

International Gas Union Research Conference 2011

**FIRST ENCOUNTER OF EXCESSIVE HEAT AND TOXIC GAS
RELEASE DURING MERCURY REMOVAL UNIT CHANGEOUT
ACTIVITY**

Salihin Mohamed Ismail

Malaysia LNG Sdn. Bhd.

Malaysia

ABSTRACT

Malaysia's PETRONAS LNG complex in Bintulu, Sarawak, comprises of MLNG (1983), MLNG DUA (1995) and MLNG TIGA plants (2003). The three plants are operated as one integrated site, all being part of the Gas Sector of PETRONAS. Each of MLNG and DUA plant consists of three independent process modules with total LNG deliverable capacity of 6.87 million tonnes per annum (mtpa) and 8.10 mtpa respectively, while MLNG TIGA having two independent process modules designed to deliver 7.68 mtpa of LNG. In 2005, upon the completion of the MLNG Revamp and Rejuvenation (MRR) project, MLNG capacity has been increased by 25% bringing the new total deliverable capacity of 8.4 mtpa while MLNG DUA is expected to contribute another additional 21% by end of 2011 after completion of MLNG DUA Debottlenecking (MDD) Project.

Each one of the 8 LNG modules in PETRONAS LNG complex has been installed with Mercury Removal Unit (MRU). This unit is located downstream of Dehydration Unit to guard the downstream equipment against corrosion effect of Mercury (Hg) in the Cryogenic section. MRU in all the modules have never pose any significant operational problems in regards to Hg breakthrough due to consistently low Hg content in the feedgas. Previous abnormalities in this unit were mainly due to elevated differential pressure (dP) caused by the upsets in the upstream units such as adsorbents carry under, severe soot formation and solvent carry over.

During Module 6 MRU adsorbent changeout in September 2007, a rather highly unusual occurrence took place where extreme heat ($>160^{\circ}\text{C}$) and toxic gas ($\text{H}_2\text{S} > 600 \text{ ppm}$) was released during unloading of spent adsorbent. The same experience happened again in August 2008 during MRU changeout activity for Module 4 with somewhat greater severity. The strange encounter was shared with other substantial Hg adsorbent users to better appreciate the technicalities but none was having comparable to MLNG DUA's experience making it the first incident ever heard of in gas processing industry.

Reasons for the abnormal encounter during the two MRU changeout activities had to be properly understood and distinguished to ensure deliverance from future recurrence. In May 2009, a team from MLNG as well as other related external technical specialists was called to participate in an integrated (Root Cause Analysis) RCA study to fully understand and systematically underline the possible root causes for the unusual episodes mentioned. In late 2009 and mid 2010, the team had 3 opportunities to implement all the improvement measures identified during RCA study for MRU changeout of Module 5 (July 2009), Module 6 (June 2010) and Module 2 (August 2010) and proved that all the root causes identified were effectively addressed.

This paper documents the detail technical explanation regarding the two unique experiences and highlight of the RCA Study. This paper also discusses on the challenges that the shut down team underwent as well as changes and improvisation to MRU changeout procedure.

TABLE OF CONTENTS

Abstract

1. Introduction
 - 1.1 Process Description
 - 1.2 Heat and Toxic Gas Release during Routine Adsorbent Changeout
2. Root Causes Analysis (RCA) Study
 - 2.1 Problem Statement and Demarcation
 - 2.2 RCA Study Findings
 - 2.3 RCA Study Conclusion
3. Challenges to Shut Down Team
 - 3.1 Isolation of Hazards & Minimize Exposure to Personnel
 - 3.2 Safe Work Execution
4. Improvement to Hg Guard Bed Changeout Activities
5. Key Learning Points
6. Conclusion
7. References
8. List of Tables
9. List of Figures

1.0 INTRODUCTION

1.1 Process Description

The purpose of MRU is to remove Hg in the feed to Liquefaction Unit in order to protect the Main Cryogenic Heat Exchanger (MCHE) against corrosion. Generally, MRU consists of one vessel loaded with high porosity catalyst (i.e. sulfur impregnated activated carbon) as adsorbent. The base carbon is made from selected grades of activated coal and suitable binders to create the unique pore structure and superior hardness necessary for the intended service.

Activation of coal is controlled to impart a coal structure that will both accept substantial quantities of impregnant component (i.e. Sulfur) while having ability to maintain access of gas being treated through the complex pore structure. After activation, the sulfur is distributed in a thin layer over the extensive internal surface area to provide it with the unique properties required for the removal of elemental and organic Mercury from natural gas.

During operation, treated and dried feed gas from the Acid Gas Removal Unit (AGRU) and Dehydration Unit passes through the Hg adsorbent bed. Hg in the gas is adsorbed by the activated carbon and chemical reaction with sulfur converts the Hg to become a stable compound known as Mercuric Sulfide (HgS). The spent adsorbent is not regenerable; therefore once its capacity has been used it will be disposed off and replaced with a fresh batch.

