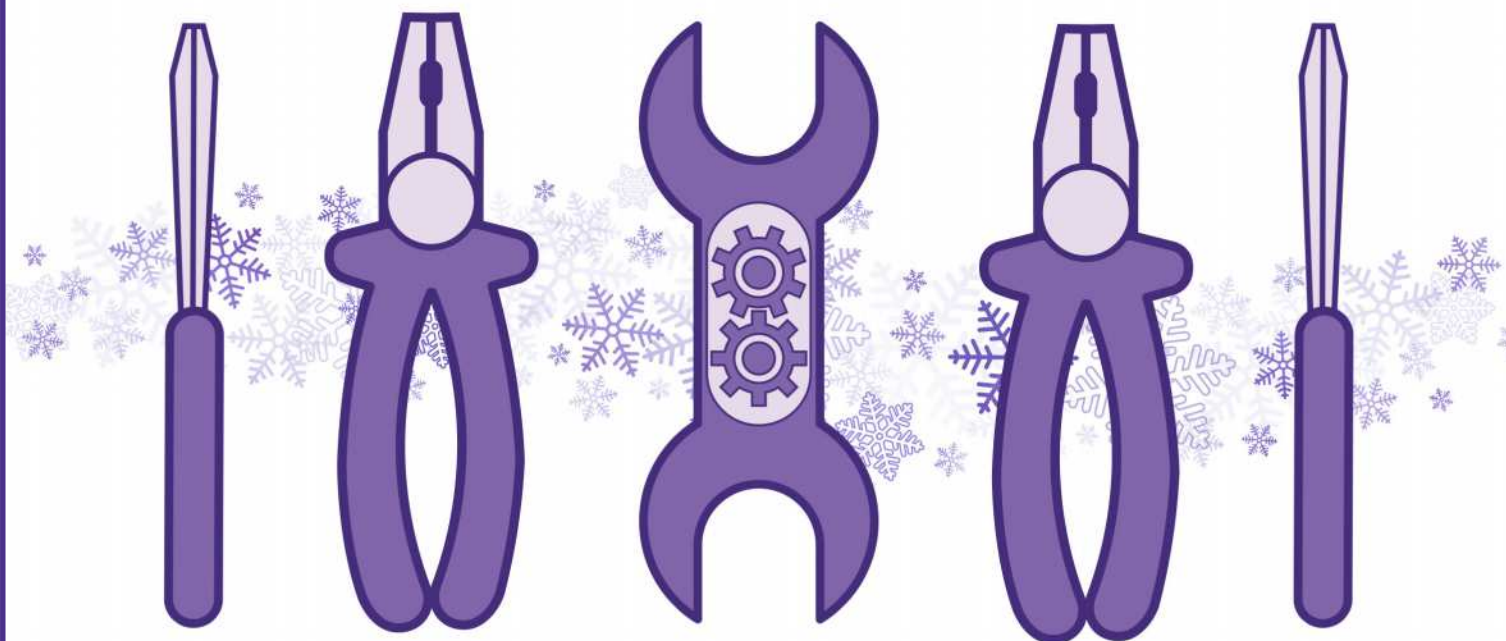# LNG TROUBLESHOOTING

David Engel, Cody Ridge, and Scott Williams, Nexo Solutions, Amine Optimization Company Division, USA, analyse cryogenic heat exchanger fouling troubleshooting at LNG facilities.

The process of treating and liquefying natural gas into LNG is a complex and often delicate operation. The profitability of a plant depends on throughput, which is maximised by maintaining stable operation, consistently meeting product specifications, and managing a number of process contaminants present in the feed gas to the facility or produced within the process.

The specifications involved with natural gas liquefaction are stringent and often difficult to maintain, as shown in Table 1. The gas purity required for liquefaction is higher than that for sales gas in several respects such as heavy hydrocarbon content, carbon dioxide (CO_2), oxygen, and water. Additional restrictions are present as well for mercury and benzene that are not of major concern in conventional gas plants.

The liquefaction process is the back end of the LNG plant and is downstream of all pre-treatment processes. In the most common process, the gas stream is cooled by propane and then further cooled and liquefied by mixed refrigerant in the main cryogenic heat exchanger (MCHE). Plant upsets caused by contaminants that often lead to shutdowns or reduced throughput can usually be remedied quickly in conventional gas plants, and the plant can return to normal flow rates shortly thereafter. LNG facilities, however, cannot recover as quickly from process upsets. Due to the design of liquefaction units, start-up can take several hours and sometimes days to get back down to the low process temperatures required to liquefy gas.

