

Technologies of Natural Gas Sweetening

Basic Research

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Amine Sweetening Plant
(courtesy of KiniderMorgan)

Chapter 1 - Natural Gas Processing

Necessary Conditions and Goals of Processing :

The types of treatments carried out on gas streams usually are:

separation;

– heating;

– inhibition.

– dehydration;

– liquid hydrocarbon recovery;

– sweetening.

Treatment needs and objectives:

The first gas treatments are temporary. Their aim is to prevent the hydrates formation, and they're classified as follows:

– separation of free water;

– increase in the temperature of gas above that of hydrate formation;

– inhibitors injection to prevent hydrate formation.

Elimination of free water

The elimination of free water in the gas is carried out through separators that are installed at the wellhead and at the entrance of the treatment stations.

This treatment removes the liquid phase from the two-phases coming out of the wellhead. The gaseous phase is saturated before the treatment and is still saturated (at pressure and temperature conditions), leaving the separator.

Gas undergoes a temperature decrease flowing within the pipe from wellhead to the treatment station and expands (decreasing in pressure, caused by head losses along the pipe and across valves and fittings). The expansion causes a temperature loss (Joule-Thompson effect), since another condensation of moisture takes place so that the liquid phase can be present at the inlet of the treatment station once again.

Gas heating

In the diagram representing the hydrates formation of a 0,7 specific gravity gas, the evidenced area defines the condition under which the hydrates can form.

From the same diagram, it is evident that we have the gas phase increasing the temperature.

The treatment is temporary because heating the gas at constant pressure increases the capacity to hold vapor. However, content is still the same.

So, when the temperature is lower than the previous values, gas returns into the hydrates formation area.

Inhibitors

Inhibitors are liquid substances that prevent and also eliminate the formation of hydrates. The inhibitors enter a solution with water, lowering its freezing point, thus

shifting the equilibrium of hydrates towards lower temperature values. The inhibitors which are generally used are:

- ethyl Alcohol;
- methanol;
- diethylene Glycol.

Other chemical inhibitors are used to hinder, in case of sour gas, the corrosion of the machinery located at the wellhead.

Both treatments are temporary since they do not eliminate the problem, but simply hand it over to the treatment stations, either for the elimination of water vapor or the removal of corrosive agents such as CO₂ and/or H₂S.

Final treatments

After temporary treatments, gas is delivered to the treatment plant and then to users, according to the requested specifications.

The final treatments eliminating harmful elements from natural gas consists in:

1. reducing water (dehydration);
2. reducing the content of superior hydrocarbons (adsorption);
3. reducing the content of hydrogen sulfide and carbon dioxide

Sweetening

The treatments mentioned above are carried out by appropriate types of plants according to the composition of natural gas. Moreover, the plants are managed to meet the user's specifications.

The maximum concentration allowed for the various undesirable components are indicated as follows:

CHARACTERISTICS OF NATURAL GAS ACCORDING TO USERS REQUESTS

(These specifications can vary depending on the customer)

WATER Content usually expressed as dew point temperature

e.g. < 5 °C at 50 bar

HYDROGEN SULPHIDE Content = 2 ppm/Vol Max

CARBON DIOXIDE Content = 1,3 Mol% Max

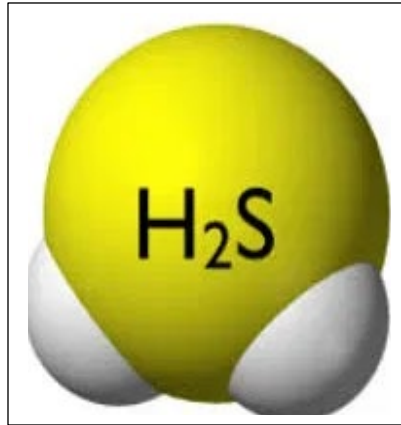
NITROGEN Content = 6 Mol% Max

GASOLINE Content usually expressed as dew point temperature

e.g. < -10 °C at 50 bar

Chapter 2 - Natural Gas Sweetening

Natural gas may contain high quantities of hydrogen sulfide H₂S and/or carbon dioxide CO₂. The presence of these compounds renders the gas a sour gas.



Primarily this is because sulfur has such adverse effects on the quality of the produced gas, that the concentration of both components has to be reduced from the gas flow before being distributed to users.

