

OPTIMIZED MERCURY REMOVAL IN GAS PLANTS

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ABSTRACT

Mercury is present in many natural gas streams. While mercury levels can vary greatly, even low levels of mercury need to be removed to avoid damage to cryogenic aluminum heat exchangers and other plant equipment.

There are two types of mercury removal materials: non-regenerative sorbents and regenerative adsorbents. With non-regenerative types of mercury sorbents, the process fluid flows through the sorbent bed for a number of years, after which the sorbent is replaced. The mercury is removed from the process fluid and stays on the sorbent. The plus side of this approach is its simplicity. The down side is the installation cost, the additional pressure drop, and the disposal cost of the used sorbent.

Regenerative mercury removal is usually practiced simultaneously with another regenerative adsorption application such as drying. By replacing some of the drying adsorbent with a dual function water and mercury removal adsorbent, both water and mercury are removed in the dehydrator. The mercury, like the water, is regenerated off the adsorbent leaving with the spent regeneration gas. The plus side of this approach is no additional equipment cost, no additional pressure drop, and the possibility of recovering most of the mercury as a separate mercury stream. However, the mercury is not permanently held on the adsorbent and the spent regeneration gas may require some secondary mercury removal treatment.

This paper will evaluate and compare the various mercury removal technologies including the discussion of a case study where multiple technologies are used at one plant.

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INTRODUCTION

Mercury, being a naturally occurring element, is often a contaminant in natural gas. The amount of mercury can vary from one production area to another and from one gas well to another. Field analyses have shown that the concentration is not steady and may vary from day to day and even hour to hour. Generally, the level of mercury in natural gas is low, being only a few parts per billion. However, even these low levels of mercury will cause problems. Mercury will damage aluminum heat exchangers commonly used in LNG plants, cryogenic hydrocarbon recovery plants, and petrochemical plants. A number of production plants have experienced sudden heat exchanger failures resulting in unscheduled plant shutdowns, costly repairs, and even fires. Mercury can also concentrate and drop out as liquid in the colder sections of the plant where subsequent plant maintenance becomes difficult. In petrochemical plants, mercury can deactivate downstream catalyst. Mercury in the plant inlet gas has caused an ammonia production gas plant explosion.^[1]

Mercury concentrations in gas are typically expressed as micrograms per normal cubic meter ($\mu\text{g}/\text{Nm}^3$) or in nanograms per normal cubic meter (ng/Nm^3). These concentration expressions are compared with the common gas plant analysis expressions in Table I.

Table I – Comparison of Mercury Concentration Expressions in Gas

| $\mu\text{g}/\text{Nm}^3$ | ng/Nm^3 | Volume % | PPM | PPB | PPT |
|---------------------------|-------------------------|-----------------|-----------|-------|-----------|
| 9,000 | 9,000,000 | 0.000,1 | 1 | 1,000 | 1,000,000 |
| 900 | 900,000 | 0.000,01 | 0.1 | 100 | 100,000 |
| 90 | 90,000 | 0.000,001 | 0.01 | 10 | 10,000 |
| 9.0 | 9,000 | 0.000,000,1 | 0.001 | 1 | 1,000 |
| 0.90 | 900 | 0.000,000,01 | 0.000,1 | 0.1 | 100 |
| 0.090 | 90 | 0.000,000,001 | 0.000,01 | 0.01 | 10 |
| 0.0090 | 9 | 0.000,000,000,1 | 0.000,001 | 0.001 | 1 |

$\mu\text{g}/\text{Nm}^3$ – Micrograms ($1 \times 10^{-6}\text{g}$) of mercury vapor per cubic meter of gas @ 0°C and 1 atm
 ng/Nm^3 – Nanograms ($1 \times 10^{-9}\text{g}$) of mercury vapor per cubic meter of gas @ 0°C and 1 atm

To protect their heat exchangers, generally everyone wants the treated gas to contain as little mercury as possible. Since $10 \text{ ng}/\text{Nm}^3$ (corresponds to about one part per trillion by volume) of mercury is the lowest level that can be readily measured in the plant, it has become the target, but not because of process requirements.

How is Mercury Measured?

A number of analyzers are available that claim capability at these low concentrations. The mercury detection mechanism may involve such means as electron fluorescence, cold vapor atomic absorbance, atomic emissions spectra, or electrical resistance. None of these analyzers can directly measure the low levels of mercury present in natural gas, not even the levels of mercury present in the plant inlet gas. All of these analyzers rely on the principle of taking some gas from the process line, passing a sample gas stream through an analytical trap, and then desorbing the mercury from the trap as a concentrated pulse into the analyzer. Some of these analytical traps may consist of gold or silver gauze, or gold-coated inert particles such as silica or sand. The trap is desorbed by heat.

Numerous analyzers are on the market utilizing the above-mentioned detectors. They will all work well if used properly. The criticality is to get a representative sample from inside the process line to the analytical detector. This task is not easy because of the extremely low concentrations and because mercury can be present in ambient air. Well-designed gas sampling points on the process lines, proper in-plant sampling techniques, and careful laboratory sample handling techniques are essential for accurate determination of the plant mercury levels.

Types of Mercury Present in Gas and Natural Gas Liquids

The mercury that is present in natural gas is predominantly elemental mercury. Mercury can also exist as mercury compounds. Mercury can be part of an organic molecule, an inorganic molecule, or be part of both, commonly referred to as organo-ionic mercury. The presence of mercury compounds in natural gas has not been clearly established. In-plant analysis for trace levels of compounds such as dimethyl mercury (CH_3HgCH_3), diethyl mercury ($\text{C}_2\text{H}_5\text{HgC}_2\text{H}_5$), mercuric chloride (HgCl_2), or methyl mercuric chloride (CH_3HgCl) etc. does not currently exist. Very sophisticated laboratory techniques are needed to differentiate one type of mercury-containing molecule from another.

Analyses of various natural gas condensates have shown that a large portion of the total mercury present in some condensates can be present in the form of the various types of mercury compounds. Thus, it would be reasonable to expect that some mercury compounds could also be present in gases associated with those condensates. However, since mercury and mercury compounds are quite soluble in liquid hydrocarbons, the gas phase concentrations of mercury compounds may not be very high.

To date, there has not been a need to develop analytical capability for in-plant analyses of trace levels of mercury compounds, since only the elemental mercury is known to damage the heat exchangers. The mercury analyzers using previously mentioned mercury analytical detectors are marketed as elemental mercury analyzers. However, in actuality they most likely act as total mercury analyzers. An analytical study was conducted by Dumarey and others at the Institute of Nuclear Sciences in Gent, Belgium.^[2] They studied the mercury collection and desorption efficiency of various media used in analytical traps for measuring mercury in air. When using gold-coated sand, they reported essentially 100% efficiency in trapping elemental mercury and all of the mercury compounds previously mentioned. The analytical traps used with most current mercury analyzers utilize gold, and the traps should perform similarly in natural gas. Since the detectors will measure all mercury, the analytical result from the analyzer should represent the total mercury content of the gas. So, if the analyzer shows essentially no response to the sample, then it can reasonably be assumed that the process stream is essentially mercury-free.