In MLNG DUA, the design Hg content in feed is 800 mg/Nm³ while the treated gas downstream of MRU has a strict low Hg content specification of 0.1 mg/Mm³. MRU is located downstream of Dehydration unit to gain the benefit of superior adsorption performance under dry condition. Adverse adsorption performance will be experienced if the adsorbent bed is wet. For drying operation (normally upon start-up) dry defrost gas is introduced from defrost gas connection at the outlet of MRU flowing backward through the bed and routed to flare via the RV bypass.

1.2 Heat and Toxic Gas Release during Routine Adsorbent Changeout

MRU operation in all the modules have never posed any significant operational problems in regards to Hg breakthrough due to consistently low Hg content in the feedgas. Previous abnormalities in this unit were mainly due to elevated differential pressure (dP) caused by the upsets in the upstream units such as molsieve carry under, severe soot formation and solvent carry over. MRU is also commonly referred as the Hg guard bed. Changeout requirement of Hg guard bed will depend on the remaining Hg adsorption capacity left or the dP across the bed. However the normal changeout will be scheduled every 3 or 6 years depending on Hg guard bed performance to match the Department of Occupational, Safety and Health (DOSH) statutory shutdown requirement (i.e. once every 3 years)

During scheduled Module 6 MRU adsorbent changeout in September 2007, a rather highly unusual occurrence took place where extreme heat (>160°C) and toxic gas (Hydrogen Sulfide - H₂S > 600 ppm) were released during unloading of spent adsorbent. The same experience happened again in August 2008 during MRU changeout activity for Module 4. Due to early detection and immediate actions to isolate the exposure of hazards, there were no casualties encountered during both of the incidences.

Having no clear-cut technical explanations from other substantial Hg adsorbent users and technical advisors, the uniqueness of these two incidents has triggered a call for an integrated Root Cause Analyses (RCA) study. It was conducted in May 2009 to fully understand and systematically underline the possible root causes for the unusual occurrence. The study was also intended to generate improvement measures to ensure deliverance from future recurrence of such incidents.

2.0 RCA STUDY

All the information and data gathered before and during the two incidents were presented and thoroughly discussed during the RCA study session. A number of possible root causes that would contribute to the occurrence of extreme heat and toxic gas release were assessed. Accordingly, evidences to support or eliminate the possible root causes were identified.

2.1 Problem Statement and Demarcation

Since the study was participated by internal and external parties, an accurate definition of problem statement has to be decided to ensure that the discussion being steered in the right direction. The following problem statement was agreed and used as the starting point for the RCA study:

“Excessive and Uncontrolled Heat Release (>160°C) & Toxic Gas Release Detected by H₂S meter (> 600 ppm) during Spent Activated Carbon Unloading Activity of Hg Guard Bed for Module 6 (2007) and Module 4 (2008)”

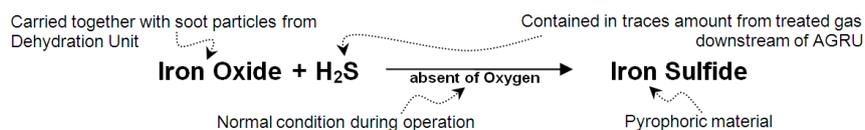
2.2 RCA Study Findings

The root causes determined during RCA study were:

- Oxidation Reactions
- Reduction Reaction Converting S to H₂S
- Desorption of Traces of H₂S and RSH
- Oxidation of FeS/FeS₂ to SO₂
- Vaporization of S

2.21 Oxidation Reaction of Pyrophoric Material

One of the most probable oxidation reactions that may lead to heat release as high as recorded during the incidents would be pyrophoric oxidation. Pyrophoric oxidation reaction requires presence of pyrophoric material as well as air. Since presence of air can be confirmed during unloading activity, the team further explored on possibility of having pyrophoric material formation in the system. From the evidence gathered, it was found that all the ‘ingredients’ required for pyrophoric material formation (specifically Iron Sulfide – FeS) should have been present during operation before the shut down. Iron Sulfide formation was believed to have been formed under the following condition:



The above reaction matched the generic chemical reaction for Iron Sulfide formation:



When exposed to air (i.e. Oxygen), Iron Sulfide undergoes oxidation reactions that results in heat release:



Soot Migration from Dehydration Unit to MRU. Dehydration Units in MLNG DUA have been known to suffer from significant soot generation due to exposure of regeneration gas to higher temperature in the waste heat recovery heat exchanger. Consequently the MRUs in all the DUA modules were subjected to the impact of soot migration. Evidence of soot migration to MRU was confirmed when the MRU downstream filters were seen to register frequent filter element changeout due to black debris (i.e. soot) fouling.

In the previous study, the soot samples collected at Hg guard bed downstream filter were sent for micro-structural and elemental analyses [1]. It was found that the soot samples portrayed some distinguished magnetic properties which later determined to be magnetite (i.e. Iron(II,III) Oxide – $\text{FeO} \cdot \text{Fe}_2\text{O}_3$). Both MRU for Module 4 and 6 have been subjected and exposed to the soot for 3 years before their respective shutdowns. This finding confirms the presence of Iron Oxide in the system.