The regulations allow a maximum of H₂S equal to 0,002 gr./Nmc (1,31 PPM). The amount of CO₂ in the gas produced will depend on the amount required by the regulations. Typical values allow a maximum concentration of carbon dioxide and other inerts to 4% molar of the gas. If the content of CO₂ is within these values, the process selected to remove the hydrogen sulfide has to avoid the removal of the carbon dioxide.

Gas sweetening technology using alkanolamines to remove sour (acid) components from hydrocarbon-rich gas have been in operation for many years. The alkanolamine processes are particularly applicable where acid gas partial pressures are low or low levels of sour gas are needed in the sweet gas. Alkanolamines are used because they form essential solutions when mixed with water and chemically enhance the absorption of H₂S and CO₂ in the aqueous solution. The necessity of an efficient natural gas sweetening process is due to the following reasons:

- the toxicity of the hydrogen sulfide.
- sulfur dioxide is formed after the gas combustion;
- the corrosive action of sulfur compounds in metals especially with the presence of water even under the form of steam.
- the corrosive action of carbon dioxide
- the problem of hydrogen embrittlement of the vessels containing the gas.
- to reduce corrosion in pipelines and processing equipment
- for economical transportation of gas over long distances

Typically, natural gas desulphurization processes can be grouped into 9 technology categories. These technology categories are as follows:

- 1- Chemical Solvents
- 2- Physical Solvents
- 3- Combination Chemical and Physical Solvents (Hybrids)
- 4- Fixed Beds (Adsorption)
- 5- Cryogenic Distillation
- 6- Membranes
- 7- Direct Conversion (Liquid Redox)
- 8- Scavenging technology
- 9- New Processes – Hybrid (Membrane and Amine, Liquid Redox and Amine)

The first six are used for bulk removal of acid gas and can be tailored to a wide range of outlet concentration. Direct conversion is used for low amounts of H₂S, and scavenging is used for small throughputs or trace removal. A combination of processes can be used for a particular processing requirement. Chemical solvent processes involve the absorption by chemical solutions at preferably high pressure and near ambient temperature. The solvent in an aqueous solution, bonds with the acid gas component, and removes them from the feed gas, the sour gas components are then released when the temperature of the solvent is increased or/and the pressure is reduced. Several alkanolamines solutions have been widely used in the gas sweetening system, including:

1. Monoethanolamine (MEA)
2. Diethanolamine (DEA)
3. Diglycolamine (DGA)
4. Di-isopropanolamine (DIPA)
5. Methyl diethanolamine (MDEA)
6. Triethanolamine (TEA)
7. Glycol plus amine solution.

MEA and DGA react with H₂S, CO₂, and COS directly. DEA and DIPA react with H₂S, CO₂, and some COS directly. While MDEA and TEA are reacted with H₂S directly, CO₂ indirectly and a little COS. The following factors should be considered for evaluation and decision making as a general approach to all sour gas sweetening treatment installations:

1. Air pollution regulations regarding H₂S removal;
2. Type and concentration of impurities in sour gas;
3. Specification of treated gas (sweet gas);
4. Temperature and pressure at which the sour gas is available and at which the sweetened gas should be delivered;
5. The volume of the gas to be treated;
6. Hydrocarbon composition of sour gas;
7. Selectivity required for acid gas removal;

8. Capital cost and operating cost;
9. Liquid product specifications.

Below are discussed some alkanolamines which use in the gas sweetening system. Common chemical solvents include aqueous solutions of amines, inorganic salts, or mixtures of them. The amines more commonly used are Monoethanolamine (MEA), Diethanolamine (DEA), Methyldiethanolamine (MDEA) and Diglycolamine (DGA). The inorganic salts are mostly essential carbonate solutions and caustic soda.

In general, the selection of a proper gas treating process involves consideration of the following factors:

- Gas composition, including CO₂, H₂S, and trace sulfur components.
- Inlet pressure and temperature.
- Treated gas purity specification. Avoid removing more CO₂ than required to meet Specs.
- Need for selectivity.
- Co-absorption of hydrocarbons.
- Process Capital and Operating costs, including the cost of solvents and their availability.
- Process royalty fees, if any.
- Corrosion/Metallurgy Requirements.
- Process experience with similar treating requirements.
- Chemical degradation and evaporation losses.
- Process support from the licensor, availability of chemicals/spares at a location.
- Environmental performance, disposal of effluents.
- Water content for raw and treated gas.