Mercury Removal Methods in Gas Plants

All of the current methods for removing mercury from natural gas and hydrocarbon liquids use fixed beds of mercury removal materials. The gas, or liquid, flows through the fixed bed. The mercury reacts with the reactive reagent in the mercury removal material and stays in the vessel, while the effluent gas or liquid hydrocarbon is mercury-free. There are two types of mercury removal materials: non-regenerative mercury sorbents, and regenerative mercury adsorbents.

Non-Regenerative Mercury Removal

In non-regenerative mercury removal, the process fluid flows continuously through the bed of mercury sorbent for a number of years. When mercury is detected in the effluent, or when the pressure drop becomes excessive, the sorbent needs to be replaced. A number of different mercury removal sorbents are available with various tolerances to operating temperature, liquid hydrocarbons, and liquid

water. This operation is simple since no regeneration equipment and special valving is required. The mercury once sorbed stays on the sorbent and does not leave the adsorber. However, this method requires additional adsorption vessels and it adds to the pressure drop on the process stream. Also, the eventual disposal of the used sorbent can be expensive since the sorbent not only picks up the mercury, but it will often contain other hazardous material such as benzene and other hydrocarbons and may even accumulate some other trace hazardous materials that are not detected by feed gas analyses.

Types of Non-Regenerative Mercury Sorbents

These types of sorbents include:

1. Elemental sulfur dispersed within a porous carrier such as activated carbon granules or pellets^[3]

The elemental mercury reacts with the sulfur to form mercuric sulfide which stays in the sorbent. This type of product was the very first mercury removal product to be used in the natural gas industry when the Badak LNG plant started in the late '70s. The mercury removal bed was installed downstream of the molecular sieve gas dehydrator.

Currently, a number of manufacturers offer this type of product. The performance of the product depends on the quality of the activated carbon support and on the technique used to disperse the sulfur within the activated carbon particle. The activated carbon support has to have a high internal pore surface and the sulfur must be properly dispersed without causing any internal pore blockage. This maximizes the sulfur surface available to the mercury and retains the sulfur on the activated carbon, especially if the operating temperature is above ambient. If the sulfur is not properly dispersed, all of it will not be available to the mercury, resulting in poor mercury removal. Also, sulfur that is not properly dispersed will not be held tightly by the activated carbon. This sulfur will be stripped by the hydrocarbon gas, especially at higher temperatures. Loss of sulfur will decrease the mercury removal performance and may contaminate downstream process equipment and recovered LPG.

These products can be used in both water-containing and dry natural gas streams. Because elemental sulfur is highly soluble in liquid hydrocarbon, this product can be used only for gas. Also, great care must be taken to prevent any liquid hydrocarbons from contacting the adsorbent during upset conditions. Liquid hydrocarbons will wash off the elemental sulfur and reduce the sorbent's capacity for mercury.

2. Metal sulfide or mixed sulfides dispersed within a solid carrier such as activated carbon or alumina

The mercury reacts with the sulfide and stays on the sorbent. Metal sulfides and polysulfides were found to be effective in removing elemental mercury.^{[4], [5]} Copper and zinc are the predominant metals used as well as other proprietary metals. In some cases where trace H₂S removal is required, the metal oxide version is used to remove the H₂S that converts the oxide into the sulfide, which then removes the mercury. A number of different products are being offered by various manufacturers. Most are available in the pellet form. The particle sizes generally vary from 0.9 to 4mm pellets. The smaller particles offer better mercury removal efficiency, but give a higher pressure drop, while the reverse is true for the larger ones. These products can be used in both gas and liquid hydrocarbon service and they are also not damaged by contact with liquid water.

3. Halide-impregnated activated carbon particles

These particles are used to remove mercury from liquid hydrocarbons.^[6] The mercury reacts with the halide, such as iodide, to form HgI_2 that stays on the sorbent. The product cannot be used where there is the danger of liquid water contacting the sorbent since liquid water will wash off the halide and may cause vessel corrosion. Some other products are available that contain proprietary ingredients and which are claimed to offer improved performance in treating natural gas liquids and which are not damaged by liquid water.

4. Ion-exchanged resins

These resins remove mercury from liquid naphtha feeds to petrochemical plants with mixed results.

Regenerative Mercury Removal

The regenerative mercury removal works the same way as does other thermally regenerated adsorption processes. Usually it is practiced simultaneously with dehydration or some other contaminant removal process. Since nearly all cryogenic plants use molecular sieve dehydrators, the mercury removal function can be easily added to the dehydrator performance by replacing some of the molecular sieve with a mercury removal adsorbent. The mercury is sorbed during the dehydration step, and then regenerated off the adsorbent and the mercury leaves the vessel with the spent regeneration gas. Depending on the amount of mercury present in the feed fluid, and on the process conditions in the spent regeneration gas knockout separator, much, and potentially all, of the mercury can be collected and recovered as liquid mercury.

The benefit of this method is that there is no need for additional adsorption vessels. Also, mercury protection can be quickly added simply by replacing some of the existing molecular sieve without compromising the drying performance. Another benefit is that there is no additional pressure drop introduced on the process stream. This avoids the 5 to 10 psi or higher pressure drop that is commonly experienced when using non-regenerated mercury removal sorbents. Since the mercury does not accumulate on the adsorbent, it presents no spent adsorbent disposal issues. The trade-off is that there will be mercury left in the gas from the spent regeneration gas separator; however, this can be addressed by process options as discussed later.

HgSIV™ Adsorbents

This is a regenerative mercury removal product developed, manufactured, and marketed by UOP. It has greatly enhanced mercury removal properties. This is a molecular sieve product that has been modified with silver. HgSIV adsorbents retain their full properties for removing water and other conventional adsorbates. Silver has been deposited only on the surface of the molecular sieve. Mercury from the gas, or from a liquid stream, contacts the silver and amalgamates with it. By having the silver on the surface and readily available to the mercury, the mercury atom does not have to diffuse through the pore structure, which would greatly slow the rate of mercury removal. When the adsorbent is heated to the normal dehydrator regeneration temperature, the mercury is released from the silver and it leaves with the spent regeneration gas. Because these surface mercury removal sites are regenerated each cycle, the product retains a high rate of mercury removal.

Normally, only a fraction of the dehydrator adsorbent bed volume must be replaced with HgSIV adsorbent to achieve the desired level of mercury removal. This product is usually located at the bottom of the drier. The life of HgSIV adsorbent often exceeds the life of the dehydration grade sieve and can be reused. Currently, there are over 30 units containing HgSIV adsorbent in gas and liquid service in LNG plants, cryogenic hydrocarbon recovery plants, and petrochemical plants.

