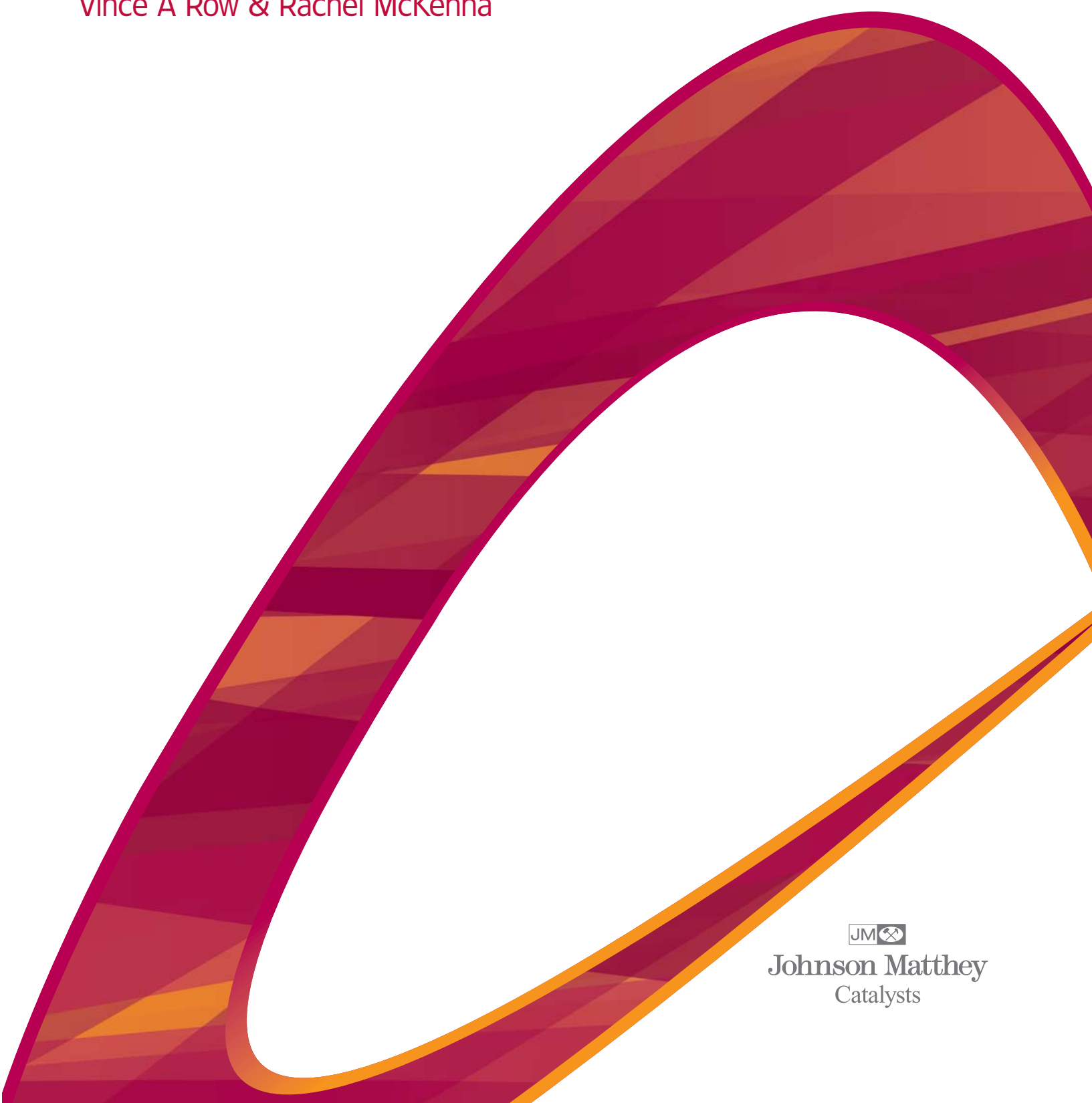


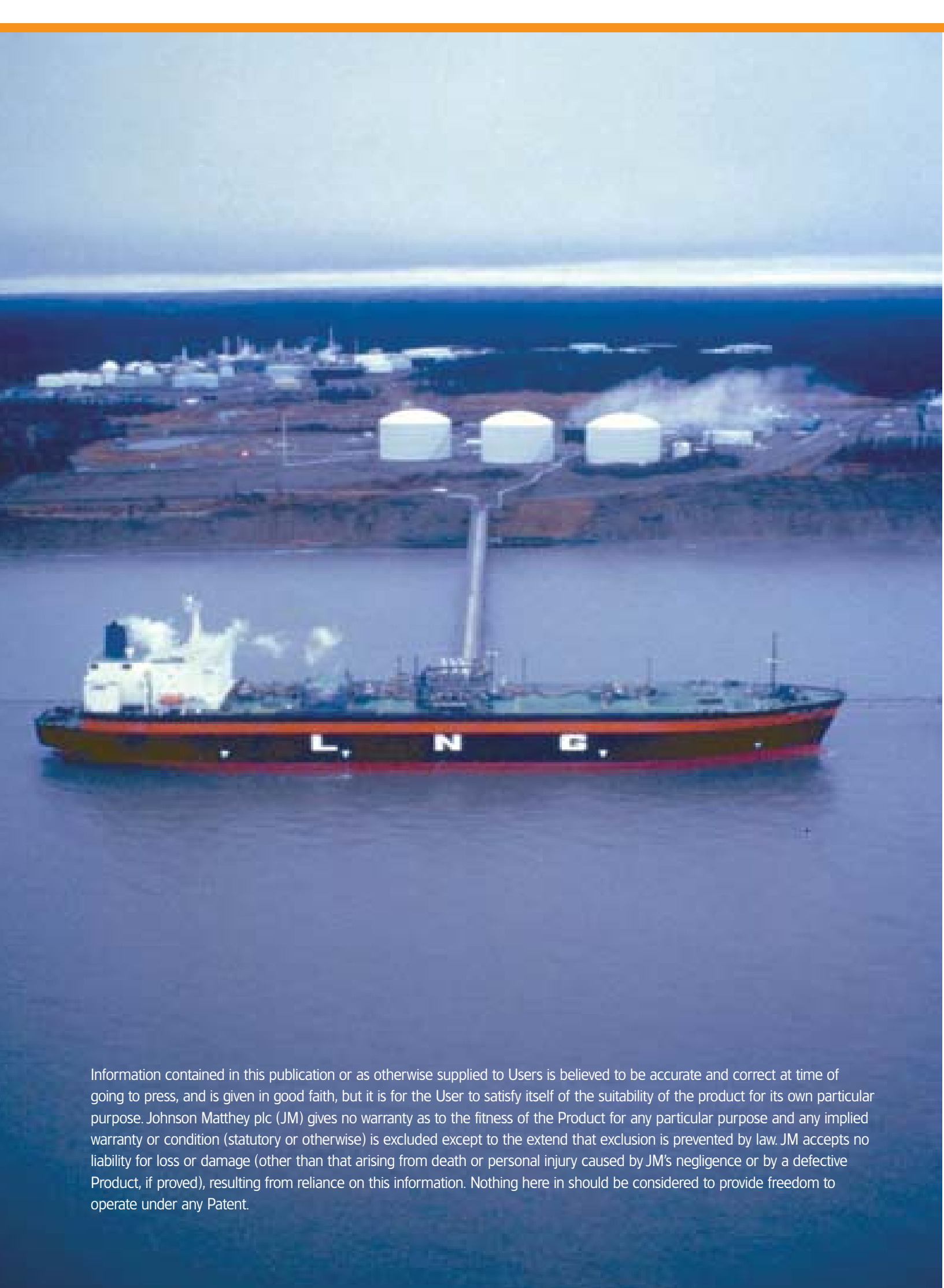


A re-think of the mercury removal problem for LNG plants

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Abstract

Following the mercury induced catastrophic failure of a heat exchanger at Skikda in 1957, the LNG industry had to move quickly to install mercury removal units (MRUs) prior to liquefaction. At that time, the choice of absorbent was limited and MRUs had to be installed at the final stage of purification immediately prior to the cold box. This was not the best arrangement. By not treating the raw gas, mercury was left in co-produced NGLs and might also be released to the atmosphere during processing. Commissioning of new beds lengthened start up and the choice of location added to compression costs.