Process Advantages and Disadvantages Chemical Solvent Process Monoethanolamine (MEA) Process

Monoethanolamine (MEA)



MEA is the strongest base of alkanolamines and reacts most rapidly with acid gasses, and this is why MEA is the first choice in gas sweetening system. MEA have 1.7 times more capacity for acid gases on a weight basis than DEA or DGA. Therefore a lower amine solution circulating rate can be used when amine treating with MEA compared to treating with DEA or DGA. MEA has a good thermal stability, can easily be reclaimed from contaminated solutions, good COS removal and less expensive than DEA and DGA.

There some things that should be considered when using MEA:

1. MEA should commonly be used as a 10 to 20% solution in water.

2. The acid gas loading should usually be limited to 0.3 to 0.4 moles acid gas per mole of amine for carbon steel equipment.
3. MEA's degradation products are very corrosive. COS, CS₂, SO₂ and SO₃ can partially deactivate MEA, which may essentially require to be recovered with a reclaimer.
4. MEA has a high pH that makes MEA produce gas containing less than ¼ grains H₂S per 100 S.ft³ of acid gas at very low H₂S partial pressures.
5. MEA will easily reduce acid gas concentrations to Pipeline Specifications (0.25 grains per 100 S.ft³). By proper design and operation, the acid gas content can be reduced as low as 0.05 grains per 100 S ft³).
6. The heat of reaction for CO₂ in MEA is about 1930 kJ/kg of CO₂ (460 kcal/kg of CO₂).

Advantages

- High reactivity.
- Low solvent cost.
- Good thermal stability.
- Ease of reclamation.
- Low hydrocarbon content of acid gas produced.
- Lower plant investment compared to other amine processes.

Disadvantages

- Inability to cope with and gas containing O₂, CS₂.
- Will remove all the CO₂.
- Higher vaporization losses than DEA, MDEA.
- Ineffective for removing mercaptans.
- High residual acid gas concentration in lean amine.
- Non-selectivity for removing H₂S in the presence of CO₂.
- Higher utilities than hot pot and most physical solvent processes.
- Most corrosive amine.
- Freeze point 50°F – Transportation of 15% water solution may be required (Freeze point 9°F).
- If gas is not saturated reverse osmosis water or equivalent is needed to maintain amine concentration, it will re-hydrate dry gas. This is a general point for amines.

Diethanolamine (DEA) Process

DEA is a secondary alkanolamine, it has a reduced affinity for H₂S and CO₂. DEA has very low vaporization losses and excellent stability in the presence of CO₂, COS, and CS₂. Degradation reaction with CO₂, COS, and CS₂ proceed at a much slower rate, and the products are non-corrosive, thus reclaiming is not need to control the level of DEA degradation products.

DEA is not selected when the absorber feed stream contains high levels of a strong acid (chlorides, SO₂, SO₃, thiocyanic acids), organic acids (formic, acetic, nepthanic acids),

CO, oxygen, and cyanides. Because they react with DEA to form heat stable salts (HSS), which are stable at regenerator conditions. HSS can cause loss of DEA, solution foaming, and localized corrosion.

DEA is seldom chosen for application where reclaiming will be needed to control the buildup of HSS due to DEA's low volatility need a high vacuum reclaimer to avoid excessive reclaiming temperature. Some things that should be considered when using DEA:

1. DEA is commonly used in the 25 to 35 mass percent ranges.
2. The loading for DEA is limited to 0.3 to 0.4 mole/mole of acid gas for carbon steel equipment.
3. When using stainless steel equipment, DEA can safely be loaded to equilibrium. This condition can be considered for carbon steel equipment by adding inhibitors.
4. The degradation products of DEA are much less corrosive than those of MEA.
5. COS and CS₂ may irreversibly react with DEA to some extent.
6. DEA has a reduced affinity for H₂S and CO₂. As a result, for some low pressure gas streams,
7. DEA cannot produce Pipeline Specification gas.
8. DEA will be selective toward H₂S and will permit a significant fraction of CO₂ to remain in the product gas.
9. The heat of reaction for DEA and CO₂ is 151 kJ/kg of CO₂ (360 kcal/kg of CO₂) which is about 22% less than for MEA.

Advantages

- Resistance to degradation by COS and CS₂.
- Lower vaporization losses and regeneration energy required.
- Less corrosive.

