

# Advanced mercury removal technologies

**New technologies can cost-effectively treat 'wet' and 'dry' natural gas while protecting cryogenic equipment**

**N. ECKERSLEY**, UOP LLC, A Honeywell Company, Des Plaines, Illinois

**M**ercury is present in many of the world's natural gas fields. Process plants with brazed aluminum heat exchangers, including liquefied natural gas (LNG) facilities and nitrogen-rejection units, are particularly susceptible to corrosive attack by mercury. More awareness on the part of gas processors is necessary to assure better protection of their assets and to address environmental concerns by removing mercury. At present, mercury levels have increased from 30  $\mu\text{g}/\text{Nm}^3$  or 40  $\mu\text{g}/\text{Nm}^3$  to levels exceeding 1,000  $\mu\text{g}/\text{Nm}^3$  in the Pacific Rim.

## PROCESSING SOLUTIONS

In supplying purification solutions to the gas-processing industry, a number of approaches for mercury removal have been developed. Several process options using both regenerable and non-regenerable fixed-bed technologies are available. The protection of aluminum heat exchangers can be accomplished by using a layer of silver-containing molecular sieve inside the dehydration vessels. The active silver forms an amalgam with any mercury present, and its zeolitic substrate adsorbs moisture in the treated gas. This approach offers flexibility in being regenerable, as the mercury-containing gas is bypassed around any cryogenic equipment. If necessary, condensed mercury can be collected, and the mercury-entrained gas treated with a small non-regenerable guard bed.

Another approach uses non-regenerative metal sulfides to remove mercury from the raw gas upstream of the dryers and the amine unit. Utilizing larger vessels, this approach also protects the brazed-aluminum heat exchanger and ensures less mercury contamination in and around the process plant.

A comparison of mercury-removal processes will be described via several case histories that examine regenerative zeolitic and non-regenerable metal sulfide-based solutions. Plant-specific drivers for each approach will be discussed as well as the efficacy for each technology.

**Contaminants of concern.** Process systems designed to purify hydrocarbon feed streams are commonly used in the natural gas (NG) industry and are becoming increasingly important. Historically, NG components such as sulfur, carbon dioxide ( $\text{CO}_2$ ) and water ( $\text{H}_2\text{O}$ ) have been effectively removed by using regenerable molecular sieves, non-regenerable fixed-bed absorbents, membrane systems and amines.

Mercury is a naturally occurring element found in small but measurable concentrations in many oil and gas fields. This metal

is most frequently detected in its elemental form and is prevalent in NG processing and LNG facilities. Due to advances in detection systems, mercury can now be accurately measured down to nanogram levels in the case of gases and to parts per billion (ppb) levels in liquid hydrocarbons.

**Metal embrittlement issues.** Mercury, when present, can cause severe and catastrophic corrosion of aluminum heat exchangers, which are commonly used in gas-plant cryogenic systems. Deposition of liquid elemental mercury in heat exchangers can compromise their structural integrity. One mechanism is referred to as liquid-metal embrittlement (LME). LME has been responsible for a number of failures of aluminum heat exchangers over the past 40 years. LME can cause crack initiation and propagation within such equipment, particularly in the proximity of a weld.<sup>1</sup> Several examples of mercury causing equipment failure in gas processing facilities have been documented in North America, North Africa and, more recently, in Asia Pacific.<sup>2</sup> Understanding the effects associated with LME is particularly important as it is difficult to detect prior to failure.

To avoid potential equipment failure, tight limits have been placed on allowable mercury levels in NG passing through aluminum heat exchangers. The current typical level of mercury removal commonly required is 10 nanograms/ $\text{Nm}^3$  of NG passing to the cryogenic section of a processing plant. This specification can be achieved by using two types of mercury-removal technology, located immediately upstream of the cryogenic unit:

- Regenerable molecular sieve
- Non-regenerable absorbent
- Molecular sieve plus non-regenerable absorbent.

