

<p>KLM Technology Group</p> <p>Practical Engineering Guidelines for Processing Plant Solutions</p>	 <p>Engineering Solutions</p> <p>www.klmtechgroup.com</p>	Page : 1 of 120
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<p>KLM Technology Group P. O. Box 281 Bandar Johor Bahru, 80000 Johor Bahru, Johor, West Malaysia</p>	<p>Kolmetz Handbook Of Process Equipment Design</p> <p>MERCURY REMOVAL UNIT SELECTION, SIZING AND TROUBLESHOOTING</p> <p>(ENGINEERING DESIGN GUIDELINES)</p>	<p>Co Authors</p> <p>Rev 01 - Mochamad Adha Firdaus Rev 02 – Utami Ledyana Daulay</p> <hr/> <p>Author / Editor</p> <p>Karl Kolmetz</p>

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INTRODUCTION

Scope

Mercury exists naturally in hydrocarbon reservoirs, Typically in low levels and low concentrations. Nevertheless, this small amount of mercury could causes significant problems flowing to a process unit . Table 1 shows the concentration of mercury from it's sources such as oil and gas wellheads.

Table 1 Mercury in Natural Gas by Region

Location	Mercury Concentration	
	Gas	Liquids
	($\mu\text{g m}^{-3}$)	($\mu\text{g kg}^{-1}$)
Europe	100 - 150	-
South America	50 - 120	50 - 100
Gulf of Thailand	100 - 400	400 - 1200
Africa	80 - 100	500 - 1000
Gulf of Mexico (USA)	0.02 - 0.4	-
Overthrust Belt (USA)	5-15	1 – 5
North Africa	50-80	20–50
Malaysia	1- 200	10- 100
Indonesia	200 - 300	10 - 500

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Mercury usually occurs in gas plant streams as an elemental (metallic), organic and also inorganic compounds. The presence of the mercury may not be tolerated in the presence of the process streams that contain certain types of equipment.

Mercury can cause severe and hazardous corrosion of aluminum heat exchangers, which are commonly used in ethylene and 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 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. Mercury could also cause a failure during to its corrosive attributes.

Mercury is toxic, could dissolved in aqueous streams through a water waste stream and also poison the catalysts of downstream facilities from gas plant processing. Based on a variety of process schemes, a number of mercury removal options are now available to the gas processor. The study is designed to assist the industry in the selection of suitable economical and safe solutions.

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General Design Considerations

Natural gas produced from either a gas reservoir is a complex mixture with different compounds of hydrocarbons (primarily methane and varying amounts of ethane, propane, butane, and even higher molecular weight hydrocarbons), an amount of water vapor, small amounts of nonhydrocarbon gases (hydrogen sulfide, mercury, carbon dioxide, and mercaptans such as methanethiol and ethanethiol), and even neutral gases such as nitrogen and helium, etc.

The gas composition depends on the geological area, as well as the underground deposit type, depth, and location. The gas that is finally transported in pipelines must meet the quality standards specified by pipeline companies. Those quality standards vary from pipeline to pipeline and are usually a function of a pipeline system's design, its downstream interconnecting pipelines, and its customer base. In general, these standards specify how a commercially acceptable natural gas should be :

- a. It must be within a specific Btu content range. For example, in the United States, it should be about $1,035 \pm 50$ Btu per standard cubic foot (at 1 atmosphere and 60°F)
- b. It should be delivered at a specified hydrocarbon dew point temperature level. This would prevent liquids to condense and form liquid slugs which could be damaging to the pipeline.
- c. The gas should not contain more than trace amounts of compounds or elements such as mercury, hydrogen sulfide, carbon dioxide, mercaptans, nitrogen, water vapor, and oxygen.
- d. The water vapor must be removed (dehydrate the gas) sufficiently to prevent corrosion and the formation of gas hydrates in the processing plant or the pipelines.

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e. All particulates must be removed.