The arrival of new high activity mercury absorbents has allowed the re-thinking of the purification process. The MRU can now be located at the front of the plant to treat the raw gas thus avoiding mercury in NGLs or in emissions. The high activity allows smaller beds to be used and the use of radial flow reactors allows significant savings in compression costs over the traditional axial flow design. The new absorbents can be recycled through an audited disposal route.

This paper draws on data from actual operating MRUs to suggest how the design of LNG plants could be improved.

Introduction

Almost all hydrocarbons contain mercury. In the case of natural gas and natural gas liquids it is likely to be present as elemental mercury. In the case of crude oil it may also be present as organo-metallic and ionic mercury.

The concentration of mercury in natural gas varies widely from 450 to 5000 $\mu\text{g}/\text{Nm}^3$ in some fields in North Germany ^[1] to less than 0.01 $\mu\text{g}/\text{Nm}^3$ in some parts of the US and Africa. Reported levels of mercury found in some well known gas fields are given in Table 1

Mercury has a high boiling point (356.7°C) but has a high vapour pressure at ambient temperature and is surprisingly mobile.

Although the levels of mercury recorded are low, the tonnages of liquid hydrocarbons handled are enormous so downstream processing equipment is exposed to a substantial amount of mercury. Thus a typical 10,000 tes/day LNG plant would use 600 mmscfd of natural gas and if this contained 100 $\mu\text{g}/\text{Nm}^3$ mercury the plant would receive 582 kg mercury per year.

The main concerns are:

- Corrosion of process equipment.
- Exposure of workers to high levels of mercury during maintenance operations.
- Difficulty in disposal of mercury contaminated equipment.
- Emissions to the environment.
- Potential liabilities resulting from mercury contaminated product streams.

These can cause serious financial losses for the plant operator.

Table 1: Reported levels of mercury in specific gas fields.

Gas field	Amount ($\mu\text{g}/\text{Nm}^3$)
Groningen	180 - 200
Arun	250 - 300
Albatross & Askeland	1.0
Niger Delta	10
North & East Coast Trinidad	12
Goodwin, N Rankin & Perseus	38
Saih Nihayda & Saih Rawl	60

Mercury-induced corrosion

Two major types of mercury corrosion can be observed. These are amalgam corrosion and liquid metal embrittlement (LME). Amalgam induced corrosion is shown by any metal capable of forming an amalgam with mercury. Most metals owe protection from corrosion to the presence of an oxide layer. If this protective layer is damaged in the presence of liquid mercury, the metal can show its full reactivity and attack by air or water is rapid.

LME involves the diffusion of mercury into the grain boundaries and results in cracks developing along the grain boundary. This type of attack does not involve air or water and once initiated progresses rapidly. This type of corrosion affects a broad range of materials (aluminium alloys, copper based alloys eg Monel 400 and some types of steel eg 316 L). Figure 1 is a photomicrograph showing mercury embrittlement on a failed heat exchanger ^[2 & 3].

Corrosion is a particular concern for LNG plants and for this reason a mercury limit of $< 0.01 \mu\text{g}/\text{Nm}^3$ is set on the feed.