Mercury Removal Options in a Typical Gas Processing Plant

In the gas plant flow scheme, there are options as to where and how the mercury should be removed. Some of the selection criteria include:

- Treated stream Hg content requirement. When heat exchangers need to be protected, the elemental mercury should be removed to the lowest practical level.
- Amount of mercury present in the inlet streams. If there is much mercury, perhaps most, or all of it, could be recovered and the need to dispose of large amounts of potentially hazardous waste avoided.
- Are both gas and liquids introduced into the plant? If the low molecular weight liquids are fed into the cold box, this stream will also have to be mercury-free.
- What are the gas or liquid stream treating processes ahead of the dehydrator? If there is mercury in the inlet streams, there will be some mercury in the off gases. Will this be a problem?
- What are the local environmental concerns?

Generic simplified gas plant flow schemes are presented to illustrate the mercury removal options. The first case is shown in Figure 1. Here, natural gas containing $1 \mu\text{g}/\text{Nm}^3$ of mercury first goes through an acid gas removal unit, then through a drier containing MOLSIV™ dehydration grade molecular sieves made by UOP LLC, and then into the cryogenic section for hydrocarbon recovery. For the purpose of showing the mercury balance in the plant, we have assumed that there will be no change in the mercury content of the gas as it goes through the acid gas removal unit. That is, the removed acid gas will have the same mercury content as the plant inlet gas. Information does not exist as to how much mercury it may actually have. Mercury is very soluble in liquid hydrocarbons.^[7] It would be reasonable to expect that when organic solvents are used, the acid gas will have some mercury. The mercury removed may well depend on the amount and type of amine in the solution. Mercury has very low solubility in water so the acid gas from water solutions such as hot potassium carbonate, could be expected to be low in mercury.

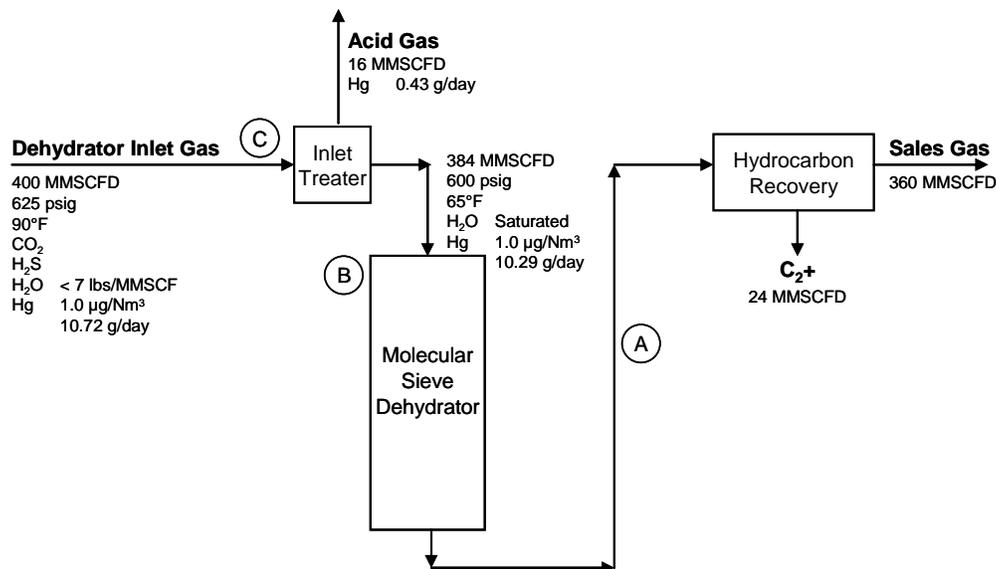


Figure 1 – Mercury Removal Options in a Typical Gas Plant with Low Inlet Mercury
Simplified Flow Scheme

In this example, with a plant inlet gas rate of 400 MMSCFD and 1 $\mu\text{g}/\text{Nm}^3$ of mercury, there are 10.72 grams of mercury coming into the plant each day. If 4% of the gas is removed as acid gas, then 4% or 0.43 grams of mercury could go with the acid gas. The remaining mercury will go into the molecular sieve dehydrator. Most of this mercury will go through the dehydrator and into the cold box unless the mercury is removed.

There are three options. Option A – install a non-regenerative mercury removal unit (MRU) downstream of the dehydrator. Option B – convert the dehydrator to the dual function of water and mercury removal by replacing some of the dehydration molecular sieve with HgSIV adsorbent. Option C – install non-regenerative mercury removal at the plant inlet.

Options A and C will require separate vessels and add approximately 5 to 10 psi pressure drop. Usually, the vessels are of the same number and about the same size as the number of molecular sieve dehydration vessels that are in the drying mode. For instance, a three-vessel dehydrator, with two on drying and one being regenerated, needs two vessels for the non-regenerated mercury sorbent. Option A will give good mercury removal performance and sorbent life, since being after the dehydrator, the gas will never have any liquid entrainment. Option C will insure that there is no contamination of the plant with mercury. However, because the example case has relatively low inlet mercury level, this option may be of limited benefit.

Option B requires no new vessels or piping and does not add to the pressure drop. There are a number of ways to practice Option B. Option B-1 is shown in Figure 2. In this case, the dehydrator is regenerated with a small slip stream of the plant residue gas. The spent regeneration gas is cooled to knock out most of the water and put back into the sales gas line. Essentially all of the mercury goes into the sales gas line. This option will raise the residue gas mercury concentration from the 1.0 of the plant inlet gas to about 1.06 $\mu\text{g}/\text{Nm}^3$. In summary, the dehydrator acts to divert all of the mercury and some of the water around the cold box. The recovered hydrocarbons, of course, will be mercury-free.