The natural gas produced from wells must be processed and treated before it can be delivered to the pipelines. Natural gas that is not within certain specific gravities, pressures, Btu content range, or water content levels will cause operation problems, and pipeline deterioration such as corrosion and fouling. The purpose of gas processing is to produce a gas stream that meets sales requirements and specifications including heating value and the recovery of maximum amount of NGLs (Natural Gas Liquids). The processing of wellhead natural gas into pipeline-quality natural gas (e.g., 99.9% methane) can be quite complex and usually involves several processes.

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A generalized gas processing schematic is shown in Figure 1.

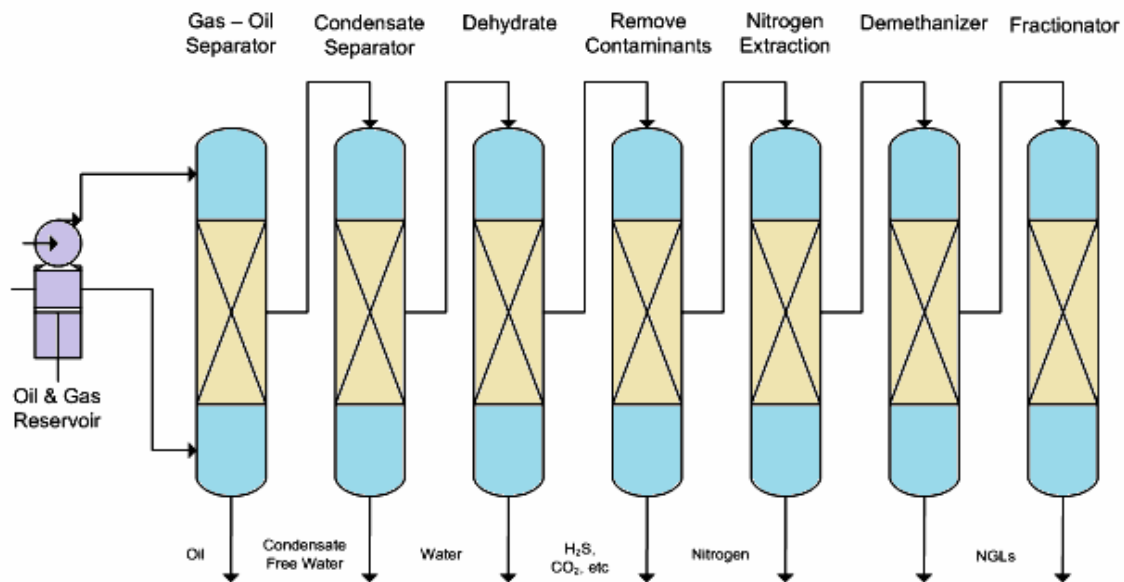


Figure 1 Generalized gas processing schematic

In addition to those four processes (to remove oil, water, compounds, or elements such as sulfur, helium carbon dioxide, mercury and natural gas liquids), it is often necessary to install scrubbers and heaters at or near the wellhead. The scrubbers serve primarily to remove sand and other large particle impurities. The heaters ensure that the temperature of the natural gas does not drop too low to form a hydrate with the water vapor content of the gas stream. Natural gas hydrates are crystalline solids that block the passage of natural gas through valves and pipes.

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Treating of Natural Gas

Natural gas is produced at the well site in compositions of considerable variety. The objectives of natural gas treatment are correspondingly diverse. The composition range that must be encompassed is shown in Table 6 for selected examples. Besides its primary constituent methane, natural gas may contain various amounts of impurities, which lead varying problems during production and transportation :

- a. Water
Condensed water forms solid hydrates with hydrocarbons or hydrogen sulfide, or in addition leads into liquids slugs in pipelines and to corrosion.
- b. Higher Hydrocarbons
If natural gas contains higher concentration of C₂₊ hydrocarbons, the recovery of liquid petroleum gas (LPG) and gas condensate is economically important. The desired Wobbe Index and calorific value could also require a reduction in the concentration of higher hydrocarbons. Even very low concentrations of higher hydrocarbons can condense in pipelines (retrograde condensation). These condensed hydrocarbons can attack plastic pipes and control devices.
- c. Hydrogen Sulfide
Hydrogen sulfide together with free water can cause corrosion, particularly stress corrosion and hydrogen-induced cracking. Removal of hydrogen sulfide is performed almost exclusively in centralized treatment plants.
- d. Carbon Dioxide
Carbon dioxide together with free water causes pitting corrosion in carbon and low-alloy steels. Some natural gases that contain significant amounts of O₂ must be treated to increase the methane concentration prior to sales.