Figure 1 below illustrates some pictures of clogged filter elements and sample of black debris (i.e. soot particles) followed by snapshots [1] of soot particles under different magnifications.

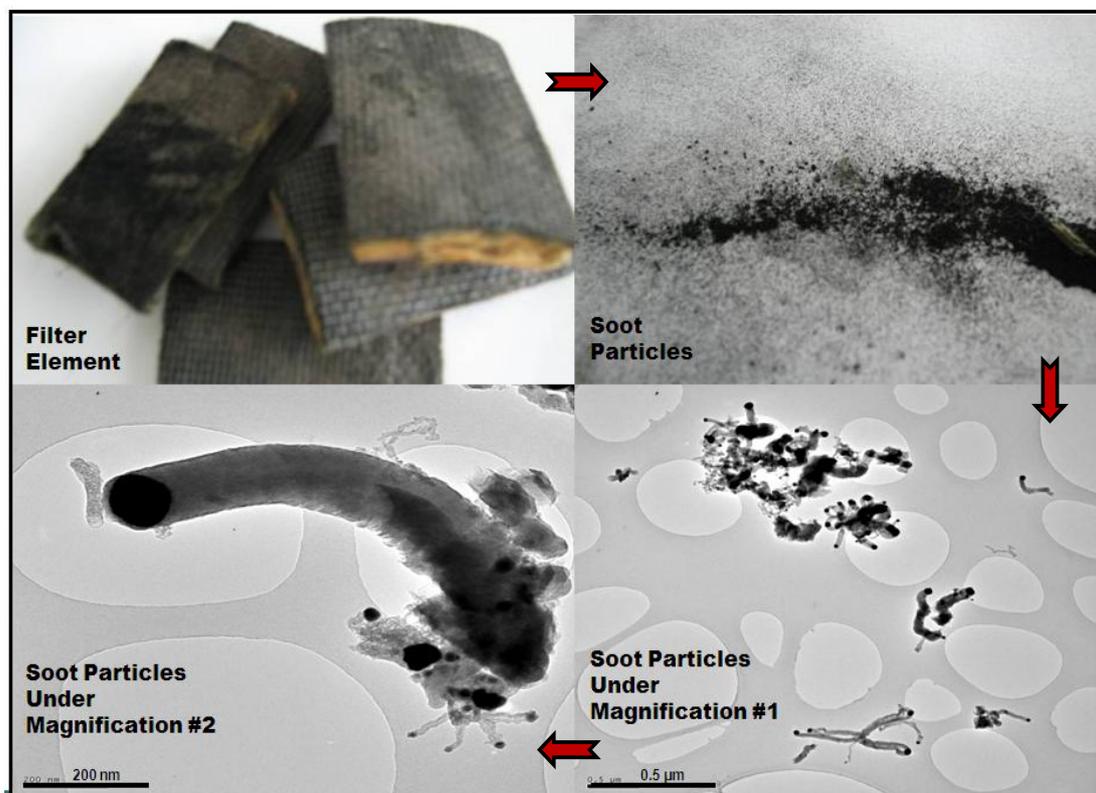


Figure 1 – Pictures of Clogged Filter Element and Soot Particles Sample Before and After Magnifications.

Presence of H₂S. The second element required for pyrophoric formation under reaction above (i.e. reaction 1) is the presence of H₂S. Even though MRU is located downstream of AGRU, the treated gas specification has been design to allow maximum traces of H₂S breakthrough as high as 3.3 ppm. During normal operation, the treated gas from AGRU has been seen to contain approximately 0.5 ppm of H₂S. Figure 2 below shows the concentration of H₂S in feed gas to MLNG DUA against the treated gas quality downstream of AGRU.

