MERCURY REMOVAL FROM NATURAL GAS AND LIQUID STREAMS

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ABSTRACT

Mercury is often present in natural gas, petrochemical and some refinery feed streams. While difficult to measure, UOP has made recent advances in low level mercury analysis, which aid in the detection of mercury in these hydrocarbon streams. Mercury is known to damage aluminum heat exchangers to the point of catastrophic failure and therefore its removal is desired. UOP™ HgSIV™ regenerative mercury removal adsorbents not only dry these streams but also remove mercury to less than 0.01 micrograms per normal cubic meter. Since the sorption sites for mercury removal are separate from and additive to the dehydration sites, mercury removal is accomplished by replacing a portion of the dehydration grade molecular sieve with HgSIV adsorbents. The dryer bed size does not have to be increased to remove both water and mercury. Hydrocarbon process stream dryers containing HgSIV adsorbents have the same performance life as typical molecular sieve dryers.

Mercury is completely removed from HgSIV adsorbents at conventional dryer regeneration temperatures. Properly regenerated HgSIV adsorbents can be disposed of as non-hazardous waste. Mercury can be removed from the regeneration gas by condensation when the mercury level in the feed gas is high. Treatment of the HgSIV spent regeneration gas is usually not needed for low to moderate mercury feed gas levels. This paper also discusses process solutions for removal of mercury from HgSIV adsorbent dryer spent regeneration gas.

BACKGROUND

Mercury is present in nature and is also present in most natural gas streams to varying levels. In UOP's recent analytical experience the levels in natural gas have ranged from less than detectable to 120 $\mu g/Nm^3$ of gas.

The primary reason for removing mercury from natural gas is to protect downstream aluminum heat exchangers, such as those used in cryogenic hydrocarbon recovery natural gas plants and in natural gas liquefaction plants. Mercury has caused numerous aluminum exchanger failures. It amalgamates with aluminum, resulting in a mechanical failure and gas leakage. Since the level of mercury that can be tolerated is not established, most operators want to remove it "all." That is, remove it to a level where it can not be detected with the available analytical capability. Currently, this means reducing the mercury to less than 0.01 $\mu g/Nm^3$, which corresponds to about 1 ppt by volume.

Another reason for removing mercury is to produce mercury-free product streams. If ethane or propane is used as feed for an ethylene plant, the mercury needs to be removed to prevent heat exchanger and catalyst deactivation problems in the ethylene plant.

Mercury in natural gas is present predominantly as elemental mercury. However, in theory, the mercury could be present in other forms: inorganic (such as $HgCl_2$), organic (such as CH_3HgCH_3, $C_2H_5HgC_2H_5$) and organo-ionic (such as $ClHgCH_3$) compounds. UOP has acquired the analytical capability to analyze liquid samples, such as naphthas and natural gas condensates, and has developed a method to differentiate between the various species. Some amounts of these other types have been found.

Precise information still does not exist on how mercury distributes when a liquid stream, such as a natural gas condensate, is fractionated. We did have the opportunity to learn the following at one natural gas plant: We measured the natural gas from the plant inlet separator, and then we analyzed the liquid. Since the separator was at pressure and the mercury analysis was done at atmospheric conditions, a portion of the liquid flashed during sampling. By developing appropriate techniques we were able to analyze both the remaining liquid and the flashed gas which was predominately C_2-C_5 hydrocarbons:

