|-----------------------|---------------------|---------------------------|
| Sample ID  | Type      | Sample Vol (Liters) @ 1 atm, 25°C | Trap A Mass (ng) | Trap B Mass (ng) | Total Hg Mass (ng) | Total Hg Concentration (µg/scm) | Paired Trap Agreement |                     | Average Total Hg (µg/scm) |
|  |           |                                   |                  |                  |                    |                                 | RD%                   | Within QA/QC Limits |                           |
| 2 Inch Test Flange Baseline Data                                       |           |                                   |                  |                  |                    |                                 |                       |                     |                           |
| fgs002 test app d  | Duplicate | 10.2                              | 5.779            | 0.000            | 5.779              | 0.567                           | 19.1%                 | Yes                 | 0.700                     |
| fgs003/4 test app a/b  | Primary   | 10.7                              | 8.926            | 0.42             | 9.342              | 0.834                           |                       |                     |                           |
| Chemical Phase I (MMS100 Chemical Circulation Post Verification Data)  |           |                                   |                  |                  |                    |                                 |                       |                     |                           |
| fgs004 test app vtest 1  | Primary   | 10.7                              | 4.666            | 0.000            | 4.666              | 0.436                           | 27.2%                 | No                  | 0.599                     |
| fgs003 test app vtest 1 d  | Duplicate | 10.6                              | 8.073            | 0.00             | 8.073              | 0.762                           |                       |                     |                           |
| Chemical Phase II (MMS200 Chemical Circulation Post Verification Data) |           |                                   |                  |                  |                    |                                 |                       |                     |                           |
| fgs004 test app vtest 2  | Primary   | 3.2                               | 0.675            | 0.000            | 0.675              | 0.211                           | 18.5%                 | Yes                 | 0.259                     |
| fgs003 test app vtest 2 d  | Duplicate | 3.1                               | 0.952            | 0.00             | 0.952              | 0.307                           |                       |                     |                           |

The first test case is representative of field conditions and limitations associated with decontaminating carbon steel pipe and appurtenances that have been subjected to mercury contamination for an extended duration. Although the defused mercury concentrations measured by CVAFS were quite low, the surface concentrations that were measured were relatively high. Soluble mercury was measured in each post treatment verification chemical phase from both test cases but higher mercury levels were measured in the second test case.

No governmental standard exists in the USA regulating surface concentrations of mercury but recent well intervention work has been performed in the GOM using 157 micrograms of mercury per square meter as a conservative standard protective of health and the environment. It is not practical to clean subsea pipelines, separators, and demethanizers, etc. to this standard; however, it is more realistic to use this standard for temporary service equipment (frac tanks, pumps, and down-hole equipment, etc.)

The results from Test Apparatus I highlight the need to design chemical cleaning programs to fit the expectations and requirements of each project. Remediation and chemical cleaning work performed in the USA typically follow recommendations provided by the ACGIH (25 µg/m<sup>3</sup>). This is not a remediation standard for produced mercury in gas processing equipment. Even though both chemistries applied to Test Apparatus I generated mercury mass and concentration reductions measured mercury remains complexed in the micro-scale layer of the test flange.

A correlation exists between the amount of surface mercury removed as measured from wipe sampling (Graph 3) and defused mercury concentrations in gas (Graph 1). This signifies that depending on remedial action criterion selected, chemical cleaning programs should consider more aggressive chemistries to remove micro-scale layers.

The second test case is representative of field sampling and analysis equipment subjected to mercury for several days as opposed to several years and designed to resist chemical exposure to mercury. The defused mercury-in-gas concentrations from Test Apparatus II were high considering the limited exposure time and equipment resistance. Measuring surface concentrations using wipe sampling methods was not practical on this test case. Dissolved mercury was measured in each chemical phase at higher concentrations than the first test case.