**Mercury removal process options.** These options meet the required mercury specifications and each offers operational advantages. The molecular sieve option relies on a portion of the dryer vessel containing a silver impregnated molecular sieve, which forms an amalgam with mercury. During the heating cycle of the drying vessel, the mercury is desorbed into a regeneration stream and bypassed around downstream cryogenic equipment.

Rather than removing mercury at a point immediately upstream of the cryogenic unit, some operators have opted to purify gas as it enters the plant. In this case, the heat-exchanger mercury specification can be met using a larger, fixed-bed mercury-removal absorbent to treat raw gas as it enters the facility.

A recent variation in using either a silver-impregnated molecular sieve or a non-regenerable absorbent now combines the two approaches. Installing a small vessel of non-regenerable absorbent to treat desorbed mercury from the molecular sieve unit permanently removes any mercury from the sales gas. Recognizing and understanding the drivers involved in the decision-making process when selecting the best available technology is the key and often varies markedly from plant to plant.

**Analysis and typical global levels.** Table 1 lists the results from a number of mercury surveys conducted over the years on a diverse range of product streams found in Asia-Pacific, Europe, North and South America, Middle East and Africa.

**Analyzing the NG feeds.** Mercury surveys were conducted using two different analysis systems:

- Cold vapor atomic fluorescence spectroscopy
- Atomic absorption spectroscopy with Zeeman correction.

The cold vapor atomic fluorescence spectroscopy is typically used to measure mercury in gases and the atomic absorption spectroscopy has been used to measure mercury in both gaseous and liquid streams. Accurately measuring mercury in the field presents a complex challenge and requires a significant degree of analytical understanding, including not only sample analysis but also sample collection. Metallic sample collection containers should be avoided when considering liquid samples since mercury will readily plate out on metal surfaces. Sample line conditioning is crucial, since mobile mercury will accumulate on the inner wall pipe-work. The presence of different mercury species and other chemical interference can also impact the measurements.

**Non-regenerable absorbent technology.** In addition to forming amalgams with several metals, mercury is very mobile and will adsorb onto pipeline surfaces and other equipment commonly found in gas processing plants. Mercury can then desorb back into gas streams, passing through contaminated pipelines, and prolonged periods can elapse between the installation of an upstream mercury removal unit (MRU) and the complete purging of a pipeline.<sup>3</sup>

MRUs have been developed to take advantage of the affinity that the contaminant has with certain surfaces. Both metallic and carbon-based sorbents have been developed to remove mercury from a variety of hydrocarbon feeds. Collectively, these systems can be termed “non-regenerable” as opposed to regenerable molecular sieves. Non-regenerable sorbents contain sulfur, present as metal sulfide in the case of metallic systems and impregnated sulfur in the case of carbon. Potassium iodide promoted activated carbon has also been used but is much less common in NG processing.

Although sulfur-promoted activated carbon MRUs have prevailed in gas processing plants, these units have recently been superseded by metal-sulfide systems, for several reasons. Sulfur-promoted carbon is only effective in treating dry gas. The extensive micro-porous nature of activated carbon means that capillary condensation is a problem when operating at or close to the dew point of a gas.<sup>4</sup>

Sulfur-promoted carbon is also prone to sulfur dissolution when exposed to “wet” gas streams. This leaching of sulfur off the carbon leads to sulfur slip from the MRU, potentially damaging downstream equipment and reducing useful mercury capacity. The presence of water in the gas to be treated has been shown

**TABLE 1. Reported elemental mercury levels detected in natural gas**

| Region         | Mercury concentration / $\mu\text{g}/\text{Nm}^3$ |
|----------------|---|
| North Africa   | 1–100   |
| North America  | 1–20  |
| South America  | 1–105   |
| Southeast Asia | 10–2,000  |
| Middle East    | 1–10  |
| Europe         | 1–50  |