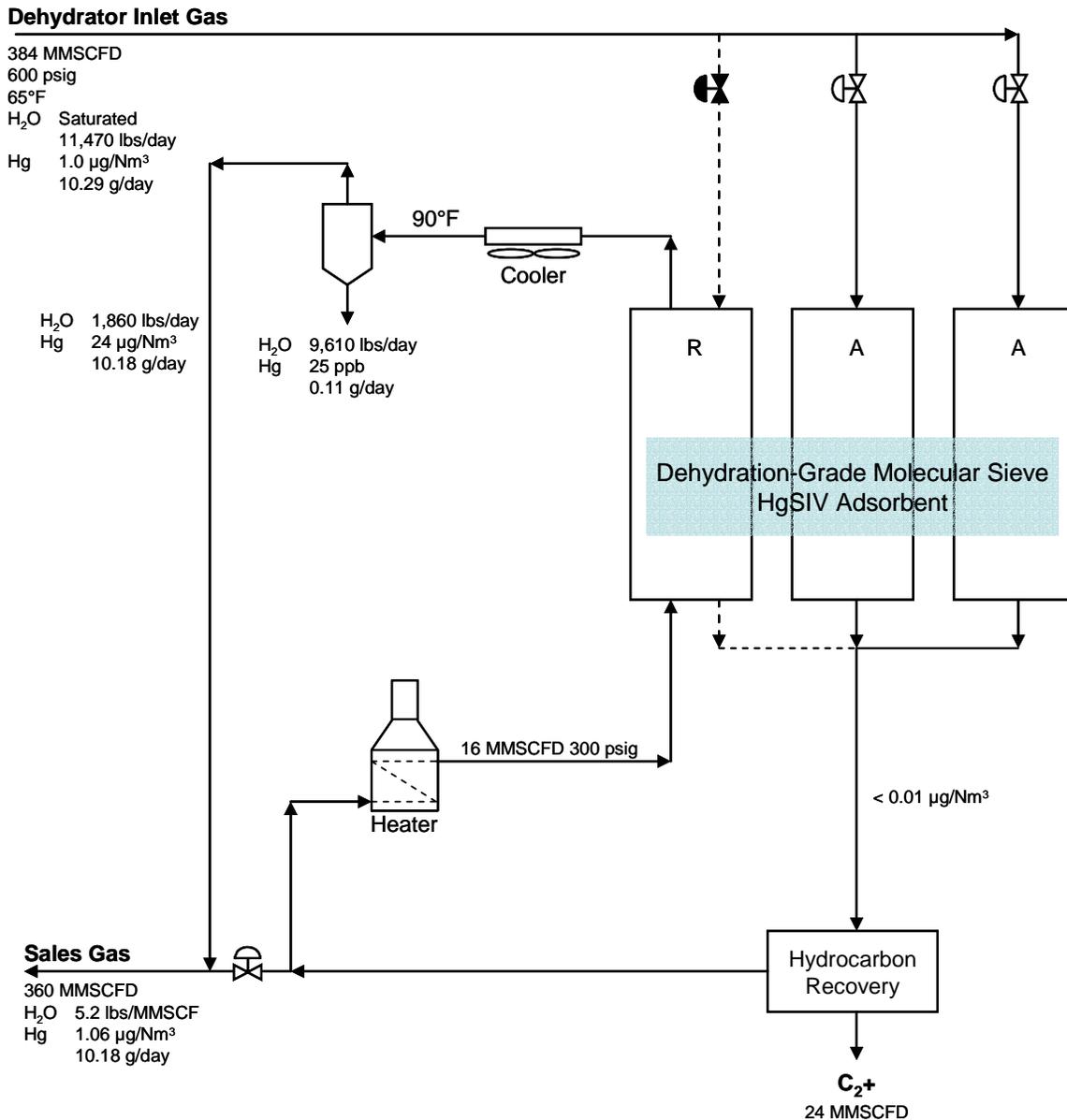


Figure 2 – Option B-1
Use of HgSIV Adsorbent for Mercury Removal

The water balance around the dehydrator is also shown in Figure 2. If the water from the regeneration gas separator would be saturated with mercury, it would contain about 25 parts per billion of mercury or approximately 0.11 grams of mercury per day. Most likely the water will not be saturated with mercury for two reasons. First, most of the mercury and most of the water come off the dehydrator at different times. The HgSIV adsorbent is at the bottom of the bed (heating inlet end) and sees the heat first. The bottom of the bed contains the water mass transfer zone and is only partially loaded with water. Most of the water comes off during the middle and latter part of the heating period. This is shown in Figure 3. When most of the mercury is passing through the spent regeneration gas cooler and separator, there is no condensing water. When most of the water is being condensed, most of the mercury is gone. Secondly, in this case, with only 1 µg/Nm³ in the inlet gas, there will not be enough mercury to condense.

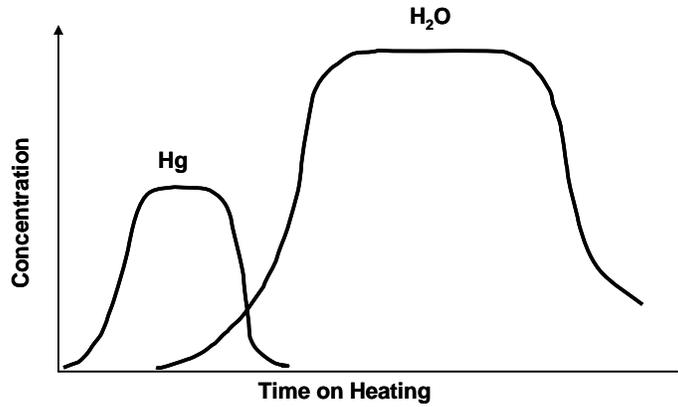


Figure 3 –MOLSIV and HgSIV Regenerative Adsorbents Desorption Profile

Option B-2 is shown in Figure 4. The spent regeneration gas is treated for mercury removal before it is put into the sales gas line or used for local fuel. This option will require a separate vessel, but a much smaller one, since the mercury is now in a much smaller volume gas stream of only 16 MMSCFD, instead of 384 MMSCFD, going into the cold box.