Disadvantages

- Lower reactivity.
- Higher recirculation rates.
- Higher solvent costs.
- In CO₂ only services, it will degrade and be very corrosive.
- Lack of selectivity for H₂S and CO₂.
- If gas is not saturated reverse osmosis water or equivalent is needed to maintain amine concentration, it will re-hydrate dry gas.
- Freeze point 80°F – Transportation of 15% water solution may be required (Freeze point 28°F).
- Difficult to reclaim – Vacuum distillation, ion exchange.

methyldiethanolamine (MDEA)

Advantages

- High selectivity of H₂S over CO₂.
- High acid gas loading per mole of solvent.
- High solvent concentration.
- Low regeneration energy.
- Low solvent circulation.
- Low degradation due to contaminants.
- Selectivity not affected by low pressure

Disadvantages

- Higher solvent cost.
- Loss of selectivity for H₂S over CO₂ as the concentration of H₂S is increased.
- Little increase in allowable loading with an increase of pressure.
- Tends to be foamy due to hydrocarbon co-absorption.
- If gas is not saturated reverse osmosis water or equivalent is needed to maintain amine concentration, it will re-hydrate dry gas.
- Reclamation process more complicated.

Diglycolamine (DGA) - Econoamine

Diglycolamine (DGA)

DGA is a primer alkanolamine; it has much high molar concentration that can be used in solution without excessive DGA losses due to degradation and without excessive corrosion rates. This allows more acid gases to be absorbed per gallon solution in lower solution circulation rates (cost-saving and investment savings). DGA has a very low the freezing point, which is good for cold climates. Also provides partial dehydration of the stream being treated. DGA has good thermal stability, can be reclaimed from contaminated solutions, and good COS removal. DGA is better mercaptan removal due to of high concentrations of DGA in solution which increases the solubility for higher molecular weight mercaptans in the DGA solution.

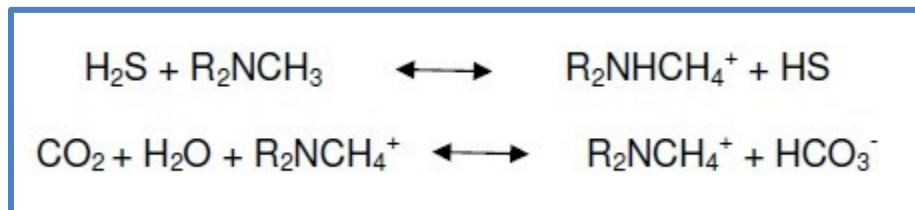
The advantages of DGA are its high solubility of gaseous and liquid carbon especially in C₅+ hydrocarbons. It will result in higher hydrocarbon losses in the vapor from the rich solution hydrocarbon flash/skimming drum and in regenerator overhead acid gas stream.

Higher hydrocarbon levels in the DGA regenerator overhead acid gas increase the risk of operating problems in the downstream sulfur recovery unit. Some things that should be considered when using DGA:

1. DGA is generally used as 40 to 60 mass percent solutions in water.
2. For gas streams with acid gas partial pressures, absorber bottoms temperatures as high as 82°C and above can occur. This will reduce the possible loading.
3. DGA has a tendency to preferentially react with CO₂ over H₂S.
4. DGA has a higher pH than MEA and thus can easily achieve 6 mg H₂S/ Sm³ gas (0.25 grains per 100 S.ft³) except in some cases where large amounts of CO₂ are present relative to H₂S.

The following factors should be considered when selecting an amine for a sweetening application as outlined here in under:

1. The pressure and acid gas content of the sour gas as well as the purity specification for the product gas.
2. MEA is used for plants where the inlet gas pressure is low and Pipeline Specification gas or total removals of the acid gases are required. MEA is not preferred for its high heat of reaction and lower acid gas carrying capacity per unit volume of solution.
3. DEA is used for its lower heats of reaction, higher acid gas carrying capacity and resultant lower energy requirements. Its potential for selective H₂S removal from streams containing CO₂ has not fully been realized.
4. DGA has very high gas carrying capacity usually produces very reasonable net energy requirements although has high heat of reaction. DGA also has a good potential for absorbing COS and some mercaptans from gas and liquid streams, and because of this, DGA has been used in both natural and refinery gas applications.
5. MDEA, with its some outstanding capabilities, resulting from its low heat of reaction, can be used in pressure swing plants for bulk acid gas removal. MDEA is currently best known for its ability to preferentially absorb H₂S.