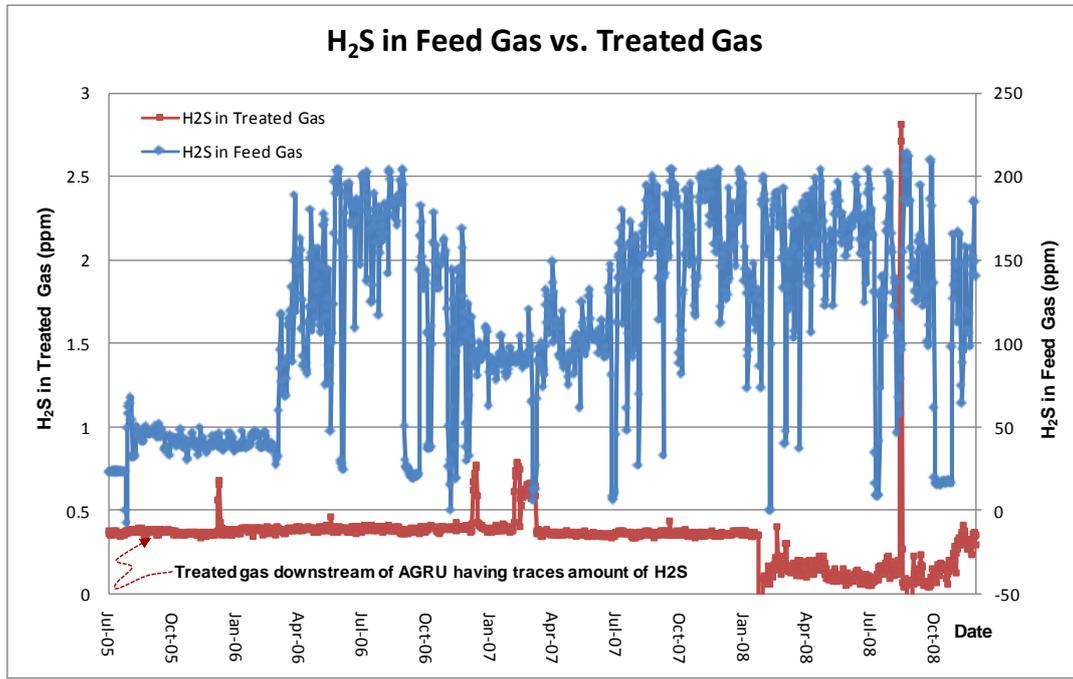


Figure 2 – H₂S in Feed Gas vs. Treated Gas for MLNG DUA since July 2005

The evidences presented above (i.e. presence of Iron Oxide and H₂S in the complete absence of Oxygen) substantiate the Iron Sulfide formation mechanism during operation. During changeout activities of the Hg guard bed for Module 4 and 6, the spent adsorbent contaminated with Iron Sulfide (pyrophoric material) was exposed to air and consequently resulted in release of heat. Measurement taken using a pyrometer indicated that the spent adsorbent temperature went up to 160°C (average).

During the second incident, the hot spent adsorbent has melted the tarpaulin sock (used to funnel the spent activated carbon into disposal drum) and caused some amount of spent activated carbon to freely spill on the ground. To control the surrounding heat, the shut down crew sprayed firewater onto the spilled activated carbon and this resulted in sudden generation of steam cloud. Figure 3 below depicts some photographs taken during the incident.



Figure 3 – Several Photographs Taken During Incident in Module 4 (2008)

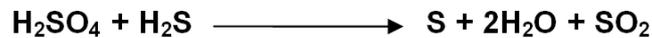
2.22 Side Oxidation Reaction

Presence of water and its associated impact to spent activated carbon was further explored to determine other reaction that could result in either heat or toxic gas release. According to the activated carbon specialist [2], several side reactions could be initiated in the presence of water. At constant temperature, water will have higher adsorption affinity with activated carbon as compared to H₂S. Therefore any presence of water during changeout will displace co-adsorbed H₂S (during operation) and will form a “water layer” on the carbon pore surface. The water layer will in turn dissolve freed H₂S and consequently the following oxidation reactions are expected to take place:

Main Reaction :



Side Reaction :



The above reactions are exothermic and consequently heat release would be anticipated. Presence of water (as catalyst) is needed for these reactions to take place. Based on discussion, during the two changeout activities, presence of water in the spent adsorbent bed could potentially originate from accidental water ingress (water leak from top canvas cover during heavy downpour), higher relative humidity (during rainy days), and/or moisture condensation at internal vessel wall (due to warmer bed temperature during unloading activity).

The RCA study team believed that the occurrence of side oxidation reactions was possible since no evidence can be found to eliminate either presence of water or presence of H₂S. However, the team also believed that the above reactions should only be the contributor to the extreme heat release during the incident as the same condition may have also be present during other MRU changeout in other modules.

2.23 Verification of Toxic Gas

One of the expectations from the RCA study was to find out the reason(s) for release of gas that triggered different types of H₂S analyzers during the two incidents. To materialize that, a batch of fresh and spent sample was analyzed to determine if the gas release was as per detected by MLNG H₂S analyzers.

For the experiment [3], the adsorbents (fresh and spent activated carbon) were heated with gradual incremental temperature and any gas release was sampled in the *Tedlar* sampling bag. Surprisingly both gas detectors showed evidence of H₂S release at relatively low temperature. Figure 4 summarizes the experiment results.

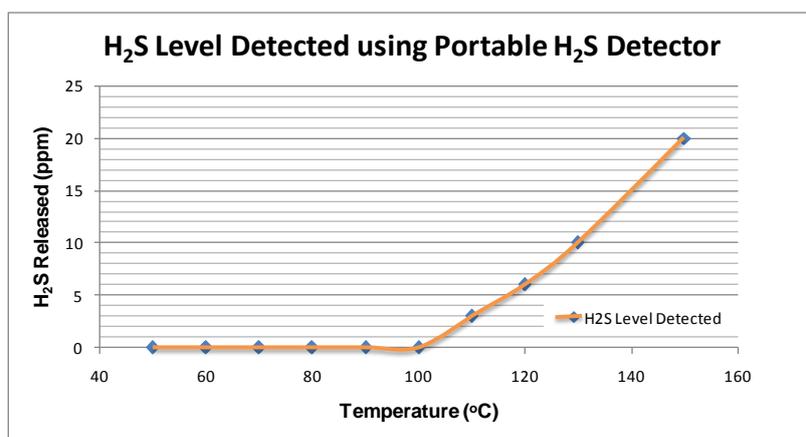


Figure 4 – Effect of Temperature to Spent and Fresh Activated Carbon

Verification of the above findings on the authenticity of H₂S gas was done by repeating the experiment and testing the gas using two standard methods which are the IP 103 and the Drager Tube Method. The analyst was able to prove that, no significant amount of H₂S gas being detected using the Drager Tube when the adsorbent was heated to >130°C, and the result was in agreement with another method (i.e. IP 103).

