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		Rev: 01
		February 2014
KLM Technology Group #03-12 Block Aronia, Jalan Sri Perkasa 2 Taman Tampoi Utama 81200 Johor Bahru Malaysia	MERCURY REMOVAL UNIT (ENGINEERING DESIGN GUIDELINE)	Rev 01 - Mochamad Adha Firdaus
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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

Location	Gas ($\mu\text{g}/\text{m}^3$)	Liquids ($\mu\text{g}/\text{kg}$)
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

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 it's corrosive attributes.

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Mercury is toxic, could dissolved in aqueous streams through a water waste stream and also poison the catalyts 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.

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 :

- 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)
- 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.
- 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.
- 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.
- All particulates must be removed.

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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. A generalized gas processing schematic is shown in Figure 1.

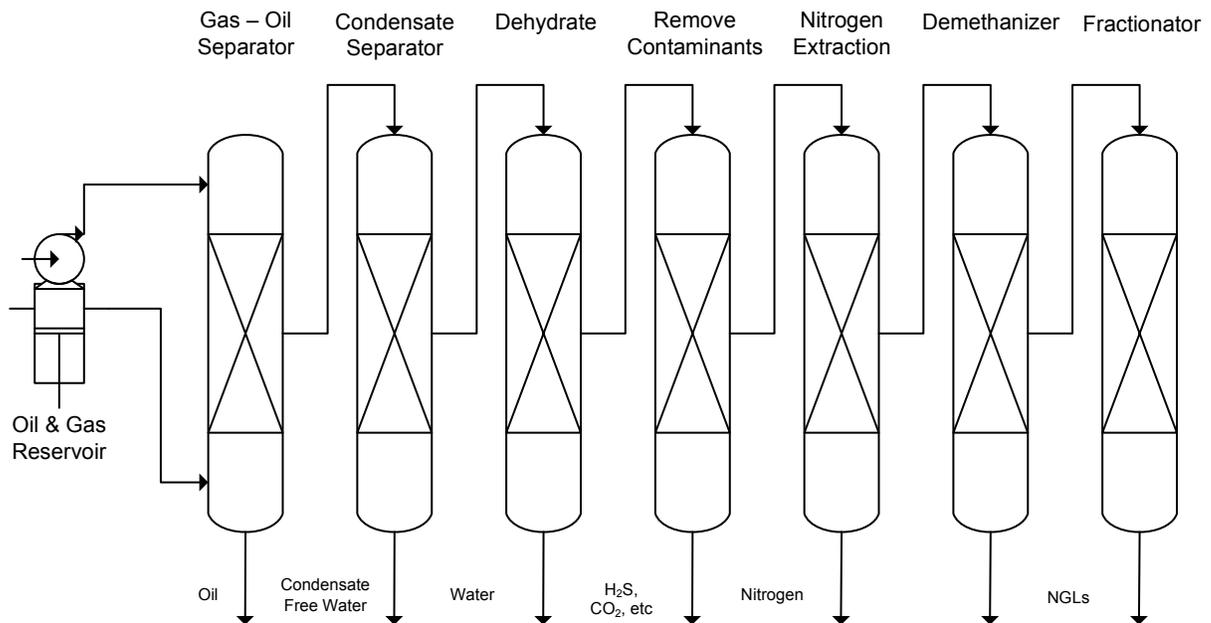


Figure 1. Generalized gas processing schematic.

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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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.

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.

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NOMENCLATURES

<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

Properties

Mercury metal is widely distributed in nature, usually in quite low concentrations. The terrestrial abundance is on the order of 50 parts per billion (ppb), except in mercuriferous belts and anthropogenically contaminated areas. In soils, the average mercury content is about 100 ppb, ranging from 30 to 500 ppb. In rocks, mercury content ranges from 10 to 20,000 ppb. Surface waters, except where special geological conditions prevail or where anthropogenic sources occur, generally contain less than 0.1 ppb total mercury. The average mercury content of sea waters has been found to range from 0.1 to 1.2 ppb.

Mercury has a uniform volume expansion over its entire liquid range. This, in conjunction with high surface tension, i.e., inability to wet and cling to glass, makes mercury extremely useful for barometers, manometers, thermometers, and many other measuring devices. Mercury also has a propensity to form alloys (amalgams) with almost all other metals except iron, and at high temperatures, even with iron. Because of low electrical resistivity, mercury is rated as one of the best electrical conductors among the metals. Mercury has a high thermal neutron-capture cross section ($360 \times 10^{-28} \text{ m}^2$ or equals to 360 barns), enabling it to absorb neutrons and act as a shield for atomic devices. Its high thermal conductivity also permits it to act as a coolant. The physical and chemical properties of mercury are given in Table 2.