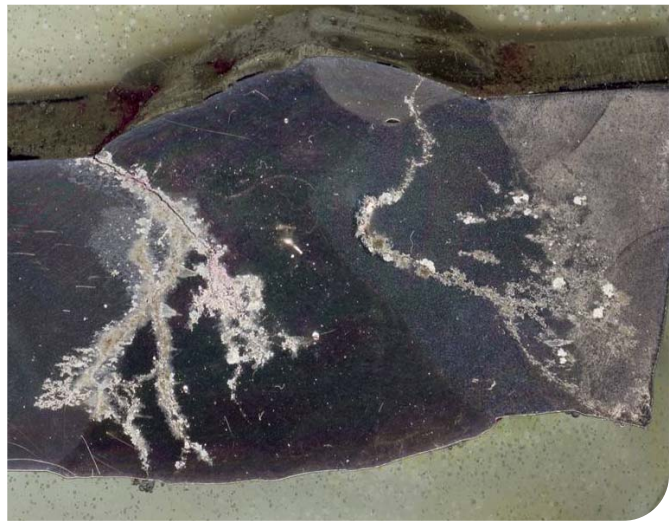


Figure 1: Liquid metal embrittlement failure on brazed aluminium heat exchanger

Health and safety issues

Mercury is a toxic metal and has a relatively high vapour pressure. Consequently, on opening mercury contaminated equipment, workers will be exposed to mercury vapour levels well in excess of the Threshold Limiting Value (TLV) and the Maximum Allowable Concentration (MAC). Suitable personal protective equipment is required during maintenance work. The European Union Scientific Committee on Occupational Exposure Limits proposes 0.02 mg/m³ as an 8-hour time-weighted average and 0.01 mg/l in blood as biological limit values ^[4].

Atmospheric measurements carried out during maintenance on the gas fields in northeast Netherlands have found localized levels of mercury as high as 1500 µg/Nm³ when cleaning tanks and filters ^[5].

Disposal of mercury contaminated pipe work

Because of the ease with which mercury bonds to metal surfaces, pipe work used to carry mercury containing gas becomes coated with mercury. In extreme cases a “mirror” surface is formed. This makes it harder to dispose of scrap steel. Tests have shown that

mercury can penetrate up to 1mm and many smelters set a limit of 2 mg/kg for scrap steel to avoid damage to the off-gas clean-up filters. Table 2 gives the levels of mercury found on a sample of contaminated steel from a failed reactor ^[6].

Table 2: Mercury content near surface of a failed steel reactor.

Depth (mm)	Concentration (µg/g)
Surface to 0.3	0.8
0.3 to 0.4	0.2
0.4 to 0.5	0.1

Emissions to the environment

Most of the operational concerns about mercury are focussed on the problems it causes for the hydrocarbon product streams. However, the surprisingly high volatility of mercury means that it is released to the atmosphere during the processing stages. Thus, up to half of the mercury present in the raw gas is likely to be removed on the acid gas removal and drying stages. Acid gas removal stripper gas is released to the atmosphere either directly or via an incinerator. Molecular sieve regeneration gas is usually added to the fuel gas.

EU Directive 2000/76/EC sets the air emission limiting value for incineration plants of 0.05 mg/m^3 , as an average value over a minimum period of 30 minutes and a maximum of 8 hours. There is a risk that fuel gas derived from molecular sieve regeneration gas may exceed this limit.

TEG and MEG flash gas and regeneration gas is released to the atmosphere. All of these releases are from low level stacks and studies have shown that there is an accumulation of mercury in fauna and flora adjacent to the plants processing mercury containing gas ^[7].

Mercury in product streams

There are increasing concerns about the presence of mercury in the feedstocks supplied to petrochemical plants (LPG and naphtha). Here the worries are not only for corrosion of cryogenic equipment but also the poisoning of precious metal catalysts. Many users are setting limits of < 1ppb.

A further complication is the risk of contamination during shipment. This can easily happen if the same vessel is used for shipments of clean and mercury containing product. Mercury is only slowly removed from contaminated pipework.

Location of MRU

There are three possible locations for the MRU. These are shown in Figure 2 and are after the molecular sieve driers (C), before the molecular sieve driers (B) and before the acid gas removal (A).