Source and survey from UOP

to elongate the reaction zone (mass transfer zone) resulting in mercury slip over and above the required outlet specification. At the same time, more gas processors are requesting that mercury removal takes place either at the well head or close to the front of the gas plant, where the gas can be “wet.” **The objective is to prevent mercury migration to various locations within a gas plant and to avoid any subsequent partitioning into processed NG and condensate streams.**<sup>5</sup>

The handling of mercury-contaminated pipe-work, which is classified as hazardous waste must be considered in the context of existing occupational health guidelines. Although mercury has a high boiling point, it also has a relatively high vapor pressure. This combined with its inherent toxicity means that extreme caution is required when handling mercury contaminated pipe-work. The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned mercury vapor a threshold limit value (TLV) of  $0.025 \text{ mg}/\text{m}^3$  of air as a time-weighted average (TWA) for a normal 8-hour workday and a 40-hour workweek.<sup>6</sup> This TLV has itself halved since 1991, when the previous assigned level was  $0.05 \text{ mg}/\text{m}^3$ .

When “up-front” mercury removal is required on raw gas, the challenge becomes one of how to treat NG that is not necessarily “bone-dry.” In cases where a carbon-based MRU is positioned on raw moist gas, the effective utilization of the carbon is compromised. Co-adsorption of moisture into the micro-porous carbon substrate proceeds, leading to a decline in mercury removal. The length of the mass transfer zone of an adsorbent is an indication of the rate of reaction the adsorbent has with the target contaminant. As little as 3 wt% to 4 wt% water adsorbed onto the carbon MRU extends the mass transfer zone of the adsorbent by 12%.<sup>4</sup> In addition, since sulfur (S) is soluble in liquid hydrocarbons, the presence of liquid hydrocarbon in natural gas leads to dissolution of sulfur from the carbon. This loss of active sulfur diminishes mercury (Hg) removal capacity of the activated carbon, thus shortening the service life of the bed. The reaction between Hg and S is stoichiometrically 1:1 according to:



A 100% utilization of active S results in the removal of 1 mole of mercury for every mole of sulfur. Table 2 looks at the effects of entrained liquids on mercury adsorption capacity in an NG application using a sulfur-promoted activated carbon MRU. The achieved lifetime of the carbon MRU was half that of the estimated lifetime quoted by the supplier.

The degree of liquid adsorbed onto carbon during the life of the MRU is shown in terms of total wt% volatiles (200°C). Layer 1 represents carbon recovered from the inlet portion of the bed and layers 2, 3 and 4 represent subsequent layers. **Clearly,**

the carbon has co-adsorbed a significant quantity of liquid (20%–30%) from the raw NG causing its shortened service life. This is not surprising since activated carbon has long been used in hydrocarbon dew point control because it has a high affinity with  $C_{4+}$  in NG.

The total wt% of active sulfur was measured on each layer of discharged carbon. While sulfur levels on newly installed activated carbon are typically 10 wt% to 18 wt%, the levels on spent materials were measured at 6 wt% to 9 wt%. To measure the mercury removal efficiency of supplied carbon, the percentage of utilized sulfur was also measured on a molar basis. The percentage of sulfur utilized in the equilibrium section of the vessel (layers 1, 2 and 3) was measured at approximately 4 wt%. By comparison, on a dry NG without the attendant issues of liquid entrainment, this percentage utilization would be expected to be >10 wt%. The data confirms that sulfided carbon is prone to sulfur dissolution and micro-pore blocking when treating wet gas.

Apart from the basic requirement to ensure that adequate mercury removal can be achieved on gases at or close to their dew points, from the point of capital expenditure, it is important to ensure that MRU reactor volumes are minimized where possible. This is particularly important when positioning an MRU offshore where spatial constraints are critical. The contact times required by sulfided-carbon products often lead to a larger than practical MRU footprint. The drive to reduce capital budgets and avoid large volumes of spent material has led to gas processors examining technologies other than sulfided carbon.

After carbon is discharged from an MRU, it is usually sent to a specialized plant where mercury is reclaimed via vacuum distillation. There is no useful purpose for the remaining carbon and it undergoes high-temperature incineration.