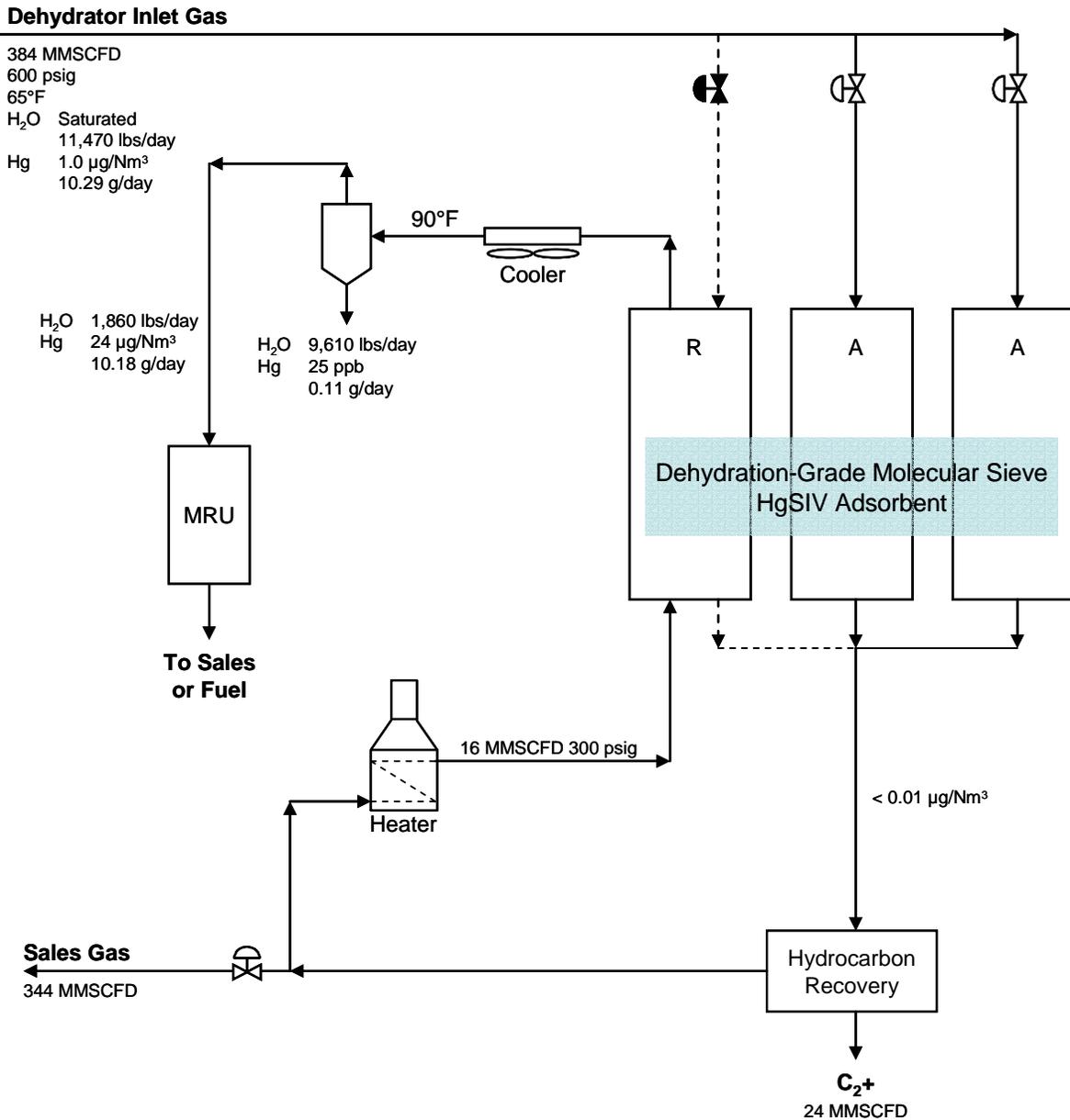


Figure 4 – Option B-2
 Use of HgSIV Adsorbents for Mercury Removal

Another example is presented in Figure 5. This is the same flow scheme as shown in Figure 1, but with a higher inlet gas mercury concentration of 70 µg/Nm³. In this example, at a flow rate of 400 MMSCFD, 750 grams of mercury enters the plant each day. Approximately 30 grams/day of this mercury could be going with the acid gas, while the remaining 720 grams would need to be removed from the gas before entering the cold box.

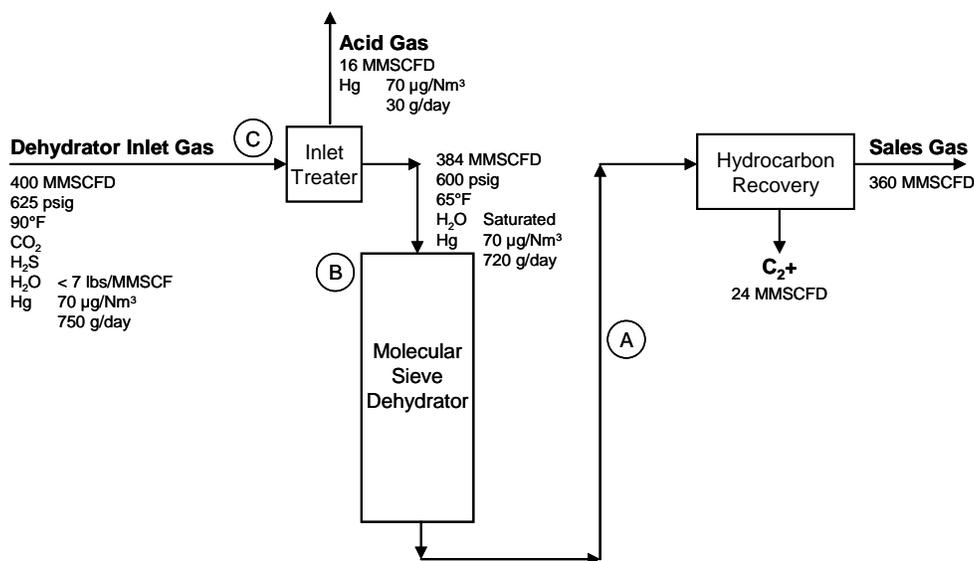


Figure 5 – Mercury Removal Options in a Typical Gas Plant With High Inlet Mercury
Simplified Flow Scheme

All three locations for mercury removal (A, B and C) are still feasible, but because of the much larger amount of inlet mercury, some new issues need to be addressed. The amount of mercury going with the acid gas needs to be established to confirm that there are no environmental issues. Also, with the increased amount of mercury to be removed, there will be an increased usage rate of the non-regenerative mercury removal sorbent. Some of the product manufacturers claim mercury loadings of 20 wt-%, or even higher. Allowing for the reaction zone and for the less-than-perfect flow distribution that frequently can exist in a packed bed, the average mercury loading on the total bed is usually about 10% before some mercury appears in the effluent and the bed needs to be recharged. Thus, with the 750 grams of mercury in the inlet gas, the mercury sorbent usage and waste generation rate will be about 7.5 kg per day, or roughly 2740 kg (6,000 lbs) per year. This corresponds to 60,000 lbs if the MRU has been designed for a 10-year life.

Option A is feasible, but there are some drawbacks beyond the need for vessels, and the pressure drop increase. With the MRU being located downstream of the dehydrator, the cold box will be protected, but there will be mercury in the acid gas as well as in the molecular sieve regeneration gas. With Option C, the mercury will be removed at the plant inlet. However, mercury removal at the plant inlet can be difficult. If any liquids would happen to get on the sorbent particles due to a plant upset condition or inlet line pigging operations, some mercury could be passed. Even if the sorbent is not permanently damaged, if liquids coat the sorbent particles, the mercury now has to diffuse through the liquid film to get to the reaction site. This greatly slows down the mercury removal process. All sorbents are affected by this. Also, if the upset is severe enough to cause liquids to be carried through the MRU, these liquids are sure to have dissolved mercury in them.

There are a number of ways to practice Option B at this higher mercury level. Option B-3 (shown in Figure 6) is similar to what was done at the lower mercury level. Here there is enough mercury to condense most of the mercury and collect it in the dehydrator spent regeneration gas separator. In the example shown, the spent regeneration gas is chilled to 60°F. At this temperature and the regeneration pressure of 300 psig, the maximum mercury concentration in the spent regeneration gas after the cooler will be about 430 µg/Nm³. Of the 720 grams of mercury present in

the dehydrator inlet gas and desorbed from the dehydrator, approximately 535 grams will be condensed and collected as liquid mercury, while the remaining 180 grams will be in the separator outlet gas. Thus, about 74% of the mercury is recovered. If the separator outlet gas is added into sales gas line, it will result in the sales gas having a mercury content of about $19.2 \mu\text{g}/\text{Nm}^3$. This is much below the $70 \mu\text{g}/\text{Nm}^3$ present in the plant inlet gas. However, if this amount of mercury is not acceptable, then the spent regeneration gas can be treated as shown previously in Figure 4.