Another test was also conducted to gauge the level of interference to electrochemical sensors of the gas detectors by simply heating elemental sulfur at 130°C and as expected, the detectors started to trigger the alarm indicating high level of H₂S where clearly only SO₂ and sulfur fumes may be present. Figure 5 (a) and (b) below showed the 2 verification tests conducted in a fume cupboard.

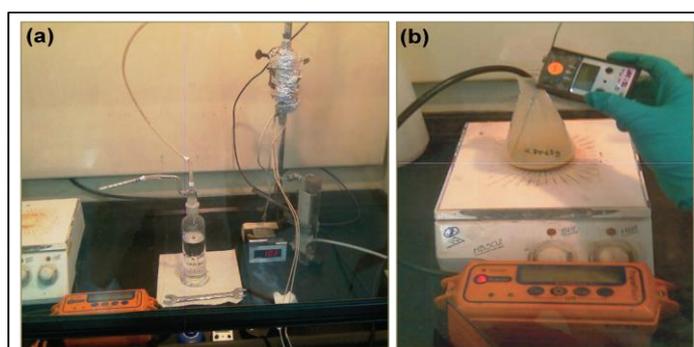


Figure 5 – (a) Drager Tube Method for Verification of “H₂S Gas” Released and (b) Vapor from Heated Sulfur Triggered the H₂S Detectors

The above finding was shared with gas detector manufacturer and it was discovered that 'cross interfering gasses' are not uncommon to be detected and translated as H₂S reading. Some of the common cross interfering gas are Carbon Monoxide, Sulfur Dioxide, Nitric Oxide, Nitrogen Dioxide and even Hydrogen. The magnitude of H₂S cross interference gas differs from one gas to the other. For instance, Sulfur Dioxide at 5 ppm may get translated into approximately 1 ppm of H₂S while 10,000 ppm of Hydrogen gas may interfere with the sensor and translated into approximately 15 ppm of H₂S.

Having the knowledge that other gas may also cross interfere with the H₂S gas detector electrochemical sensor, the team further brainstormed on every possible reaction or occurrence that may lead to release of gasses listed above.

2.24 H₂S Release via Reduction Reaction Converting S to H₂S

Another batch of activated carbon sample was sent for some customized analyses [4] to see the temperature effect to the activated carbon and to study the differences between the fresh and the spent activated carbon. During this experiment, when the spent activated carbon being subjected to hot (> 200°C) and dry Nitrogen gas (N₂), the resultant vapour was found to contain high amount of H₂S. This was repeated using fresh activated carbon but the extent of H₂S released was much less.

The analysis was again conducted using wet N₂ and tested against spent as well as fresh activated carbon. The findings revealed the same pattern as above with relatively lower H₂S concentration (i.e. higher H₂S release for spent activated carbon and much lower release with fresh activated carbon). Figure 6 below has been reproduced from the analyses [4] outcome and summarizes the results.