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e. Sulfur

Gases containing hydrogen sulfide can also contain elementary sulfur as vapor. Some gas fields, primarily in Canada, Germany, and the United States, contain such high quantities that the sulfur, depending on pressure, temperature, and gas composition, can precipitate and plug the production pipe, which then become blocked. Furthermore, elemental sulfur and free water corrosive.

f. Mercury

Natural gas can contain mercury in concentrations up to several milligrams per cubic meter, the bulk of which exists in elemental form. Separated liquid mercury causes mercury-induced corrosion in pipes and fittings, corrosion damage to aluminium heat exchangers in cryogenic plants, and damage to measuring and control valves containing nonferrous metals by amalgam formation. Mercury must also be removed because of its toxicity.

g. Other Components

In Alabama, for example, cyclic hydrocarbons such as adamantane and diamantane are found in natural gas, these compounds are inclined to sublime and must be removed by injection of oil. Some gases contain high amounts of nitrogen, which must be separated to obtain a sales gas with the required combustion properties.

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Mercury concentration in natural gas

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.

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 7.

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Table 2 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.

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DEFINITIONS

Absorption – A physical or chemical process in which atoms, molecules, or ions enter some bulk phase – gas, liquid, or solid material.

Adsorbent – Thin film at the surface of substance due to the adsorption process.

Adsorption – The adhesion of atoms, ions, or molecules from gas, liquid, or dissolved solid to a surface.

Amalgam – Substance formed by the reaction of mercury with another metal.

Catalyst – Substance that participate increasing the rate of a chemical reaction.

Chemisorption – Kind of adsorption which involves a chemical reaction between the surface and the adsorbate.

Corrosion – The gradual destruction of materials, by chemical reaction with its environment.

Drying – A mass transfer process consisting of the removal of water or another solvent by evaporation from a solid, semi-solid or liquid.

Hydrocarbon – An organic compound consisting entirely of hydrogen and carbon.

Liquefied Natural Gas – Natural gas which predominantly methane that has been converted to liquid form.

Mercury – Chemical element with the symbol Hg, commonly known as quicksilver.

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Nonregenerative Process – A sulfur-impregnated carbon adsorbent for mercury removal.

Regenerative Process – A process that utilizes silver on molecular sieve to chemisorb elemental mercury while providing dehydration at the same time.

NOMENCLATURE

<i>bp</i>	Boiling point (°C)
Btu	British Thermal Unit
<i>C_p</i>	Heat Capacity (J/mol)
Emf	Electromagnetic Field (Volt)
<i>fp</i>	Freezing Point (°C)
MCF	Million Cubic Feet
MMSCFD	Million Metric Standard Cubic Feet per Day
log <i>P</i>	Vapor pressure of compound (kPa)
<i>P_c</i>	Critical Pressure (MPa)
ppb	Part Per Billion
ppbw	Part Per Billion of Weight
ppbv	Part Per Billion of Volume
ppm	Part Per Million
<i>S₂₉₈</i>	Entropy standard at 298 K
Vol%	Percent Volume (%)
<i>V_t</i>	Volume Expansion (m ³)
ΔH_c	Heat of Combustion (J/mol)
ΔH_r	Heat of Formation (J/mol)
ΔH_p	Heat of Polymerization (J/mol)
ΔH_v	Heat of Vaporization (J/mol)
¢	Cent

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THEORY

Forms of Mercury

Mercury occurs naturally in soil and rock throughout the earth's crust, including the formations that comprise oil and gas reservoirs. Mercury occurs at varying concentrations, and in various forms. A brief review of the forms of mercury, as well as the reactions of each form, is given below. These reactions are important because of the potential for mercury to change forms during the refining process.