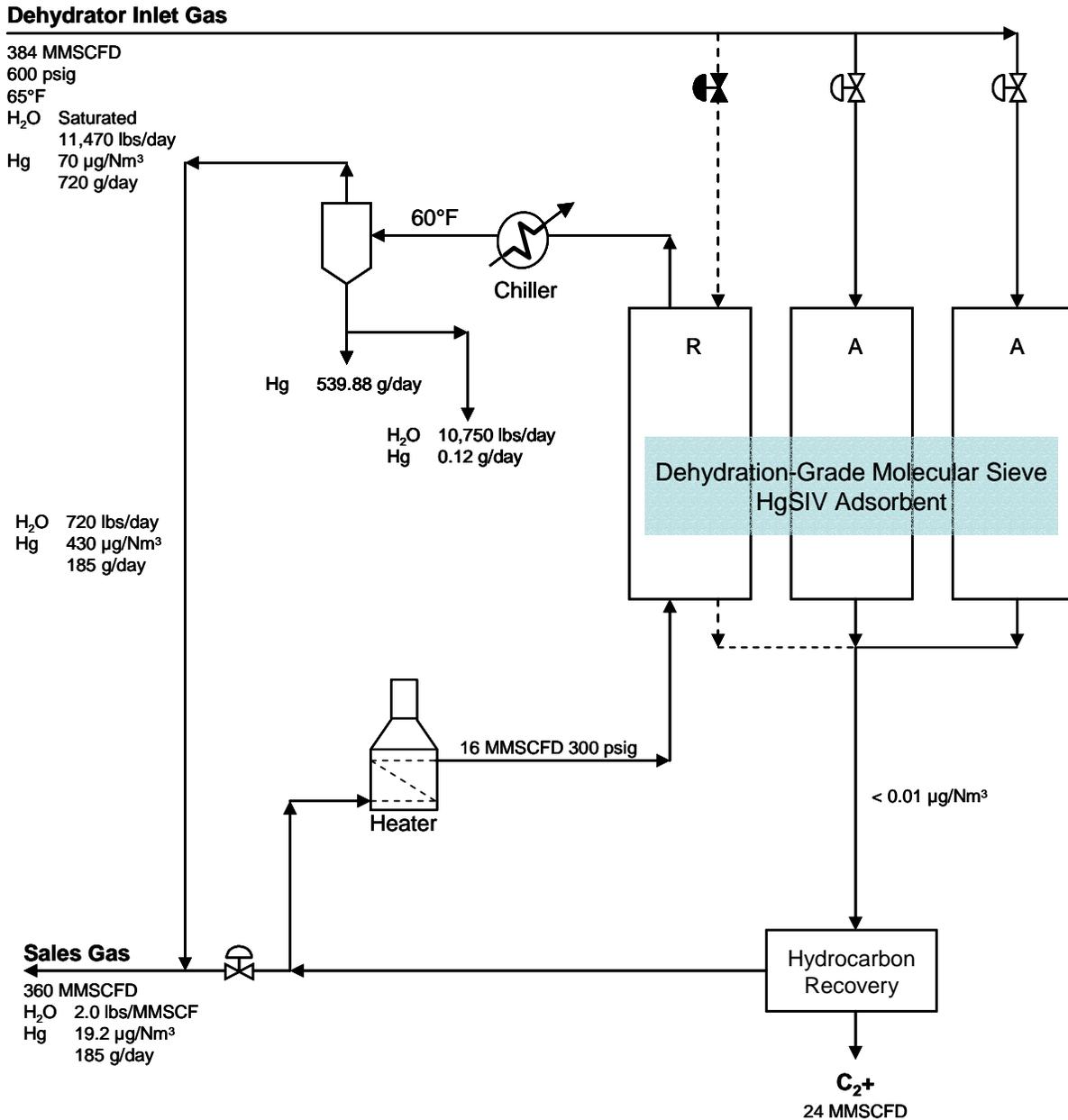


Figure 6 – Option B-3
Use of HgSIV Adsorbent for Mercury Removal

There is another way to practice Option B. This is shown as Option B-4 in Figure 7. This shows closed cycle regeneration of the dehydrator with the product gas. The gas from the separator

with the uncondensed water and uncondensed mercury is returned to the dehydrator feed line. With the regeneration done essentially at the dehydrator pressure and at the 65°F separator temperature, there will be some 290 $\mu\text{g}/\text{Nm}^3$ of mercury in the returned gas. This will raise the dehydrator inlet mercury level from the original 70 to 79 $\mu\text{g}/\text{Nm}^3$. All of the mercury present in the gas is now recovered. Since the normal regeneration in a natural gas dehydrator is at reducing conditions and there is no oxidation of the mercury, the recovered mercury is shiny and fresh looking. The mercury can be drawn off the separator and collected. This process does require good cooling and a recycle compressor. This type of closed-cycle regeneration is a common method used in natural gas dehydration service.