Undoubtedly the easiest duty is after the molecular sieve driers as the gas is cleanest and the rate lowest. However, there are concerns about this location. Mercury will have contaminated all of the upstream plant equipment and mercury will be released to the atmosphere. Plant measurements have found up to 30,000 ng/m³ in the acid gas removal stripper gas. In the case of molecular sieves, mercury is released throughout the regeneration cycle with peaks of up to 60,000 ng/m³ [7]. Acid gas removal stripper gas is likely to be vented locally. Molecular sieve regeneration gas will enter the fuel gas system but the water removed together with entrained mercury

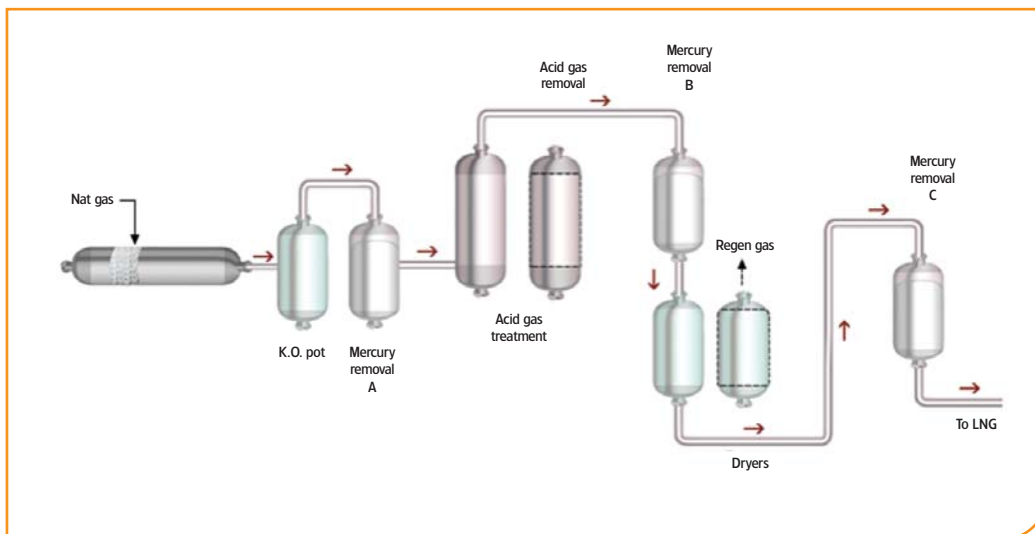
will go to drain. Flash gas and stripper gas from MEG and TEG dryers is likely to be vented locally.

It is possible to use small mercury removal units to treat some of the emissions [8].

Location upstream of the driers will reduce some of the mercury emissions and avoids any delays to start up. However, this location will carry the risk of fouling by carryover.

Treatment of the raw gas is undoubtedly the preferred location. This avoids emissions of mercury to the atmosphere and contamination of plant equipment. This will ensure any NGLs produced are free from mercury. However, this location is more of a challenge for the mercury removal absorbent.

Figure 2: Possible locations for MRU.



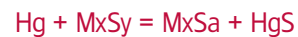
Choice of absorbent

Traditionally mercury has been removed using sulphur impregnated carbon. Typically this will contain 10 to 15% w/w sulphur and mercury is removed by reaction to form HgS. The reactivity with mercury depends on the allotrope of sulphur present on the carbon. This can vary from S⁸ down to S² with the lower allotropes having higher activity but these are the harder to form as they require higher impregnation temperatures ^[10]. There are other problems inherent with this type of absorbent.

- Sulphur Loss – sulphur is lost in service by sublimation and leaching by liquid hydrocarbons. LNG operators have found sulphur at the top of the bed of a discharged reactor to be as low as 3.7 to 4.2%. Whilst this is still enough to trap mercury there must be a concern as to where the sulphur has gone. Table 3 shows the solubility of sulphur in liquid hydrocarbons.
- Capillary condensation – the nature of the material and the method of manufacture give a high surface area support (typically 1000 m²/g with average pore size <20Å). This type of material is vulnerable to capillary condensation by C⁵⁺ hydrocarbons with aromatic compounds a particular concern ^[11].