The second test eliminates the aforementioned surface dynamics associated with long-term mercury exposure and iron oxide scale thickness, and provides valuable data for limited exposure chemistry and equipment. Components of the second test apparatus were last used measuring mercury concentrations in wet-gas; and were more impacted by surface contamination from pipeline chemistry and micro-particulates, as opposed to lasting mercury complexes within the silica coated system.

| Table 2 QA/QC DATA Test Apparatus 2                                    |           |                                   |                  |                  |                    |                                 |                       |                     |                           |
|--|-----------|-----------------------------------|------------------|------------------|--------------------|---------------------------------|-----------------------|---------------------|---------------------------|
| Sample ID  | Type      | Sample Vol (Liters) @ 1 atm, 25°C | Trap A Mass (ng) | Trap B Mass (ng) | Total Hg Mass (ng) | Total Hg Concentration (µg/scm) | Paired Trap Agreement |                     | Average Total Hg (µg/scm) |
|  |           |                                   |                  |                  |                    |                                 | RD%                   | Within QA/QC Limits |                           |
| Sulfinert Mak2 Sampling Components Test Apparatus Baseline Data        |           |                                   |                  |                  |                    |                                 |                       |                     |                           |
| fgs002/3 test app base a/b   | Primary   | 3.3                               | 120.017          | 7.402            | 127.419            | 36.369                          | 9.9%                  | Yes                 | 40.348                    |
| fgs004 test app base d   | Duplicate | 3.8                               | 168.441          | 0.00             | 168.441            | 44.327                          |                       |                     |                           |
| Chemical Phase I (MMS100 Chemical Circulation Post Verification Data)  |           |                                   |                  |                  |                    |                                 |                       |                     |                           |
| fgs002 test app t1 pv1 a   | Primary   | 4.7                               | 285.971          | 0.000            | 285.971            | 60.845                          | 2.7%                  | Yes                 | 57.013                    |
| fgs003 test app t2 pv1 a   | Primary   | 5.1                               | 267.848          | 0.000            | 267.848            | 52.519                          |                       |                     |                           |
| fgs004 test app t3 pv1 a   | Primary   | 5.0                               | 288.367          | 0.000            | 288.367            | 57.673                          |                       |                     |                           |
| Chemical Phase II (MMS200 Chemical Circulation Post Verification Data) |           |                                   |                  |                  |                    |                                 |                       |                     |                           |
| fgs002 test app t1 pv2 a   | Primary   | 2.7                               | 17.816           | 0.000            | 17.816             | 6.598                           | 15.5%                 | Yes                 | 8.010                     |
| fgs003 test app t2 pv2 a   | Primary   | 3.2                               | 26.934           | 0.000            | 26.934             | 8.417                           |                       |                     |                           |
| fgs004 test app t3 pv2 a   | Primary   | 2.8                               | 25.238           | 0.000            | 25.238             | 9.014                           |                       |                     |                           |

### Conclusions and Applied Chemistry

Further research is forthcoming that will include mercury speciation and additional chemistries on new test cases from several sources. The research and development team at MM<sup>S</sup> is dedicated to developing innovative chemical cleaning solutions to remove mercury from contaminated process systems.

A correlation also can be seen from the second test case by comparing the data from Graph 2 to the summary table of results depicting mercury concentrations measured in post treatment verification chemicals. Mercury was measured in higher concentrations in chemical cleaning solution after the first chemical phase indicating that mercury was adhering to particulate matter or relatively soluble. Post treatment mercury concentrations measured in gas phase increased after the first chemical phase was likely due to residual chemical foam remaining in the system after the purified air purge. Graph 2 shows mercury concentrations were reduced considerably after the first chemical phase as measured by CVAFS and as measured in the post treatment chemical solution.

The research supports both applied chemistries were successful in removing mercury from each test apparatus. Increased mercury concentration reductions are likely with increased residence times and temperatures.

In developing full-scale chemical cleaning programs several steps should be considered to ensure success. Where applicable residual liquid mercury should be removed (physical decontamination) first followed by a hydrocarbon removal chemical phase. Typically an oxidation chemical phase would be performed next to deactivate pyrophoric materials. A mercury reactive chemical phase could be performed next to meet a range of selected cleaning objectives.

For pipeline cleaning abrasive pigging followed by various chemical slugs could achieve appreciable mercury concentration reductions. Down-hole equipment and other contaminated maintenance equipment can be cleaned using a variety of chemistries including the ones tested using manual or high pressure spray application methods. A final chemical cleaning plan would consider the objective of cleaning (i.e., EH&S, process risk reduction, decommissioning) and associated costs. Ultimately, both chemistries tested can be applied in industrial settings using existing equipment and techniques.

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