Variations in feed gas composition can have a significant effect on the liquefaction process. The amount of high molecular weight hydrocarbons separated from the feed gas and used at a heavy hydrocarbon recovery unit (HRU) can affect the overall removal efficiency of the unit. A feed gas that is leaner than the anticipated design can actually result in more heavy hydrocarbons entering the liquefaction stage and causing a series of fouling problems.

Ingression of mercaptans and other sulfur species can also cause fouling in the cold plant section and affect the specifications for total sulfur.

Even minute amounts of liquids contamination or condensable hydrocarbons in the liquefaction stage can cause fouling or freezing in the MCHE, leading to reduced heat transfer and, eventually, plant shutdown. The potential for hydrocarbon condensation must be considered carefully, and removal of any solids and free or aerosolised liquids in the gas must be done with very high efficiencies.

LNG contaminants

Contaminants are most usefully classified according to their source, as the source is the best location to implement a solution for removal or mitigation. The most common sources of contamination in liquefaction units are the feed gas, process solvents, process materials and chemical additives, and process-generated contaminants.

Feed gas contamination levels are generally lower in LNG feed gas compared to conventional natural gas plant feed gas because of the pipeline gas quality used, but it can still significantly affect the LNG process. Contracts for feed gas supply to LNG facilities often have stricter requirements for gas quality and composition, but not all contaminants have specifications or are even considered. In some respects, the feed gas to LNG facilities can be just as contaminated as unprocessed natural gas. Table 2 demonstrates some of the most commonly observed contaminants in gas feeds to LNG facilities. Some of the contaminants in the table, such as acid gases and mercury, are accounted for with process technologies at each plant. Other contaminants such as surfactants and chemical additives have no dedicated solution that is effective for their removal or mitigation, so special precautions must be taken to prevent their ingression or mitigate any detrimental effects.

Any carryover of process solvents into the liquefaction unit will cause problems including fouling, corrosion, reduced heat transfer, and missed product specifications. In addition to the solvent itself, build-up of contaminants from other sources within the process may also be present. It should be noted that water is perhaps the most important solvent used for LNG processing and also the most susceptible to contamination. The most common problem with water is the presence of metals, foam, suspended solids, and emulsified hydrocarbons.

Materials used within the LNG process must be fully compatible with the process streams they contact. Incompatible materials can be considered contaminants because they are undesired components introduced to the system that cause a detrimental effect. The detrimental effect may be a release of some material into a process stream, or a reaction or degradation of the material leading to new contaminants or reduced performance of the related system. Molecular sieve dust, for example, may carry over from the bed past the dust filter to the downstream liquefaction stage and foul the MCHE. Filters and adsorbents that were not properly cleaned, use incompatible materials, or do not have the proper efficiency, may not remove contaminants effectively and may also release residues that cause downstream problems.

Contaminants that are process-generated are components that were created as a result of reactions that occurred within the unit itself. Corrosion products are one of the most commonly referenced process-generated contaminants. Eliminating the source of corrosion is the best method of prevention and requires knowledge of low-risk process conditions and corrosive contaminants. Contaminated recycle streams feeding back to certain units at an LNG facility may also be considered process-generated and can cause unexpected issues when not considered. Gas used to regenerate molecular sieve beds is frequently recycled to the front end of the beds and can contain elevated concentrations of sulfur species and a number of other contaminants desorbed from the molecular sieve beds. Products of unwanted and often unnoticed reactions that occur in the process are also a significant concern in many plants, such as hydrogen sulfide (H_2S) formation from mercaptans when regenerating molecular sieve beds.