**A better solution.** A range of non-regenerable absorbents has been developed to improve on existing MRU technologies. Gas streams containing thousands of micrograms of mercury can be successfully treated using advanced new absorbents. Instead of carbon, transition metal oxides and sulfides are utilized. The active component of the advanced absorbents is a metallic sulfide, and the products are supplied either in their oxide form and are sulfided in-situ by the gas to be treated or are supplied pre-sulfided.

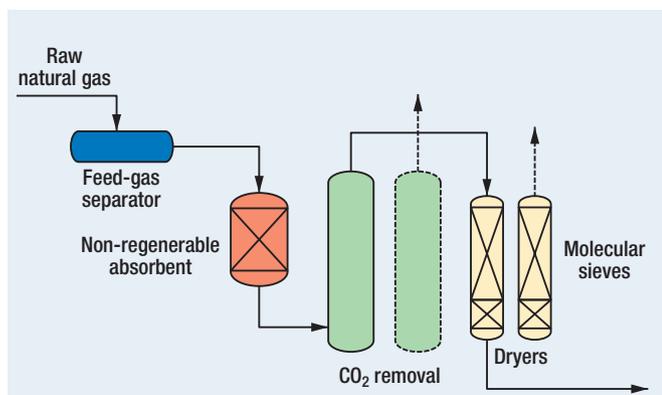
After their useful life, the discharged absorbents can have the mercury removed via vacuum distillation and sold into specialist applications for re-use. Since the remaining active metal is compatible with metal recycling programs, it is sent for recovery via a smelting process and then sold back onto the open market. This process ensures that the MRU product is handled in an environmentally friendly way.<sup>7</sup> The absorbents have been developed to treat wet and dry gases, without the same wet-gas limitations of other non-regenerable products. Fig. 1 shows a commonly suggested flow-scheme location for the advanced absorbent. This process product range is successfully treating liquid hydrocarbon streams in addition to gaseous fluids. Sulfur is anchored to the metallic substrate, preventing subsequent dissolution and slippage onto downstream equipment.

**Hg removal via regenerable molecular sieves.** Removing mercury using molecular sieve technology represents a novel and well-established approach in protecting cryogenic equipment. Using two different types of molecular sieve within the dehydration section of a gas plant, it is possible to ensure that the NG is dry and mercury-free prior to entering the cryogenic unit. Since the configuration and operating procedure of the dryers is unaffected by installing this two sieve system, ease of operation is assured. The silver-promoted molecular sieve, designed to remove mercury in addition to water, is capable of passing through thousands of regeneration cycles over the course of a long service life. Contaminant removal proceeds via temperature swing adsorption, with mercury forming a silver amalgam across the molecular sieve structure and then desorbing when hot gas is passed through the dehydration vessel. The mercury-containing regeneration gas is safely bypassed around the cryogenic unit.

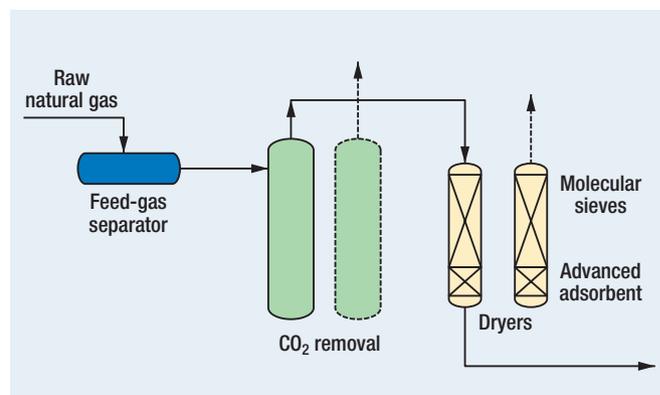
Removing mercury using silver-promoted molecular sieve in existing dehydration vessels ensures that capital expenditure is