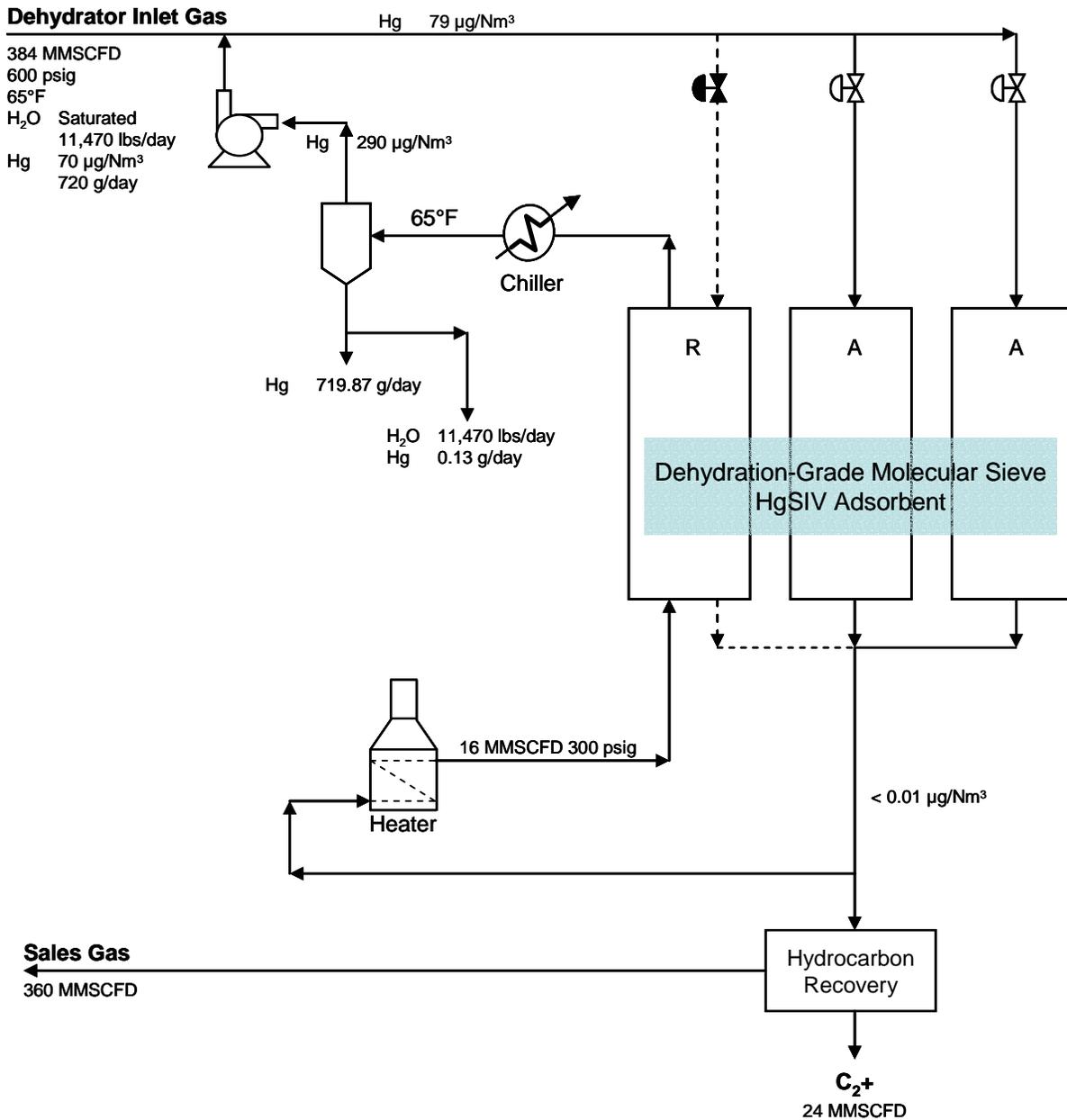


Figure 7 – Option B-4
Use of HgSIV Adsorbent for Mercury Removal

In these higher mercury content cases, there is another option worth considering. This would be to install a bulk mercury removal unit on the plant inlet gas (Option C), as well as install HgSIV adsorbent in the gas dehydrator (Option B-1). The HgSIV inventory in the dehydrator can be adjusted for the reduced mercury level. Removing most of the mercury at the inlet will avoid atmospheric mercury contamination issues. Having some HgSIV adsorbent in the dehydrator will prevent any mercury from reaching the cold box. This combination offers some benefits:

- The plant inlet MRU's performance does not have to be closely monitored for first sign of mercury breakthrough. Detecting the first sign of mercury leakage is a demanding analytical task.
- The plant inlet MRU can be run past mercury breakthrough to a pre-determined level. This will maximize the average mercury loading on the non-regenerative mercury sorbent, increase the run time, and minimize the replacement cost.
- A smaller MRU can be used. Having the HgSIV adsorbent in the dehydrators will protect the heat exchangers or other plant equipment. This can be helpful in the design of new plants, where the expected feed gas mercury content cannot be precisely predicted.
- The timing of replacement of the plant inlet MRU sorbent is flexible. The replacement can be scheduled to coincide with the normal plant turnaround, without the danger of getting any mercury in the cold box.

Gas and Liquid Feed Plants

A simplified typical gas plant flow scheme is shown in Figure 8. The gas can be treated for mercury removal at A, B, or C locations, as previously discussed.

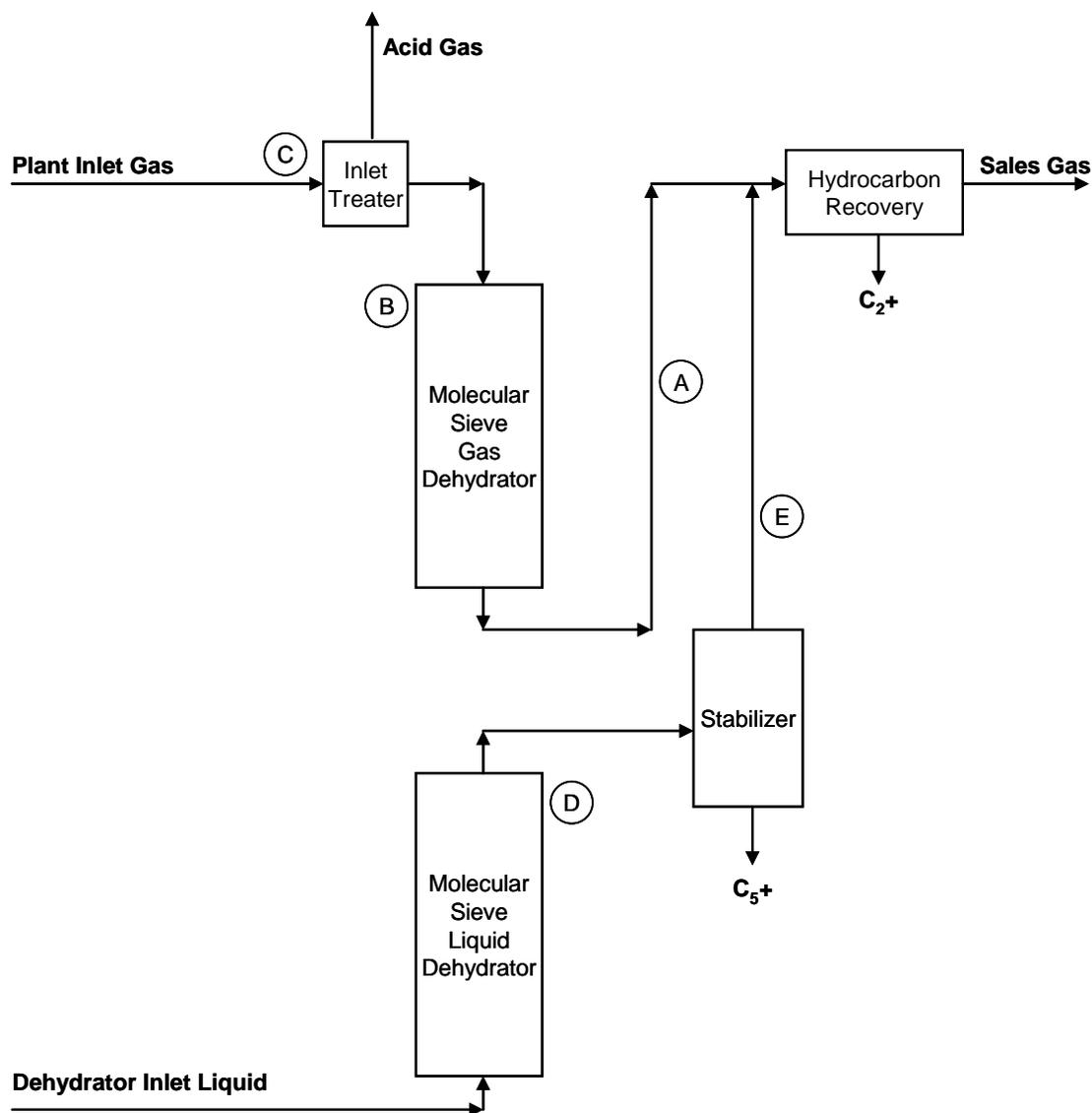


Figure 8 – Mercury Removal Options in a Typical Gas Plant with Gas and Liquid Condensate Feed
Simplified Flow Scheme

If there is any mercury in the gas, there will be mercury in the liquids. After removal of any entrained water, the liquid hydrocarbons are dehydrated with molecular sieves. The dried liquids then go into a stabilizer. The stabilizer overhead is introduced into the hydrocarbon recovery section. If the stabilizer overhead is introduced ahead of any critical heat exchangers, the stabilizer overhead stream also has to be mercury-free.