	ppb wt.	**$\mu g/Nm^3$**
Gas from Separator	4.1	3.5
Flash Gas	9.0	
Liquid	3.0	

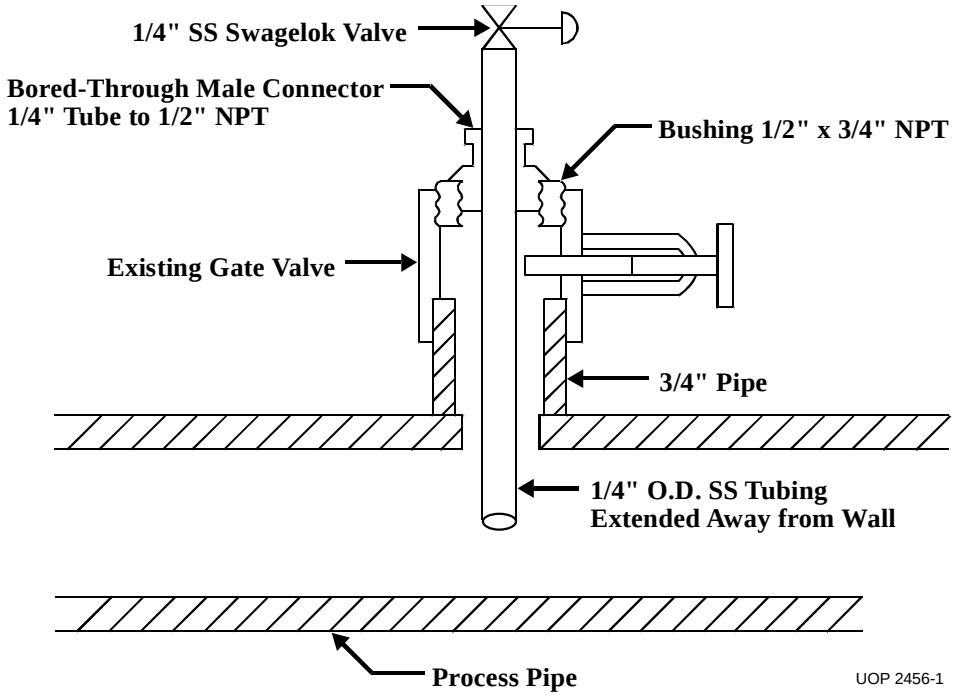
Thus, most of the mercury will be present in the LPG stream and a lesser amount will remain in the C_5^+ portion.

ANALYTICAL AND SAMPLING

With the level of mercury being so low, getting accurate analyses requires the utmost care. Ideally, getting a representative sample from a process line requires a special sample probe, as shown in Figure 1. Even a small amount of solids present in the sampling system will affect the readings for a very long time.

Figure 1

Sample Point Configuration for Hg Analysis



A number of analyzers are available. All of these analyzers utilize a gold surface trap to concentrate the mercury from the sample stream. The traps are then thermally desorbed, and the mercury pulse is swept into the analyzer, where the detector quantifies the amount of mercury. The best technology to analyze low levels of mercury is cold vapor atomic fluorescence spectroscopy (CVAFS) but its size has historically limited its use to the laboratory.

Recently, UOP purchased a new analyzer which brings this CVAFS technology to the field. As with other analyses for mercury, sample technique is critical and has been optimized through

practice in hydrocarbon gas streams. Now, UOP can consistently measure mercury concentrations down to the detectable level of 0.01 μg/Nm^3 at the plant site. The benefit to the gas processor is that each sample can now be gathered and analyzed within hours, not days or even longer as with an off-site facility. Before the analytical team departs, the level of mercury in a treated or untreated stream has been quantified. This information can determine whether streams need to be treated for mercury or to confirm that an existing mercury removal system is functioning as designed.

UOP HgSIV Adsorbents

HgSIV adsorbents were created for effective mercury removal in existing molecular sieve adsorption units. Since cryogenic plants need to have dry inlet streams, molecular sieve dryers already exist in most plants with natural gas liquid recovery. HgSIV adsorbents are molecular sieve products that contain silver on the outside surface of the molecular sieve pellet or bead. Mercury from the process fluid (either gas or liquid) amalgamates with the silver, and a mercury-free dry process fluid is obtained. Adding a layer of one of the HgSIV adsorbents to an existing dryer results in the removal of both the design water load and the mercury without requiring a larger dryer. Mercury and water are both regenerated from the HgSIV adsorbents using conventional gas dryer techniques.