**TABLE 2. Impact of liquids on mercury removal using activated carbon in the gas phase**

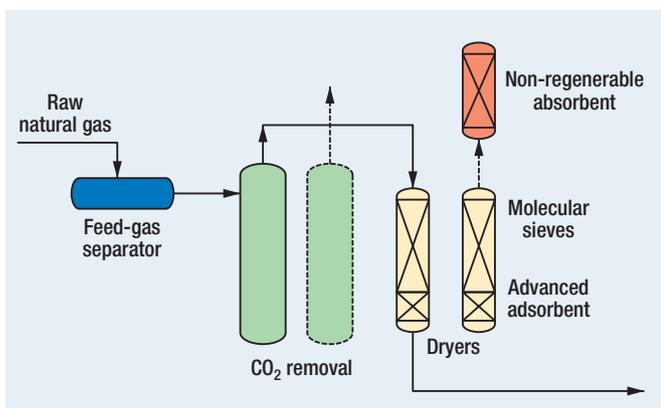
| Bed position | Total volatiles, (200°C) wt% | Total S, wt% (dry basis) | Total Hg, wt% (dry basis) | Hg/S weight basis | Hg/S molar basis | Sulfur utilization % |
|--------------|------------------------------|--------------------------|---------------------------|-------------------|------------------|----------------------|
| Layer 1      | 21.1                         | 7.02                     | 1.89                      | 0.27              | 0.0429           | 4.29                 |
| Layer 2      | 21.0                         | 6.57                     | 1.71                      | 0.26              | 0.0414           | 4.14                 |
| Layer 3      | 26.8                         | 8.32                     | 2.12                      | 0.25              | 0.0406           | 4.06                 |
| Layer 4      | 24.4                         | 7.97                     | 0.29                      | 0.04              | 0.0057           | 0.57                 |



**FIG. 1** A flow scheme for treating wet gas up-stream of process equipment using advanced absorbents.



**FIG. 2** A flow scheme for removal of mercury using regenerable silver-promoted molecular sieves.



**FIG. 3** A flow scheme for the combined removal of mercury utilizing both regenerable molecular sieves and non-regenerable adsorbents.

reduced to a minimum without the need for an additional MRU. Due to smaller quantities of the silver-promoted molecular sieve adsorbent required, plants adopting this technology can load and re-load the adsorbent quickly without any associated increase in system pressure drop. Fig. 2 represents a typical flow scheme for the silver-promoted molecular sieve adsorbents. Spent and properly regenerated adsorbent is mercury-free upon reactor discharge and since it passes the EPA Toxicity Characteristic Leaching Procedure (TCLP) test, it is classified as non-hazardous waste for disposal purposes.<sup>8</sup>

To ensure the removal of mercury from sales gas and to protect plant cryogenic equipment, some gas plant operators have taken mercury removal with silver-promoted molecular sieves one step further. By installing a vessel of advanced non-regenerable mercury adsorbent on the regeneration stream from the molecular sieve drying unit, mercury is effectively removed and captured. Fig. 3 represents a combined approach toward mercury removal using both advanced molecular sieve and adsorbent technologies. Since the regeneration gas stream has a low flowrate (typically 10% of the inlet gas), the volume of the vessel containing the non-regenerable adsorbent is small. This results in a cost-effective way of removing mercury, without the high capital expenditure associated with installing a larger adsorbent vessel upstream.

Clearly, there are several ways to remove mercury from NG processing plants. Capital expenditure limitations, equipment protection requirements and environmental factors must all be considered. Both non-regenerable adsorbents and molecular sieve technology can be used to handle a very broad range of mercury levels and process scenarios.

## CASE STUDIES

These case studies illustrate factors involved when selecting a mercury-removal system that is most applicable for a given processing situation:

**Case 1: PTT Thailand.** The PTT GSP-5 gas plant located at Map Ta Phut, Rayong, Thailand, was commissioned and started up in 2004. The onshore facility processes raw gas via a pipeline from offshore gas fields in the Gulf of Thailand. The raw gas entering GSP-5 is conditioned to remove CO<sub>2</sub>, H<sub>2</sub>O and Hg, and the total gas flow treated is 530 MMscfd. The MRU is designed to protect a natural gas liquids (NGLs) recovery plant, incorporating a cryogenic unit that includes a brazed aluminum heat exchanger.