- Start up delays – carbon based absorbents need to equilibrate with the process gas and can release sulphur during commissioning. This can delay introduction of feed gas to the cryogenic plant for up to three days. On a 10,000 tpd plant this is worth \$5.6 M in lost production.
- Disposal of spent absorbent – the material cannot be sent for landfill in most locations. It is difficult to free the spent absorbent from hydrocarbons and mercury can only be removed by a thermal process.
- Handling – the material is likely to contain dust and carries the risk of self heating.

Recognition of these problems has led to the development of inorganic based absorbents. These rely on the high reactivity of mercury with the metal sulphides of certain variable valency metal sulphides.



The reactive metal is incorporated in an inorganic support and the absorbent is supplied with reactive sulphide present or this is formed in situ by reaction with H₂S in the hydrocarbon to be treated

The “inorganic” approach has a number of advantages over the “sulphur impregnated carbon” approach:

- The spent mercury absorbent can be recycled through metal smelters. This is made possible by the use of a combination of metals with an inorganic support that is compatible with smelting processes.
- The materials can be used on wet and dry gases.

- The reactive species and the support have meso-porous structures with little affinity for hydrocarbons. There is little risk of capillary condensation even when used with gases at very high pressures (120+ bar) ^[12].
- There is no risk of sulphur migration by sublimation or dissolution.
- The absorbents can be used to process liquid hydrocarbons.

Johnson Matthey has taken this concept further by using in situ generation to allow the mercury absorbent to be generated from the H₂S present in the raw gas.

Table 3: Solubility of sulphur in liquid hydrocarbons

Hydrocarbon	Solubility (ppm)
Pentane	300
Heptane	500
Toluene	2500

Reactor design

Traditionally the mercury removal reactors have used axial flow designs. This allows for a simple design but as pressure drop is of some concern it can lead to large diameter vessels. Thus for a 50 m³ reactor the vessel diameter is likely to be 5 m. Increasing the diameter of the reactor results in thicker walls and restricts the number of suppliers. Accordingly Johnson Matthey has developed alternative designs. Radial flow reactors have a much lower pressure drop and are less susceptible to fouling. The vessels have more complex interiors but the vessel diameter is reduced. Contra-flow designs can be retrofitted into an existing axial flow design.

The savings possible in these designs are shown in Figure 4. The comparison has been made using the design conditions given in Table 4.

Self-heating is always a concern when handling carbons and metal sulphides. This is avoided by restricting exposure to air. Fortunately the reaction is slow to start and so is easily controlled.

If the MRU is upstream of the acid gas removal plant, then it is possible to use H₂S in the raw gas to form the metal sulphide in-situ. Thus making the charging operation a very simple process.

Disposal of spent material is a much more complex operation. The spent material can contain up to 15% w/w of mercury and current legislation is very prescriptive as to how this material can be disposed of. Further it is worth noting that proposed new legislation will impose tighter limits. Landfill is not allowed for mercury containing materials in most countries and the shipment of mercury containing waste has to follow a strict protocol.

Disposal of mercury-laden carbon requires thermal processing and leaves an unwanted residue.

In contrast, metal sulphides can be shipped for recycling. The spent material is collected in airtight metal drums and shipped to the smelter. Recycling may involve two stages.

Figure 3: Cut-away diagram of a radial flow reactor



Table 4: Design conditions for pressure drop comparison

Component	Mol %
N ₂	1.5
CO ₂	2.2
C1	85.1
C2	6.5
C3	3.0
C4	1.2
C5+	0.5
Total	100
Pressure	60 bara
Temperature	25°C

If the material has a very high mercury content then this is lowered by heating in an autoclave to give a residue suitable for transfer to the smelter. Materials with low levels of mercury can be fed direct to the smelter. These plants are designed to handle both mercury and sulphur and so allow a complete audit of the recycling route.