Reaction between acid gas and amine

Advantages

- High reactivity
- The solution is resistant to freezing better for cold climates
- Effective in removing RSH components
- Very high concentration solution, lower circulation rates

Disadvantages

- Absorbs heavy or aromatic hydrocarbons (an advantage in processes where traces of heavy hydrocarbons will cause problems, i.e., Benzene removal for LNG production)

- Proprietary process
- If gas is not saturated reverse osmosis water or equivalent is needed to maintain amine concentration, it will re-hydrate dry gas

SCHEME AND FUNCTIONING

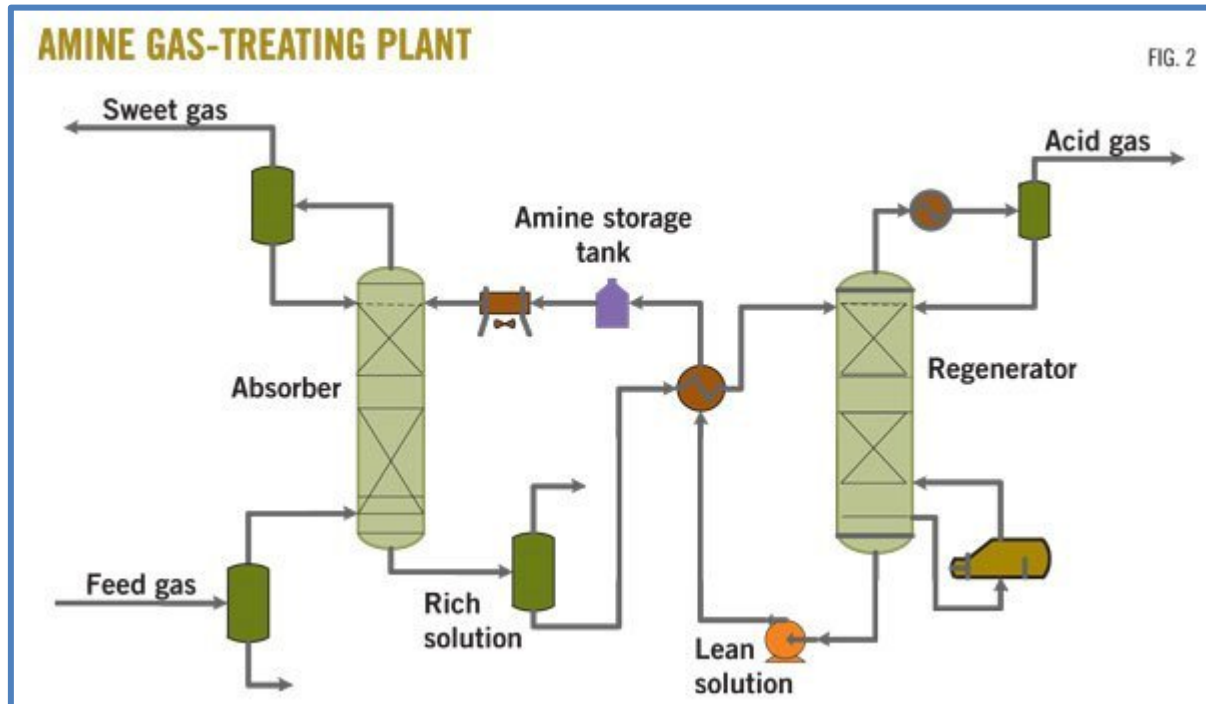
In a chemical solvent process, the acid gas components are chemically attached to the solvent. With chemical solvents, CO₂ rich gas can be treated to low levels of CO₂ without deep regeneration of the solvent. However, there is a limit to the CO₂ removal capacity of these solvents.

This limit is independent of CO₂ partial pressure, as it is determined by stoichiometry and corrosion prevention. The reaction rate H₂S with amine is much faster due to its higher acidity and is readily removed from the feed gas.

Chemical solvents are most suitable for handling gases with relatively low partial pressures of CO₂ or where a very low level of CO₂ in the treated gas is required. Usually, energy requirements for chemical solvents are relatively higher.

Most chemical solvent sweetening processes involve absorption by chemical solutions at high pressure and at low temperature. A solvent in the aqueous solution will react with the acid gas components to form a complex. The solvent bonds with the acid gas components in a chemical manner until the temperature of the solvent is increased and/or the pressure is reduced. At this time, the complex is decomposed, and the sour components released.