**FIG. 4** Parallel fixed-bed reactors using advanced adsorbents at the PTT GSP-5 gas plant, Map Ta Phut, Rayong, Thailand.

**TABLE 3. PTT GSP-5 MRU process conditions**

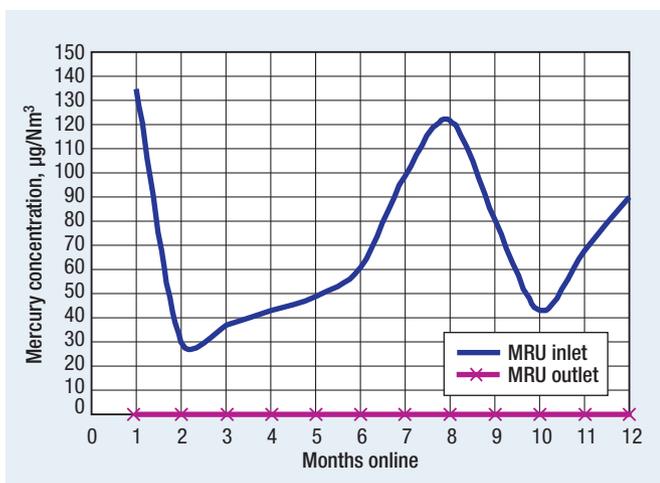
|   |             |
|---|-------------|
| Gas treated                                   | Natural gas |
| Gas flowrate, MMscfd                          | 265         |
| Operating pressure, Kg/cm <sup>2</sup>        | 48          |
| Operating temperature, °C                     | 18          |
| Hg influent range, µg/Nm <sup>3</sup>         | 50–200      |
| Hg effluent specification, µg/Nm <sup>3</sup> | < 0.01      |

The initial charge of mercury-removal adsorbent used from plant startup was sulfur impregnated activated carbon.

The gas plant MRU configuration consists of two parallel reactors, each designed to process 265 MMscfd of gas. The MRU is located upstream of the amine plant and the dryers, and is positioned to treat raw gas as it enters the facility. Historically, the gas entering the MRU contained some liquid hydrocarbon with a triethylene glycol carry-over component. The initial charge of activated carbon experienced a premature mercury breakthrough after two years in service. Table 3 provides a summary of the MRU process conditions. After the activated carbon was discharged from the reactors, the MRU was refilled with the non-regenerable advanced adsorbent. Fig. 4 shows the new installation with the parallel flow reactors at GSP-5.

Since the change-over was commissioned, the plant has continuously recorded effluent mercury levels below the required specification and maintained the start-of-run pressure drop, which was a priority for the customer. This successful performance has been achieved despite treating a liquid-entrained, water-saturated natural gas. Fig. 5 details the actual mercury influent and effluent levels at the GSP-5 facility in the first year following the startup of the new MRU. Despite fluctuating mercury inlet levels, the new adsorbent continues to meet desired effluent specifications.

**Case 2: Gasco Abu Dhabi.** The original Adnoc (now Gasco) Habshan gas plant, located in Abu Dhabi, was built in 1983 to process Thamama gas from the nearby Bab and Asab fields. Following the completion of two major development projects (OGD-1 in 1996 and OGD-II in 2001), the plant now



**FIG. 5** Mercury influent and effluent levels at the PTT GSP-5 gas plant with the new advanced absorbent system.

includes eight gas processing trains with the capacity to process 3.5 Bscfd of non-associated and associated gas. In addition to network gas, the Habshan facility produces NGLs, condensate and liquid sulfur.