Physically, HgSIV adsorbents have a similar appearance to conventional molecular sieves. They are available in a beaded or in a pelletized form. These HgSIV adsorbents are loaded into an adsorption vessel in the same way as are conventional molecular sieves. There is no need for special care, such as the use of nitrogen blanketing during the installation. For unloading, only the same precautions need to be taken as when unloading conventional molecular sieves.

The disposal requirements are also the same as for conventional molecular sieves, provided the material is properly regenerated prior to being unloaded. Analysis of fresh and used samples of HgSIV adsorbents have shown that they pass the EPA TCLP (Toxicity Characteristic Leaching Procedure) test, demonstrating these adsorbents can be safely disposed of by conventional methods.

Commercial Experience

Currently, UOP has installed HgSIV adsorbents in over 25 gas dryers and 7 liquid dryers. These units are located in the Far East, Middle East, Africa, South America and the United States. The performance of one specific natural gas dryer mercury removal unit is summarized in Table 1. Its feed gas mercury content ranged from 25 to 50 μg/Nm^3. Mercury levels in the dried natural gas were below detectable levels of 0.01 μg/Nm^3. The performance of a liquid dryer mercury

removal unit is shown in Table 2. In this unit, the mercury content of 2 ppbw in the feed liquid was reduced to a less than detectable level of below 0.02 ppbw.

Table 1

Natural Gas Purification

Feed Rate, MM SCFD	283
Temperature, °F	64
Pressure, psig	600
Inlet Impurity	
H_2O, lb/MM SCF	Saturated
Hg, $\mu g/Nm^3$	25 to 50
Product Gas Purity	
H_2O, ppmv	<0.1
Hg, $\mu g/Nm^3$	<0.01