Liquefaction unit contamination control

The liquefaction process itself usually has little to no means of contaminant removal, as LNG plants are designed to remove all contamination upstream. HRUs remove

Table 1. Sales specifications for natural gas and LNG

Parameter	Sales gas specification	LNG specification
Methane	>75 mol%	>96 mol%
Ethane	<10 mol%	<4 mol%
Propane	<5 mol%	<2 mol%
Butanes	<2 mol%	-
Pentanes+	<0.5 mol%	<0.01 mol%
Hexanes+	-	<10 ppmv
Benzene	-	<1 ppmv
Carbon dioxide	<2 – 3 mol%	<50 ppmv
Hydrogen sulfide	<4 ppmv	<1-4 ppmv
Total sulfur	<40 – 80 ppmv	<20 ppmv
Water vapour	4 – 7 lb/million ft³	<0.1 – 1.0 ppmv
Nitrogen and inerts	<3 mol%	<1 mol%
Mercury	-	<0.01 mg/Nm³
Oxygen	<1 mol%	0%

Table 2. Common contaminants in LNG feed gas streams

Solids	Liquids	Gases
Corrosion products	Compressor lubrication oil	Acid gases
Calcium/magnesium scale	Hydrocarbon condensate	Condensable hydrocarbons
Natural gas formation solids	Water and dissolved salt/metals	Mercury
Waxes, paraffins, and asphaltenes	Chemical additives and byproducts	Oxygen
Chemical additives and byproducts	Organic acids and surfactants	Surfactants and alcohols

heavier hydrocarbon fractions, molecular sieve beds and other systems remove water content from the gas, amine units remove acid gases, and mercury beds remove mercury. Trace contaminants are removed throughout the pre-treatment process via separators, filters, and coalescers. Other pre-treatment systems may also be in place but are always upstream of the liquefaction process.

Due to the low temperatures involved, the process has virtually no tolerance for contamination. When contamination is present, fouling and plugging will quickly follow, leading to decreased efficiencies and possible damage to equipment if contamination proceeds unattended. The only methods to manage contamination in a liquefaction unit are to prevent it, modify operational conditions, or shut down the plant and remove the contamination before it is allowed to damage the equipment. Modifying operational conditions usually involves reducing throughput and results in lost revenue. Increasing temperatures to melt contaminants has been used, but in several cases this protocol can result in damages to the heat exchanger.

A plant shutdown allows the plant to remove contamination and clean process equipment, but a detailed investigation of the root-cause of the contaminant presence and its associated problems is just as important. Sampling and analysis of contaminants and evaluation of the surrounding process can reveal contamination sources and allows for upstream solutions to prevent future upsets.

Proactive contamination sampling in the liquefaction unit is valuable for identifying and resolving contamination ingression before reduced throughput or shutdown becomes necessary. Testing at the liquefaction unit requires a sophisticated approach and the proper equipment, and the characteristics and levels of contaminants must be known with some degree of accuracy to implement the correct solutions. The case study presented demonstrates how proactive contamination testing prevented a plant shutdown and revealed a solution to avert further problems.

Case study

A North American LNG plant was experiencing difficulties with fouling in the MCHE. It was suspected that small amounts of contamination in the gas stream deposited in the exchanger and began acting as a seed point for further fouling and/or freezing of other contaminants. It was further suspected that contaminants could be leaching from the molecular sieve beds, where build-up and potentially the formation of contaminants was theorised to have been occurring.

To identify contamination in the feed gas and its source, three locations were chosen for testing, one immediately upstream of the MCHE and two further upstream. The objectives of testing were to isolate and quantify any contaminants present, determine their potential relation to fouling issues at the MCHE, and identify solutions to mitigate the problem.

To properly assess contamination levels in a gas stream, effective removal and quantification of all liquids in the stream is necessary. This was accomplished by using Amine Optimization's GASCO sampling unit (Figure 1). The unit uses a high-pressure housing equipped with a high efficiency gas coalescing element designed for a virtually complete separation of liquid contaminants and aerosols in the gas stream.

Accumulation of liquids was observed only once, at the MCHE inlet testing location. No liquids were isolated at the upstream testing locations (at the amine contactors and the mole sieve dust filter). Visible accumulation of approximately 70 ml of clear liquids with no observed haze or solids was transferred from the GASCO unit bottom sight glass into a pressurised gas sampling cylinder used for further analysis. The sample collected contained both liquid and gas phases from the unit.

It is important to mention that a leak at the unit the previous night forced the plant to shut down from normal operations and recirculate gas until the plant was at steady state and all temperatures were back to normal operations. The absence of liquids in the unit prior to the shutdown suggested that the ingression of liquid contamination with the feed gas was minimal or, at worst, rare and intermittent. The presence of liquids at the MCHE inlet only after the plant shutdown suggested that the ingression of liquid contamination was likely caused by the change in operation that occurred.