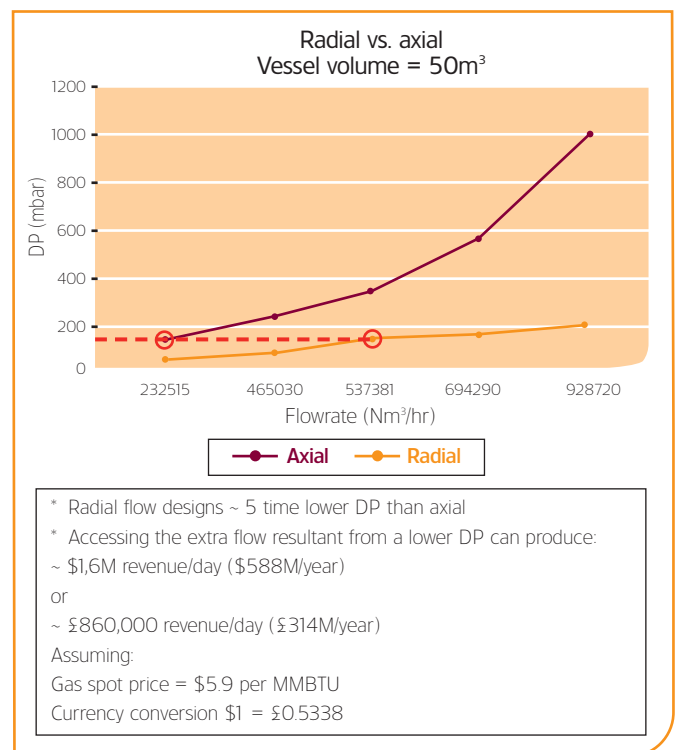
Johnson Matthey Catalysts is committed to the principles of Responsible Care and offers its **PURACARESM** programme to customers. The **PURACARE** programme guarantees users of Johnson Matthey Catalysts and absorbents quotations for disposal in an environmentally proper manner, by using a route in which the spent material is either re-processed for metals recovery or used as a secondary raw material. In solving such disposal problems in an environmentally safe way the **PURACARE** Programme provides the assurance that the user will continue to meet its environmental responsibilities in the face of growing legislative pressure on traditional methods of disposal. The cost of disposal will typically depend on the transportation cost to the nearest suitable treatment facility, the cost of treatment at the time of recovery and metal prices prevailing in the world market.

Some traditional reprocessing routes for spent catalysts such as landfill are now generally considered to be environmentally unsound. Using these facilities may therefore not be in the long-term interests of the operator even though they may be cheaper in the short-term. There is also an ever-increasing volume of environmental legislation that can make catalyst reprocessing a time consuming and daunting activity.

Features of the **PURACARE** include:

- complete commitment to recycling.
- no use of landfill or food chain related reprocessing routes.
- use of only facilities that are properly licensed and environmentally audited.
- provision of a certificate of consumption.

Figure 4: Affect of reactor design on pressure drop



All movements to the reprocessing plant are carried out under international legislation including trans-frontier shipments of hazardous waste. The material is imported into a plant that removes absorbed mercury before transfer of the absorbent itself to a final outlet that extracts the metals and recycles them into the industry.

Therefore all metals, including mercury and sulphur, are purified and returned into the chemical industry. All processes involved have been audited and trialled by Johnson Matthey Catalysts before offering to their customers for environmentally-friendly recycling of their spent mercury guard absorbents.

Conclusion

Development of new high activity mercury removal absorbents allows greater flexibility in the design of LNG plants. It is now possible to locate the MRU upstream of the main gas processing plant and thus avoid mercury emissions and contamination of any co-produced NGLs. The high activity allows for smaller beds, which coupled with new reactor designs, allows for savings in compression costs. The new absorbents can be recycled through metal smelters to give an auditable and environmentally acceptable route for disposal.

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