Table 2

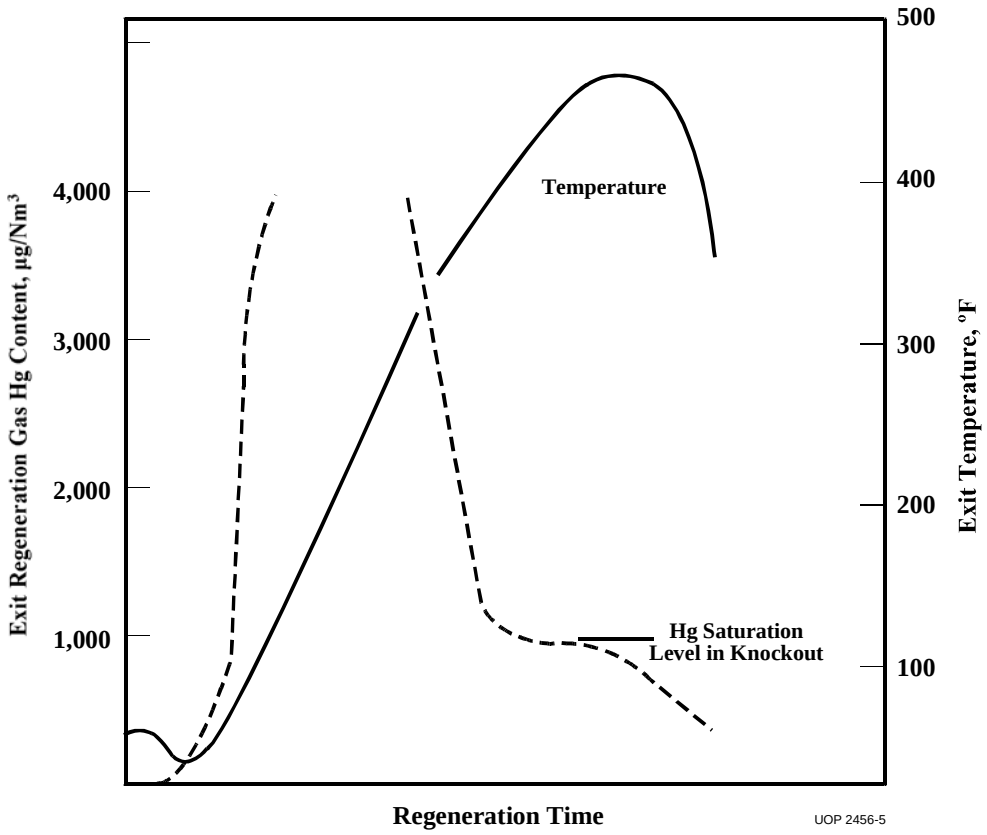
Natural Gas Liquids Purification

Feed Liquid	Natural Gas Liquids MW = 62 20°C 42 bar G H_2O Saturated Hg 2 ppbw (equivalent to 4 $\mu g/Nm^3$ in vaporized stream)
Product Liquid	H_2O less than 1.0 ppbw Hg less than 0.02 ppbw (equivalent to less than 0.04$\mu g/Nm^3$ in vaporized stream)

Regeneration temperature profiles for a natural gas dryer mercury removal unit operating with a high feed mercury content of about 40 $\mu g/Nm^3$ is shown in Figure 2. The mercury desorption profile is similar to a typical water regeneration profile, except that the mercury is completely removed from the HgSIV adsorbent well before the full regeneration temperature is reached. At the K/O drum conditions, the mercury saturation level was about 1100 $\mu g/Nm^3$. The mercury above that level was condensed and recovered as pure liquid mercury.

Figure 2

Hg Desorption Profile of a Natural Gas Dryer Using UOP HgSIV Adsorbent



PROCESS OPTIONS

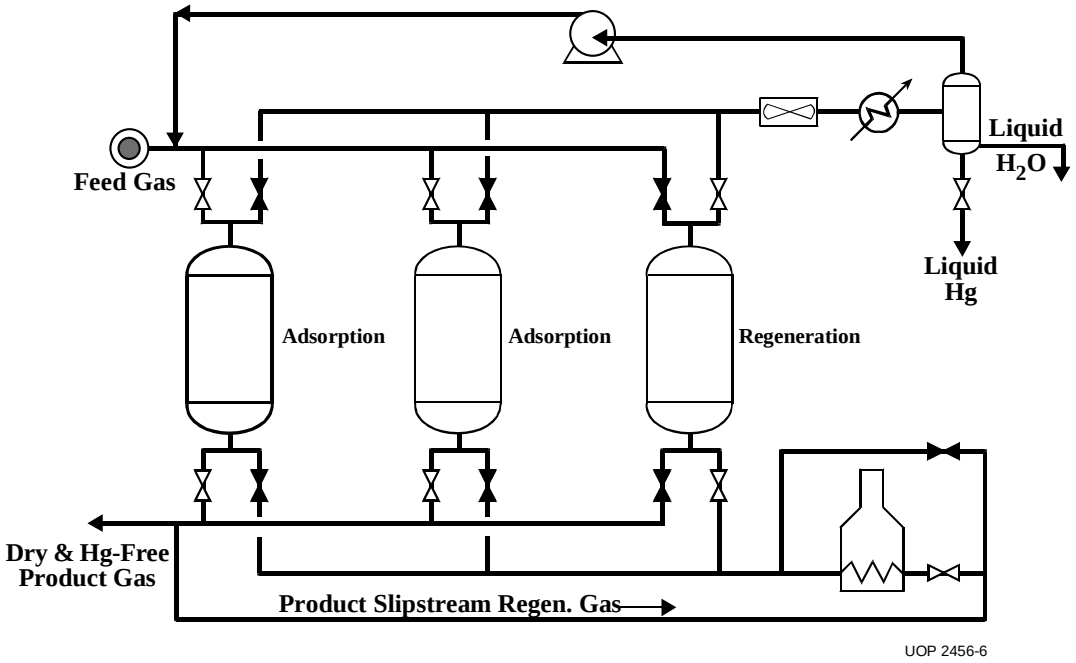
Because the readily available sorption sites are reactivated in each cycle, regenerative mercury removal with HgSIV adsorbents offer the best protection for downstream aluminum heat exchangers and other process units.