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Table 2. Physical and Chemical properties

Angle of contact of glass at 18°C	128 degrees
Atomic distance	0.30 nm
Melting point	-38.87 °C
Boiling point	356.9 °C
Triple point	-38.84168 °C
Compressibility (Volume) at 20°C	38.5 x 10 ⁻⁶ MPa
Conductivity thermal	0.092 W/cm ² .K
Critical density	3.56 g/cm ³
Critical pressure	74.2 MPa
Critical temperature	1677 °C
Crystal system	Rhombohedral
Emf, of hot Hg at 100°C	-0.60 mV
Volume expansion coefficient at 20°C	182 x 10 ⁻⁶ /°C
Latent heat of fusion	-11.80 J/g
Surface tension temp coefficient	-0.19 mN/m.°C
Viscosity at 20°C	1.55 mPa.s

The volume expansion, V_t , of mercury may be calculated over its entire liquid range by :

$$V_t = V_o (1 + 0.18182 \times 10^{-3} t + 0.0078 \times 10^{-6} t^2)$$

Where V_o is the known volume of mercury at a given temperature, t , in °C. The specific heat varies with temperature. For solid mercury it increases but in liquid mercury it drops such that the specific heat at 210°C is the same as that at -75°C (Table 3). Up to 50°C, specific heat in J/g is given by the formula :

$$0.1418 - 0.0004343 (t + 36.7)$$

For temperatures t in °C, from 50 – 150°C, the formula should be modified by an additional corrective factor of $-0.000025 (t - 50)$ and between 150 and 250°C, $-0.0000126 (t - 150)$. Values for temperatures above 150°C are not as accurate at those for lower temperatures.

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Table 3. Thermodynamic Properties of Mercury

Property	Values
Entropy, S_{298}	76.107 J/mol
Heat of Fusion	2,297 J/mol
Heat of vaporization, ΔH_v	59,149 J/mol
Liquid mercury, 25 – 357°C Heat capacity, C_p	27.66 J/mol
Gaseous mercury, 357 – 2727°C Heat capacity, C_p	20.79 J/mol
Heat of vaporization at 25°C	61.38 J/mol
Latent heat of vaporization	271.96 J/g
Specific heat	
Solid	
-75.6°C	0.1335
-40°C	0.1410
-263.3°C	0.0231
Liquid	
-36.7°C	0.1418
210°C	0.1335

The vapor pressure of mercury, P , also behaves irregularly but may be obtained for temperatures from 0 – 150°C by the following :

$$\log P = (-3212.5 / T) + 7.150$$

And from 150° – 400°C by

$$\log P = (-3141.33 / T) + 7.879 - 0.00019 t$$

where P in kPa (101.3 kPa = 760 mmHg), T is the absolute temperature in K, and t is the temperature in °C. The accuracy of these formula is believed to be within 1%. Another valuable property of mercury is its relatively high surface tension, 480.3 mN/m at 0°C, as compared to 75.6 mN/m for water. Because of its high surface tension, mercury does not wet glass and exhibits a reverse meniscus in a capillary tube.

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At ordinary temperatures, mercury is stable and does not react with air, ammonia, carbon dioxide, or oxygen. It combines readily with the halogens and sulfur, but is little affected by hydrochloric acid, and its attacked only by concentrated nitric acid. Both dilute and concentrated nitric acid dissolve mercury, forming mercurious salts when the mercury is in excess or no heat is used, and mercuric salts when excess acid is present or heat is used. Mercury reacts with hydrogen sulfide in the air and thus always be covered. The only metals having good or excellent resistance to corrosion by amalgamation with mercury are vanadium, iron, niobium, molybdenum, cesium, tantalum, and tungsten.

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 4 for selected examples. Besides its primary constituent methane, natural gas may contain various amounts of impurities, which lead varying problems during production and transportation :

- Water

Condensed water forms solid hydrates with hydrocarbons or hydrogen sulfide, or in addition leads into liquids slugs in pipelines and to corrosion.

- 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.

- 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.

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- 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.

- 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.

- 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 aluminum 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.