Mercury removal can be done as in Option D by replacing some of the molecular sieve in the liquid dehydrator with HgSIV adsorbent. This will greatly reduce the mercury level, but it may not make the stabilizer overhead completely mercury-free. Mercury removal from this liquid stream is more difficult than from the gas stream. These liquids can contain small amounts of fine solids that contain mercury. This mercury may not be permanently bound with the solid and could go into the solution.^[9] If any of these solids are present downstream of the dehydrator, they will recontaminate the liquid. Also, because elemental mercury fractionates mostly with the light hydrocarbons, any

elemental mercury that does pass through the dehydrator will be concentrated in the stabilizer overhead. These same problems would also exist if the inlet liquid hydrocarbons would be treated with a fixed bed of non-regenerative sorbents. Since the flow in the non-regenerative bed is always in one direction, if the inlet stream contains solids, irrespective of their mercury content, these solids can accumulate, restrict the flow, and increase the pressure drop.

To insure that the stabilizer overhead is mercury-free, it needs to be treated for mercury removal (Option E). This mercury removal can readily be done with a number of non-regenerative mercury sorbents. Since the stripper overhead will be at the hydrocarbon dew point and may be above the ambient temperature, provisions need to be taken to avoid condensation in the inlet line or in the sorbent bed. Even if the sorbent is not permanently damaged by liquids, the liquid film around the sorbent particle will greatly slow down the mass transfer rate and the design mercury removal performance will not be attained.

In cases of high mercury inlet concentrations, and in cases where there is a requirement for low mercury content in the stabilized condensate, using both Option D and Option E should be considered.

Case Study of Mercury at One Gas Plant

A natural gas hydrocarbon recovery plant had been in operation for about a year. The plant had an acid gas removal unit used principally for reduction of CO₂ content followed by a molecular sieve dehydrator. It recovered ethane and other hydrocarbons for use as feedstocks for adjacent petrochemical plants. The plant had an unexpected shutdown due to gas leaks in the cold box. Mechanical failure had occurred due to the unexpected presence of mercury in the inlet gas.

They replaced some of the dehydration grade molecular sieve with HgSIV adsorbent, and following the mechanical repairs, restarted the plant. They also planned to install non-regenerative mercury removal sorbent beds on the plant inlet gas, but since this required new vessels, this could not be implemented for about a year.

The mercury removal performance of the HgSIV adsorbent was evaluated before the installation of the MRU on the plant inlet gas. The gas going into the dehydrator contained 25 to 50 µg/Nm³ of mercury. The dried gas contained less than 0.01 µg/Nm³ of mercury (less than 10 ng/Nm³). Liquid mercury was collected and drawn off the dehydrator spent regeneration gas separator.

The performance of the HgSIV adsorbent was again evaluated some months after installation of the plant inlet gas MRU. The dehydrator inlet gas mercury content had dropped to about 0.5 µg/Nm³. The dried gas was still mercury-free, and there was no longer any liquid mercury in the separator. The plant has continued to operate with both HgSIV adsorbent in the dehydrator and with the inlet gas MRU. This combination minimizes the mercury contamination of the plant and provides reliable protection of the cold box.

A Second Case Study

Another cryogenic hydrocarbon recovery plant processing approximately 400 MMSCFD of natural gas had been operating for a number of years. Unexpectedly, they experienced gas leaks in their cryogenic section forcing a plant shut down. The leaks were determined to be caused by presence of mercury in their inlet gas. They replaced some of the dehydration grade molecular sieve with HgSIV mercury removal adsorbent, acquired a mercury analyzer, repaired the plant, and resumed operation. They have found the dehydrator inlet mercury levels to be about 80 µg/Nm³. The treated gas is completely dry as it was before the HgSIV adsorbent installation. Their in-plant mercury analyses show the treated gas to be below 0.1 µg/Nm³. They are happy with this purity and have not made the effort to increase the sensitivity of their in-plant mercury analyses to determine lower levels of mercury.

Other Technologies for Treating Liquid Hydrocarbons

For liquid hydrocarbon streams, such as natural gas condensates and naphtha that contain a variety of mercury compounds, some licensed process technologies are available. These are two-stage processes that first involve a conversion step to convert all types of mercury compounds that may be present to elemental mercury. The exit stream then goes through a non-regenerative sorbent bed where the elemental mercury is removed.

One process being offered uses hydrogen to hydrogenate the mercury compounds and convert them to elemental mercury. The stream is then passed through a bed of metal-sulfide non-regenerative mercury sorbent.

UOP also offers a process for total mercury removal. It is called “JGC/UOP Contaminant Removal Process.” It uses no hydrogen. The liquid inlet stream is heated and then passed through a catalytic reactor that converts the different mercury compounds to elemental mercury. The stream is then cooled and passed through a bed of mixed-metal sulfide on alumina non-regenerative mercury sorbent.

Mercury Removal from Water

As shown in the previously presented mercury balances, the amount of mercury going with the condensed water from a dehydrator containing HgSIV mercury removal adsorbent is very small. Data shows that in the absence of air where there is no oxidation of the mercury to the more soluble oxide form, the water will contain only about 25 ppb wt of elemental mercury.^[9] However, if there is a need, the mercury level can be reduced to less than one ppb wt.

A number of the non-regenerative mercury removal sorbents can be used. One product containing elemental sulfur dispersed within an activated carbon pellet has been reported to reduce the mercury content of the discharge water from a chlor-alkali plant to levels below 0.5 ppb wt.^[10]

SUMMARY

In a hydrocarbon recovery plant, as well as in an LNG plant, there are choices as to where in the process the mercury removal should be done. Should the mercury be removed at the plant inlet, or just ahead of the cryogenic section? The choice for the location for mercury removal will depend on many factors, such as inlet mercury levels, inlet gas composition, acid gas removal processes utilized, and the site environmental concerns. Both regenerative and non-regenerative mercury sorbents can be used successfully. Each offers benefits as well as some drawbacks. The best method for mercury removal in some plants may be to use a combination of both non-regenerative and regenerative mercury removal methods.

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