ADSORPTION

HgSIV adsorbents can be used in a stand-alone unit or in combination with bulk, non-regenerative mercury removal beds in the regeneration gas loop. The non-regenerative adsorbent beds are effective for bulk mercury removal, but often fail to provide complete mercury removal. A stand-alone UOP HgSIV process is shown in Figure 3. In this process option, mercury is removed from the feed stream, condensed in the regeneration knockout, and leaves the process as a separate liquid stream.

Figure 3

UOP Mercury Removal and Recovery System



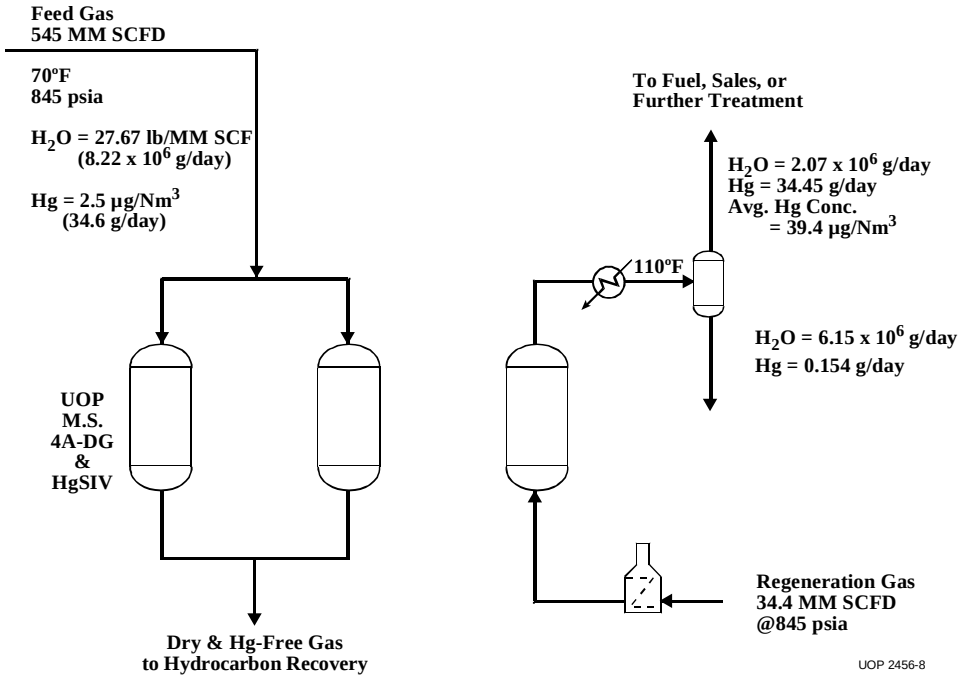
MATERIAL BALANCE

An expected mercury balance in a natural gas plant is shown in Figure 4. In drying and removing mercury from natural gas, little mercury goes with the regenerated and condensed water. Mercury has very little solubility in water at these conditions. Literature has shown that in an oxygen-free environment, the solubility of mercury in water is only about 25 ppbw. As shown in Figure 5, less than 0.5% of the inlet mercury goes with the condensed water. This fugitive mercury can be removed from the water condensed from the regeneration knockout using a non-regenerative proprietary adsorbent available from UOP. The liquid mercury decanted from the HgSIV adsorbent regeneration knockout is salable.

The balance of the mercury leaves with the spent regeneration gas. In this example of drying and purifying 545 MM SCFD of gas containing 2.5 $\mu g/Nm^3$ of mercury, this level represents only about 34.5 grams of mercury per day. The average concentration of mercury in the spent regeneration gas is about 39.4 $\mu g/Nm^3$. Often the spent regeneration gas is blended with the plant residue gas into the sales gas stream. This mixing reduces the mercury concentration to that approaching the plant inlet gas.