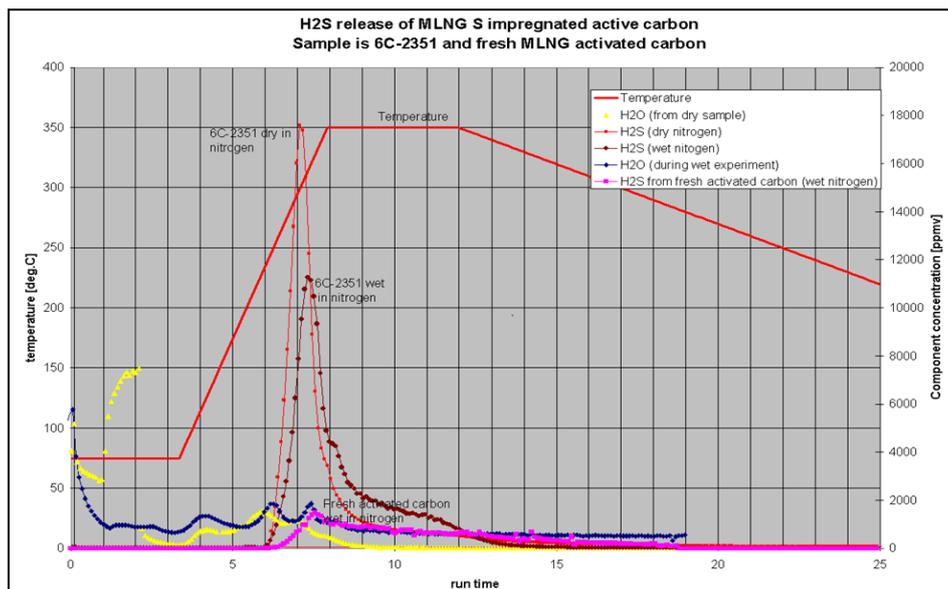


Figure 6 – H₂S Released at Elevated Temperature Even Without Presence of Oxygen

According to the analysts [4], the presence of heavy hydrocarbons in the heated spent sample should explain the higher H₂S release as compared to the fresh sample. Since Sulfur is known to be a strong oxidizer, it is indeed capable of oxidizing the co-adsorbed hydrocarbon according to the following generic relationship:



This reaction would require heat and in the case of the past two incidences, excessive heat release was evident as explained in section 2.21 above.

2.25 Desorption of Traces of H₂S

Desorption of H₂S from spent bed can take place at high temperature as well as whenever there is presence of free water. Evidence of high temperature and presence of water has been established before and the team believed that likelihood for desorption of traces of H₂S was indeed possible.

2.26 Oxidation of Iron Sulfide (FeS) to Sulfur Dioxide (SO₂)

Release of SO₂ would be highly possible following pyrophoric oxidation as well as other side reactions (elaborated in section 2.21). As it was known that H₂S gas detectors may also cross interfere with SO₂, possibility of having SO₂ to amplify the H₂S reading was considered to be credible even though the actual extent of interference during the incident could not be quantified.

2.27 Vaporization of Sulfur

Elemental Sulfur (melting point ~ 115°C) may exist in several allotropic forms but the most predominant are Rhombic and Monoclinic forms [6]. When heated to 120°C, the Rhombic (thermodynamically more stable) would slowly be converted into the Monoclinic and the bonding ring started to break-up resulting in rapid increase in viscosity once the temperature exceeding its melting point. Upon receiving localized extra energy, some Sulfur may also vaporize at lower than its boiling temperature (~ 444°C) [6].

As demonstrated in the test to verify the toxic gas (in section 2.23), some amount of SO₂ together with Sulfur fumes were generated when elemental sulfur was heated at approximately 130°C. During the past two incidents, the temperature of spent bed was measured to have exceeded 160°C. Therefore, formation of sulfur vapour together with generation of SO₂ was deemed to be highly possible and these gasses should have also been responsible for elevated H₂S detector reading during the 2 incidents.

2.3 RCA Study Conclusion

Based on the experiment and verification done, the RCA study team believed that the gas detectors have detected a mixed component of gases primarily SO₂ and H₂S resulted in H₂S alarm to trigger. Different reasons for toxic gas release explained above have been clearly linked with heat requirement. Therefore, the team agreed that the precursor to toxic gas release during the past two incidences should be initiated by release of heat while the main root cause for excessive heat release was due to pyrophoric oxidation reaction.

3.0 CHALLENGES TO SHUT DOWN TEAM

Both of the incidences have caused some significant delay to the tight shut down schedule. However, effective communication and information cascading during these incidents have minimized the delay and exposure of hazards to personnel. Despite having limited knowledge on technical explanation and solutions, the shut down team has worked together to isolate the hazards, minimize the exposure, and safely complete the tasks.

3.1 Isolation of Hazards & Minimize Exposure to Personnel

The problem was initially realized when the workers complained that the tip of vacuum hose used to withdraw the spent adsorbent melted. As soon as this was reported, all the workers were asked to stop the job and shortly after that, some personnel onsite complained about the 'rotten egg' smell followed by H₂S alarm. The above events immediately prompted emergency site evacuation.

When the H₂S reading subsided, a team from shut down crew went to the site (wearing appropriate breathing apparatus) and fully isolated the Hg guard vessel using a metal plate.

3.2 Safe Work Execution

A team (consists of technical, operations and maintenance personnel) was formed to understand the situation and provide temporary solutions until the task can be safely completed. From the discussion, it was decided to conduct a special periodical 'Nitrogen (N₂) blow technique' (with strict H₂S and temperature monitoring) during silent hours until the end of unloading activity. For this, a special metal plate with pipe and valve was fabricated to replace the metal plate used for vessel isolation.

During silent hours (midnight and common break hours), after ensuring that no other personnel working onsite, the Hg guard vessel would be slightly pressurized with N₂ followed by sudden purge from the top (using the valve). Workers allowed to be onsite for this activity were fully equipped with breathing apparatus. N₂ blow from the vessel will be repeated several time and unloading activities was allowed after the H₂S level dropped to less than 10 ppm. During unloading, continuous H₂S and temperature monitoring was done. Any increase in either the temperature or H₂S level would warrant an immediate vessel isolation and N₂ blow during silent hours. Figure 7 below is the sketch of Hg guard vessel with fabricated isolation plate for N₂ blow activity.