- 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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Table 4. Composition of natural gas

Source	C ₁ , Vol%	C ₂ , Vol%	N ₂ , Vol%	CO ₂ , Vol%	H ₂ S, Vol%	Elemental Sulfur, g/m ³	Organic Sulfur, ppm	Mercury, mg/m ³
Netherlands, Gronigen	81	2.8	14.3	0.9				0.002
Norway, Ekofisk	85	8.4	0.4	2	10 ppm		1	
Germany, Söhlingen	85	1.5	12.5	0.5				1 – 5
Indonesia, Arun	75	5.5	0.3	15	100 ppm			0.2
U.S, Texas	73.2	6.1	14.3	0.3				
Germany, Wustrow	43	0.6	56	0.3				
Germany, Süd- Oldenburg	77	0.1	7	8	8		200	
Former states of USSR, Tenguiz	42	8.5	0.8	2.6	16	0.5 – 3	1000 ppm	
Canada, Bearberry	4		1	5	90	80		

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Recovery of Components with Economic Value

Another important factor is whether additional components must be removed to meet product specifications, or whether the recovery of these products is of economic interest. Examples of the latter include the recovery of helium, the production of sulfur sour gas, and the recovery of LPG and hydrocarbon condensates. A special case is so-called ultrasour gas. In this case the main interest is not to produce a fuel gas but rather to provide a feedstock in the production of sulfur.

In Canada, the production of gas with a hydrogen sulfide content of 90% began. In addition, the removal of carbon dioxide for enhanced oil recovery in crude oil production should be mentioned. By contrast, if these components are present only in trace amounts they are not removed because of its economic reasons, but rather to avoid corrosion, environmental, or production problems.

The individual process by which undesired gas contaminants can be eliminated depends on the composition of the gas, the amount and type of contaminant, and ultimately whether a saleable pure gas must be delivered at the well or whether the gas is piped to processing plant.

Natural Gas Wells

Installations at individual gas wells must fulfill the following objectives :

- To guarantee trouble-free gas flow in the production pipes and surface equipment.
- To separate or, if necessary, treat co-produced liquids.
- To condition the gas for transportation to the processing plant.
- To meet the required feed quality for the pipeline distribution network.
- To protect the production pipes and field installations from corrosion.

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The type and design of plants are determined by :

- Type and concentration of accompanying substances in the gas.
- Behavior the gas during pipeline transportation
- Applicable sales specifications.

A flow diagram for the most important treatment steps is shown in Figure 2. To prevent deposition of elemental sulfur, which occurs, for example, in some sour gas wells, solvents are pumped into the production pipe. Corrosion inhibitors can also be introduced in the same way. On the surface, liquids condensed under the well-head flow conditions are separated. After being depressurized and cooled to collection pipe conditions, further condensate is precipitated. If necessary, separated condensate must be treated further (phase separation, stabilizing, stripping).

If large amounts of formation water occur or considerable amounts of liquids (inhibitors, sulfur-dissolving agents) are injected during sour gas production, hydrogen sulfide may be released during depressurization and transportation of these liquids. Emissions can be minimized by high-pressure liquid stripping or by recompression of the flashed gas. When no further condensable hydrocarbons are present, the gas is dehydrated to a dew point equal to or below the dew point specified for pipeline transportation.

Removal of Mercury

Natural gas from predominantly “Rotliegenden” reservoirs often contains mercury in vapor and/or aerosol form. Natural gas fields containing mercury are known in Algeria, Indonesia, the Netherlands and Germany. Mercury has not resulted in any problems in production from sour gas fields. To avoid health hazards during treatment and use, the mercury content is lowered in separate mercury-removal plants from 5 mg/m³ to < 10 µmg/m³.

A considerable portion of the mercury has often already been removed by low-temperature separation (LTS) in the dehydration unit at the well. Mercury levels of < 5 µg/m³ are attained in downstream chemisorption fixedbed reactors with, for example, sulfur-impregnated activated carbon. Condensable components, such as water hydrocarbons, reduce the loading ability for mercury or even deactivate the adsorbent, The reactors are not regenerated. Rather, the laden adsorbent is fed to an external treatment plant. Regenerative amalgamation process are currently being tested.

These design guideline are believed to be as accurate as possible, but are very general and not for specific design cases. They were designed for engineers to do preliminary designs and process specification sheets. The final design must always be guaranteed for the service selected by the manufacturing vendor, but these guidelines will greatly reduce the amount of up front engineering hours that are required to develop the final design. The guidelines are a training tool for young engineers or a resource for engineers with experience.

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