Figure 4

Hg Removal without Treatment of the Spent Regeneration Gas



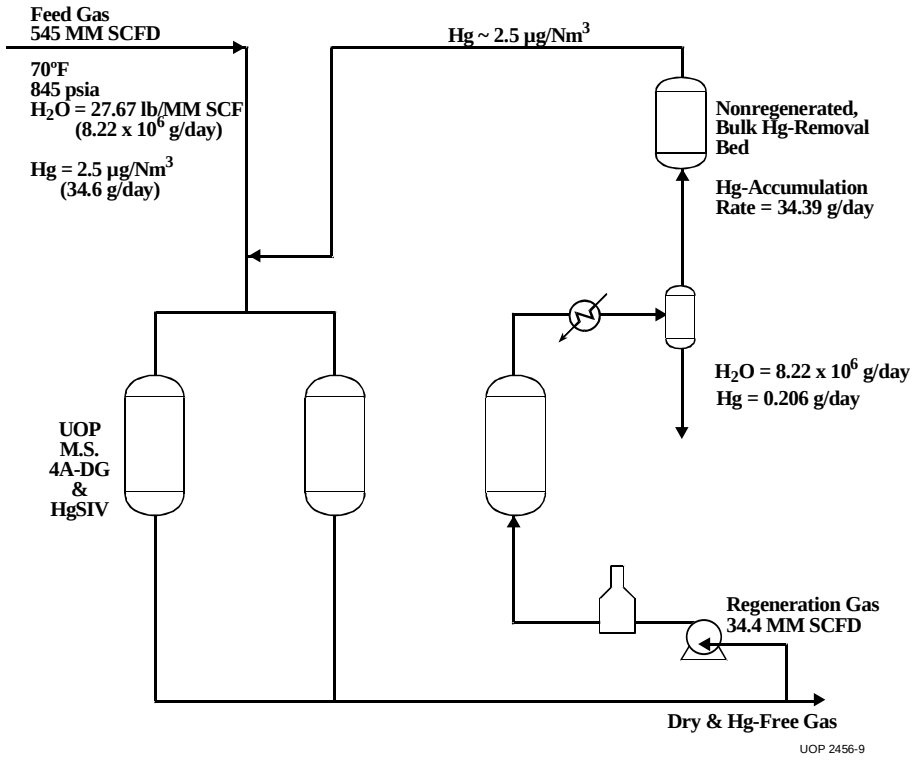
REGENERATION GAS TREATMENT

A number of techniques are available to protect the cryogenic portions of the plant, produce mercury-free LPG, and prevent any mercury from passing into the fuel system or into the sales gas line. These options incorporate the use of a small bed of non-regenerative mercury removal adsorbent. One such scheme is shown in Figure 5. Here, the spent regeneration gas, after being cooled and passed through a separator, is sent through a small bed of non-regenerative mercury removal adsorbent, such as sulfur-loaded activated carbon. Only a small bed is required for two reasons. The regeneration gas stream is much smaller in volume than the process stream. Also, only bulk removal of mercury is necessary. The mercury concentration does not need to be reduced below that of the feed gas. This means that worrying about containment of the mercury reaction zone in the non-regenerative mercury removal bed is not necessary. The sorption sites in the non-regenerative adsorbent can be loaded to higher breakthrough loading, minimizing associated replacement expenses.

While several technical options are available to remove mercury from the regeneration gas, to date not one of the natural gas companies treating for mercury have opted to remove the mercury from this stream.

Figure 5

Hg Removal with Treatment of the Spent Regeneration Gas



SUMMARY

In conclusion, adding HgSIV adsorbents to existing molecular sieve dryers can remove mercury to lower levels than non-regenerative adsorbents while also removing water. The capital expense and pressure drop increases associated with additional equipment are not required when adding HgSIV adsorbents to an existing molecular sieve drying process. The only additional out-of-pocket expense is the cost of the adsorbent itself. When the time comes, the spent HgSIV adsorbents are classified as non-hazardous for disposal purposes.