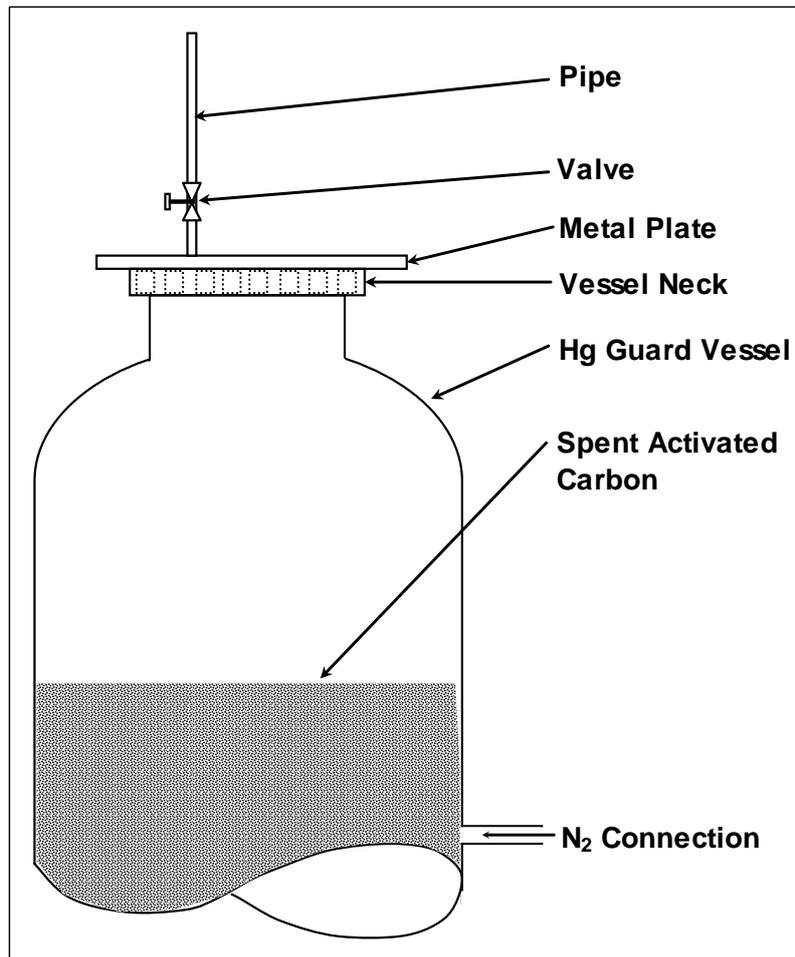


Figure 7 – Hg Guard Vessel with Isolation Plate for N₂ Blow

4.0 IMPROVEMENT TO HG GUARD BED CHANGEOUT ACTIVITY

MLNG is currently implementing the measures to rectify the issue in dehydration unit that has resulted in severe soot (and Iron Oxide) formation and migration. Until the Iron Sulfide formation mechanism in MRU (through Iron Oxide & H₂S reaction during operation) can be fully eliminated, the RCA Study team has recommended to ensure no presence of air (i.e. O₂) during unloading activity. Elimination of O₂ ingress would prevent chain of reactions that lead to heat and toxic gas release. This can be achieved by conducting inert unloading (i.e. unloading under positive N₂) of spent bed. Figure 8 below illustrates the simplified root cause linkages and basis of introducing inert unloading procedure.