Elemental Mercury (Hg)

Elemental mercury is the shiny silver-coloured liquid that most people think of when they hear the word 'mercury' (Figure 2). However, it is not the most common form of mercury, and is unstable in the presence of sulphur and some sulphur compounds. When exposed to these compounds, elemental mercury will form mercury sulphide.



Figure 2 Mercury

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Elemental mercury has some properties that are unusual for a heavy metal. For example, it is liquid at room temperature. Another unusual property of elemental mercury is its vapour pressure: unlike most heavy metals, mercury has a measurable vapour pressure at room temperature (Table 2).

Table 3 Vapour pressure of elemental mercury

Temperature		Vapour pressure	
°C	°F	Pa	psi
0°	32°	0.027	0.00004
20°	68°	0.17	0.0002
40°	104°	0.86	0.001
60°	140°	3.5	0.005

Although mercury's vapour pressure is high relative to other heavy metals, it is actually lower than most liquids. For example, elemental mercury has a much lower vapour pressure than liquid water; laboratory studies have shown that droplets of mercury do not evaporate quickly into air (Winter, 2003). This is an important factor when responding to mercury spills. In general, droplets should be left undisturbed until they can be dealt with by appropriately trained personnel using appropriate procedures and equipment.

Elemental mercury exhibits different behaviour when it is mixed with hydrocarbons. This is discussed later.

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Mercury Sulphide (HgS)

Mercury sulphide is the predominant form of mercury in nature. This is due to the strong affinity of mercury and sulphur.

At room temperature, mercury sulphide is a solid. It has very low solubility in either water or hydrocarbon. The solubility has been estimated to be less than one part per quadrillion. The affinity of mercury for sulphur is so high, and the solubility of mercury sulphide in water is so low, that samples of pure mercury sulphide created by simple mixing of mercury with sulphur have passed EPA leachability tests (Lopez, 2010). This strong affinity may be important in determining mercury's behaviour in the sulphur-rich environment that exists within many refinery processes.

However, when heated with a torch, such as during hot work, mercury sulphide will begin to decompose, liberating elemental mercury.

Mercury sulphide has lower toxicity than most other forms of mercury. Due to its low solubility in water, exposures are very low. In fact mercury sulphide was often used to make jewellery and ornamental plates.

Mercury Sulphate (HgSO₄)

Mercury sulphate is considered to be an important part of the mercury cycle in the biosphere. In open water bodies such as lakes and rivers, sulphate-reducing bacteria may play a role in the creation of organic mercury species.

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Mercury Mercaptides (RS-Hg-SR)

Mercury mercaptides are formed when mercaptans² (thiols) react with mercury. The most commonly cited way to make mercury mercaptides is the reaction of ionic mercury (Hg²⁺) with light mercaptans. For example, a 1961 paper discusses an analytical method for determining mercaptan concentrations by titrating with an aqueous solution containing Hg²⁺ (Fritz and Palmer, 1961).

The prevalence of mercaptans, plus the relative instability of mercury mercaptides, may influence the behaviour of mercury within a refinery. However, mercury mercaptides are much less stable than mercury sulphide. When the mercaptides decompose, the end products may be elemental mercury and disulphides.

Organic Mercury (R-Hg-R or R-Hg-X)³

Light organic mercury species, such as dimethyl mercury, are liquids that are somewhat soluble in both water and oil. In the environment, methyl mercury appears to be the most common form, as dimethyl mercury is relatively unstable. Methyl mercury is an ion, soluble in water.

Light organic mercury species are believed to be among the most toxic forms of mercury. Literature papers suggest that the toxicity of these forms of mercury is due to their ability to dissolve in, and ultimately pass through, cell membranes and tissue.

Species such as methyl mercury and dimethyl mercury are the result of organic processes, such as those that exist within the tissue of algae and fish. The tendency of biological processes to methylate mercury is one key reason why regulators want to limit total mercury in the biosphere. There are limits on the organic mercury concentrations in fish and seafood intended for human consumption. These limits are typically on the order of 0.5 to 1 part per million (500 to 1000 ppb).

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