The OGD-1 expansion raised output at Habshan from 450 MMscfd to 1,865 MMscfd. Three new trains were developed: two 350-MMscfd trains for the treatment of non-associated and associated gas (T1 and T2) and one 625-MMscfd train for the treatment of non-associated gas (T3). In addition, condensate recovery was raised from 5,000 bpd to 131,000 bpd. Raw gas entering OGD-1 is currently conditioned to remove CO<sub>2</sub>, hydrogen sulfide (H<sub>2</sub>S), H<sub>2</sub>O and Hg.

From plant startup in 1996, the OGD-1 gas processing trains have used molecular sieve adsorbents. In 1998 following a study effort together with Gasco, a layer of silver-promoted molecular sieve adsorbent was incorporated into each drying vessel as a retrofit solution to ensure that the gas passing to downstream cryogenic equipment was mercury free. The combination of dehydration-grade molecular sieves and advanced silver-promoted molecular sieve adsorbent products has demonstrated excellent operating performance in each of the three OGD-1 trains. Each train has successfully used silver-promoted molecular sieve adsorbent in up to six-year lifetime cycles, to reduce a design inlet mercury level of 200 ng/Nm<sup>3</sup>–250 ng/Nm<sup>3</sup> down to a cold box specification of < 10 ng/Nm<sup>3</sup>.

**Case 3: Enterprise US.** The Enterprise Meeker I gas plant, located in Colorado's Piceance Basin, started up in 2007 with an initial gas processing capacity of 750 MMscfd, incorporating 35,000 bpd of NGLs. A Phase II expansion in the form of sister plant, Meeker II, started up in 2008 and doubled processing to 1.5 Bscfd of gas and 70,000 bpd of produced NGLs.

Both Meeker I and Meeker II condition raw gas to remove CO<sub>2</sub> using amines and remove water and mercury using molecular sieve technology. Dehydration-grade molecular sieves and silver-promoted molecular sieves are utilized in the drying vessels to remove water and mercury from the raw gas prior to the treated gas passing to the cryogenic system. In addition, an advanced absorbent is used to remove mercury from the molecular-sieve

**TABLE 4. Enterprise Meeker I and II**

|  |             |
|--|-------------|
| Gas treated  | Natural gas |
| Gas flowrate to mol sieve vessels, MMscfd                          | 750         |
| Absorbent operating temperature, °C                                | 30–40       |
| Absorbent operating pressure, kg/cm <sup>2</sup>                   | 70          |
| Raw gas Hg concentration to HgSIV 1, ng/Nm <sup>3</sup>            | Up to 800   |
| Regeneration gas Hg concentration to absorbent, ng/Nm <sup>3</sup> | Up to 2,000 |
| Effluent Hg concentration from absorbent, ng/Nm <sup>3</sup>       | < 10        |

regeneration stream. The molecular sieve dryers are configured such that two vessels are in adsorption mode and one vessel is in regeneration mode at any given time. Each molecular sieve vessel processes 375 MMscfd of feed gas. Table 4 provides a summary of the mercury removal process conditions for the combination system at Enterprise Meeker I and II.

**Summary.** If mercury is allowed to reside in an NG plant unchecked, it can cause severe damage to process equipment and potentially compromise the health and safety of plant operators. Two distinctive technologies have been developed to remove mercury from various locations within a gas plant. Each technology affords maximum mercury removal and protection and includes within it a number of non-regenerable and regenerable fixed-bed solutions. The well-established silver-impregnated molecular-sieve technology ensures that the cryogenic component of a gas plant is protected against potential mercury ingress. Applying such systems can provide cost-effective (lower capital cost) options with longer service life. The latest non-regenerable products offer the option to remove mercury from raw gas as it enters the plant. Alternatively, desorbed mercury can be removed from the molecular sieve regeneration gas using a small cost-effective fixed bed. **HP**