The liquid contamination sample and the gas phase of the cylinder were analysed to determine its origin and characteristics (Tables 3 and 4).

Figure 1. GASCO sampling unit as assembled for feed gas contamination testing and sampling.

Table 3. MCHE inlet contamination analysis results (liquid phase)

Component (liquid phase)	Concentration	Units
Helium	<0.0010	% mole
Nitrogen	0.1221	% mole
Carbon dioxide	<0.0050	% mole
Oxygen	<0.0050	% mole
Methane	38.6956	% mole
Ethane	17.1773	% mole
Propane	25.9707	% mole
Iso-butane	3.4366	% mole
n-butane	6.6348	% mole
Iso-pentane	1.8470	% mole
n-pentane	1.1454	% mole
Total hexanes	12579	ppm (v/v)
Total heptanes	10611	ppm (v/v)
Total octanes	15461	ppm (v/v)
Total nonanes	11054	ppm (v/v)
Total decanes	<1	ppm (v/v)
Benzene	173	ppm (v/v)
Toluene	1016	ppm (v/v)
1,3-dimethylbenzene (m-Xylene)	<1	ppm (v/v)
1,4-dimethylbenzene (p-Xylene)	<1	ppm (v/v)
1,2-dimethylbenzene (o-Xylene)	<1	ppm (v/v)

Table 3. MCHE inlet contamination analysis results (gas phase)

Component (gas phase)	Concentration	Units
Hydrogen sulfide	<0.1000	mg/m^3
Carbonyl sulfide	<0.1000	mg/m^3
Methyl mercaptan	16.1400	mg/m^3
Ethyl mercaptan	315.4200	mg/m^3
Tert-butyl mercaptan	445.6300	mg/m^3
n-propyl mercaptan	788.7800	mg/m^3
Isopropyl mercaptan	119.0900	mg/m^3
n-butyl mercaptan	96.3700	mg/m^3
Methanol	<0.5	mg/kg
Dimethyl ether	27.8000	mg/kg
n-propyl alcohol and isopropanol	<0.5	mg/kg
Acetone	<0.5	mg/kg
Acetaldehyde	2.8	mg/kg
Isobutylaldehyde	<0.5	mg/kg
Butylaldehyde	<0.5	mg/kg
Helium	<0.0010	% mole
Nitrogen	0.2432	% mole
Carbon dioxide	<0.0050	% mole
Oxygen	0.0070	% mole
Methane	70.1234	% mole
Ethane	15.5826	% mole
Propane	11.5456	% mole
Iso-butane	0.8563	% mole
n-butane	1.2976	% mole

The sample was found to contain a significant amount of $C_1 - C_4$ mercaptans. Other components detected included heavier hydrocarbons including benzene and toluene as well as minor amounts of dimethyl ether and acetaldehyde. The sample as analysed also included some of the feed gas components, mostly methane, ethane and propane.

The heavier hydrocarbons and mercaptans at the low process temperature likely contributed to MCHE fouling. The presence of heavier hydrocarbons also suggested that the upstream HRU was not operating effectively. In fact, analysis of this small sample of liquids collected during testing was the strongest evidence of the root-cause of MCHE fouling and led to activities directed at verifying HRU operation.

Mitigation strategies and process improvements

The MCHE contamination causing fouling and freezing issues was identified as heavy hydrocarbons and mercaptans. The mercaptans were determined to be originating from the molecular sieve beds. Small concentrations of mercaptans in the feed gas to the beds likely built up slowly over time until the sieves were saturated and began to release contaminants during regeneration. Due to the closed system design, mercaptans could only be released in the treated gas over time. The heavy hydrocarbons were present because of inefficiencies at the upstream HRU. This problem was identified only because of the contamination found during gas testing at the MCHE inlet. Operations were adjusted to prevent reduced efficiency at the HRU after an upset and mitigate MCHE fouling.

After addressing the root-causes for fouling at the MCHE, solutions were established considering all the data and observations. Changes to the HRU operation solved the fouling at the MCHE. Central to the success of this onsite work was the rigorous sampling and testing of contaminants coupled with process data analysis and investigation.

Overall, it is important to understand that the contamination testing and control strategies for any process unit is a critical step for ensuring a stable and reliable plant performance. The majority of plants that do not consider this important step carefully are often challenged with high operating costs, low equipment reliability, unscheduled shutdowns, and other adverse situations with direct impacts on plant economics.