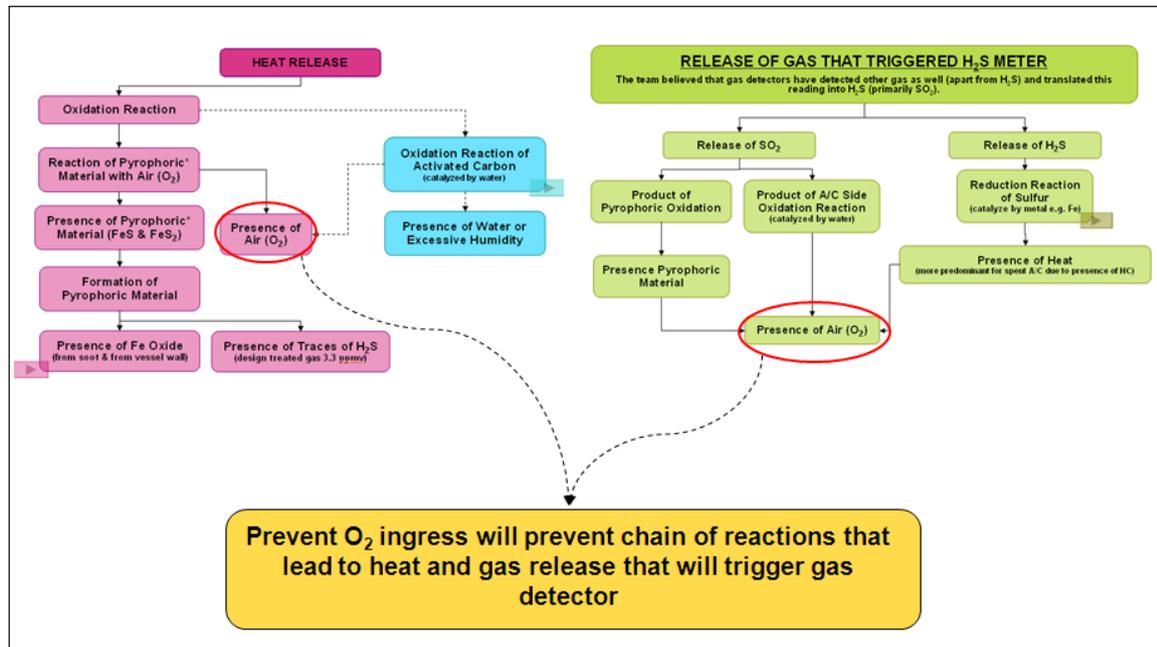


Figure 8 – Hg Guard Vessel with Isolation Plate for N₂ Blow

Apart from inert unloading, the team has also proposed few other improvements measures for the upcoming MRU changeout activities in MLNG:

- ✓ To prevent water ingress during rainy days by enhancing the canvas shed/tent on the MRU working platform
- ✓ To measure bed temperature every 30 minutes during unloading activity.
- ✓ To prolong N₂ purging duration before spading/opening (until Methane (CH₄) Lower Exposure Limit (LEL) drops below 10%).
- ✓ To ensure hoses and related equipment are dry.
- ✓ To prevent external pyrophoric oxidation and heat release by soaking the spent activated carbon in water (half filled the disposal drums with water).

4.0 KEY LEARNING POINTS

The two unique experiences that MLNG encountered have brought some significant changes to the overall perception on execution of “routine” activity. The following key learning points are shared for the benefits of all:

- Effective communication is extremely important especially in the midst of abnormal situation,
- All work must be stopped, reported and evaluated if one is unsure about the situation,
- Calibration of gas detectors alone may not necessarily ensure accurate detection of gasses in the field,
- It is important to verify the reading through bench scale lab test and simulation to determine the accuracy and nature of gas release,
- It is a good practice of a plant/site to check with gas detectors manufacturer and keep a glossary of gas detectors cross interfering gasses for future reference,
- Never bypass any safety steps and treat any routine activity lightly, they may surprise anyone in unexpected moments.

5.0 CONCLUSION

The last changeout activities of Mercury guard bed in Module 6 (September 2007) and Module 4 (August 2008) witnessed the most peculiar occurrence of extreme heat and toxic gas release during unloading of spent adsorbent beds. In May 2009, an integrated RCA study was conducted to fully understand and systematically underline the most possible root causes for the highly unusual experience mentioned. The team concluded that the primary root cause was initiated by heat release and this became the precursor to the release of gas that triggered the H₂S detectors. Heat released was believed to be the result of pyrophoric oxidation reaction while the toxic gas released was the consequential product of reactions linked to the heat release.

Findings from the RCA Study brought the team to propose few changes to the spent activated carbon unloading procedure mainly in terms of introducing the inert unloading method. In late 2009 and mid 2010, MLNG had 3 opportunities to implement all the improvement measures identified during RCA study during MRU changeout of Module 5 (July 2009), Module 6 (June 2010) and Module 2 (August 2010) and proved that all the root causes identified were effectively addressed.

6.0 REFERENCES

- [1] Blazina, D., Smith, G., ‘*Analysis Report of MLNG Black Debris Samples*’, -SGSI Lab, UK Mar 2007
- [2] Wortman R., ‘*Heat & H₂S Release*’, NORIT Application Specialist for Gas & Air, May 2009
- [3] Mercury Team, ‘*High Temperature and ‘H₂S’ Release at Mercury Removal Unit at MLNG DUA Study*’, Novel Process and Advanced Engineering, PRSB Lab, Bangi, April 2009
- [4] Last, T., Smith, K., ‘*Analysis of Spent Activated Carbon Sample from MLNG*’, SGSI Lab, Amsterdam, Sept 2008
- [5] Zumdahl, S.S., ‘*Chemical Principles – 3rd Edition*’, pp. 872, 873, Houghton Mifflin, Boston, 1998
- [6] <http://en.wikipedia.org/wiki/Sulfur>, retrieved 24th Dec 2009

7.0 LIST OF FIGURES

Figure 1	Pictures of Clogged Filter Element and Soot Particles Sample Before and After Magnifications.
Figure 2	H ₂ S in Feed Gas vs. Treated Gas for MLNG DUA since July 2005
Figure 3	Several Photographs Taken During Incident in Module 4 (2008)
Figure 4	Effect of Temperature to Spent and Fresh Activated Carbon
Figure 5	(a) Drager Tube Method for Verification of "H ₂ S Gas" Released and (b) Vapor from Heated Sulfur Triggered the H ₂ S Detectors
Figure 6	H ₂ S Released at Elevated Temperature Even Without Presence of Oxygen
Figure 7	Hg Guard Vessel with Isolation Plate for N ₂ Blow
Figure 8	Hg Guard Vessel with Isolation Plate for N ₂ Blow