#### ACKNOWLEDGMENT

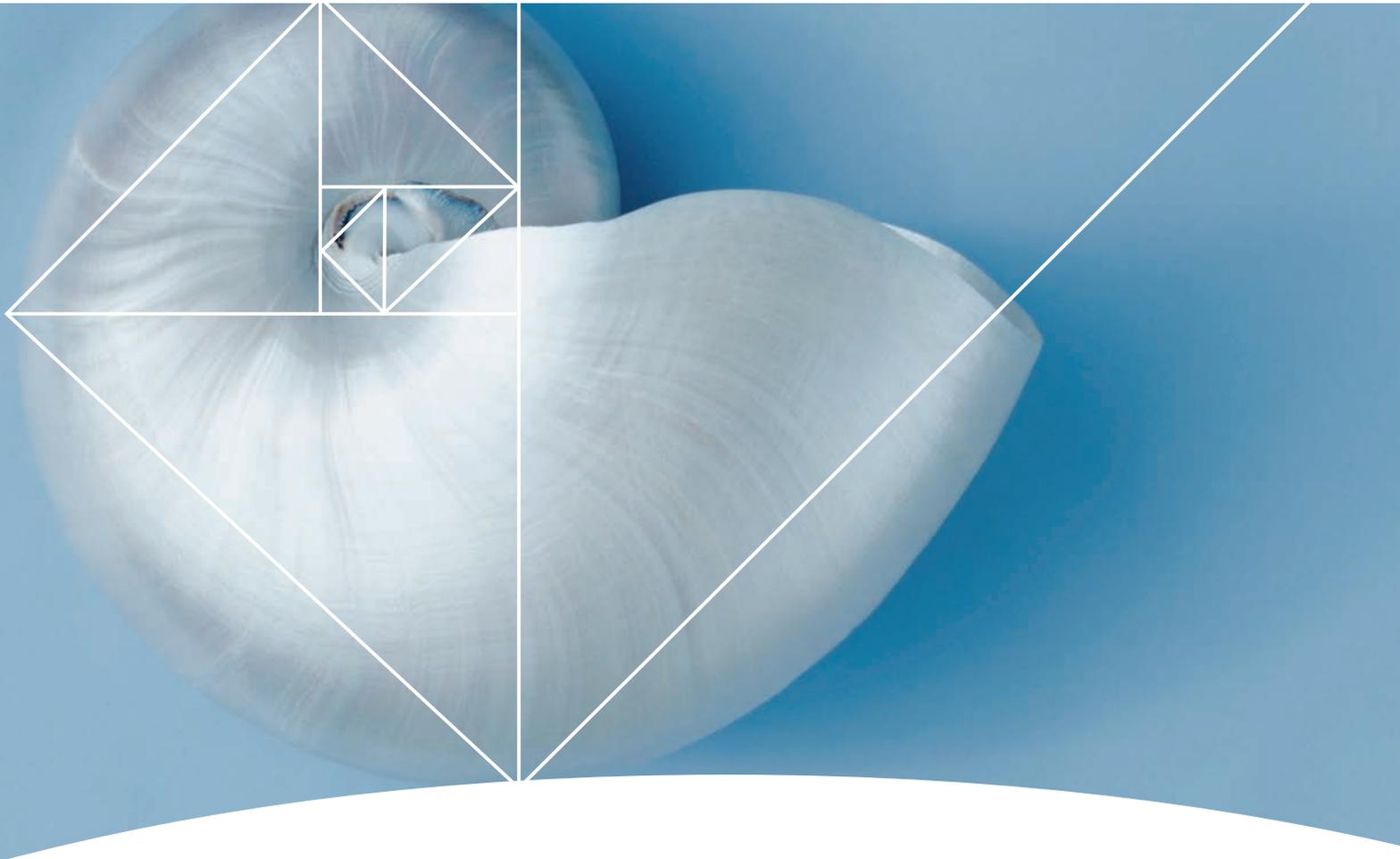
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**Neil Eckersley** is the UOP business manager for Aluminas and Specialties responsible for its complete portfolio of alumina-based solutions including mercury and sulfur removal products. He graduated from Sheffield Hallam University in the United Kingdom with a BS degree in chemistry and has worked in the areas of Research, Technical Service, Sales and Product Management.

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