A sweetening plant operation on amine consists mainly of two pieces of equipment, i.e.:
– the packed absorber or plate absorber where the gas is washed with an absorbent;



– the distillation column (de-absorber) where the absorbed substances (hydrogen sulfide, carbon dioxide) are separated from the absorbent until regeneration. With reference to the scheme, the gas containing hydrogen sulfide and carbon dioxide enters the lower part of the absorption tower. In contrast, the aqueous amine solution begins at the top in a counter-current fashion.

The sweet gas comes out of the tower top, whereas the amine rich solution, now saturated with hydrogen sulfide and/or carbon dioxide, is gathered at the bottom of the tower. The rich solution is warmed up the heat contained in the regenerated solution, its pressure reduced to allow the removal of the acid gases and then is sent to the top of a distillation tower. The rich solution is regenerated with the steam developed by the reboiler.

After the regeneration process, the solution of amine passes, as mentioned before in heat exchangers where it is cooled. Then it goes back into circulation through a pump. To cool the solution to an ideal absorption temperature, a water or air exchanger is installed between the pump and the absorption tower. The acid gases, that is hydrogen sulfide and/or carbon dioxide, exit at the top part of the regeneration tower and after having been cooled off, in a water or air exchanger. After the cooling water is formed, and , is pumped into the regeneration tower to create reflux to limit the losses of amine.

Chapter 3 - What are Hydrates and what is Hydrate Prevention

Hydrates are crystallized, compact, porous, and rather light mass, similar to compressed snow. They are made of water, hydrocarbons, H₂S, and CO₂.



Hydrate Removed from a Pipeline

Unlike ice, hydrates have an unusual characteristic: they form at a temperature that is above water freezing point. For instance, they can create at 20 °C at particular pressures.

When they are exposed to air, they dissolve chugging and fizzing because of the gas that is more or less slowly freed according to the surrounding temperature.

When they are lit in the air, they can slowly and completely burn, until they leave a small residue of water. This does not represent the quantity of water they actually contain, as part of the water content is lost through evaporation. Hydrates form quite quickly by simple contact of gas and water, and the formation is related to the conditions of temperature and pressure, according to the law of equilibrium.

They can quite frequently form in lines that gather gas from the various wells and transport it to the central treatment station where it undergoes dehydration. This formation of hydrates can partially or totally obstruct the lines, limiting or hindering the transportation of gas Hydrates can form only if the following conditions occur:

- a) presence of H₂O in the liquid state
- b) presence of hydrocarbons
- c) turbulence (created by curves, collisions, etc.)
- d) for a given pressure, only if the temperature is lower than a specific value.

Industry researchers experimented with the mixtures of gas with different compositions to determine the formation curves of hydrates.

Methods to prevent the formation of hydrates

To reduce the possible formation of hydrates in a line that transports natural gas, it is essential that:

- a) there is no free water;
- b) the temperature is higher than that required for hydrates formation.

If one of these conditions cannot be removed, it is necessary to use other systems to prevent the formation of hydrates:

- a) the use of inhibitors (anti-freezing agents), i.e., substances capable of decreasing the hydrate formation temperature.
- b) Water removal from the gas

Hydrates elimination

The method for hydrates elimination depends on the nature of the obstruction.

Partial clogging: can be located when the pressure and the gas flow in the conducts vary. This is due to a partial obstruction in the conduct.

In this case, the operator should check if a hydrate prevention system has been installed upstream the hydrate clog (i.e. a heater or an inhibitor injection system) and if it functions properly.

The interventions that can follow are:

- temperature increasing of the outlet gas released by the heater;
- Increasing of the inhibitor rate.
- The inhibitors injections upstream the choke.

Complete clogging: The complete clogging with hydrates provokes a total production shutdown, so the methods adopted in case of partial clogging are no longer valid. In this case, decompression will be the proper method for melting.

The decompression must be carefully carried out, since it can be dangerous.

First of all, the pressure upstream the choke has to be reduced by balancing the pressures upstream & downstream the choke itself. This is done in order to avoid that a higher ΔP and the hydrates clog detachment can have evident consequences on the pipeline.

Once the pressure is balanced, the contemporary released upstream and downstream depressurisation must reach the atmospheric pressure.

At this point the clog melts on its own, having absorbed the molecules of gas at the pressure level in which the hydrate had formed.

From the nature of hydrates and their formation it can be stated that, correct gas treatment must be carried out so that such dangerous formations are avoided.