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Dynamics of Solid Bed Dehydration in a Niger Delta Natural Gas Liquids Plant

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ABSTRACT

This work focuses on the study of a natural gas liquid solid bed dehydration plant in the Niger delta. The dehydration system of the plant is made of a 3-bed cycling unit placed upstream the cryogenic section of the plant to prevent hydrate formation (desired dew point of -101^{0}C). The system comprised three (3) solid desiccant beds, which are packed with molecular sieves and alumina balls. Each bed had a maximum design capacity of 300million standard cubic feet per day. The dehydrator beds are configured to operate under a timed cycle, such that two (2) beds are always online while the third bed is undergoing regeneration. During the dehydration (drying) cycle, the amount of moisture adsorbed by the molecular sieves, at different cross section of the tower varied with time. At the initial stage of the drying cycle, most of the moisture was adsorbed by the molecular sieves at the top of the bed, since the flow direction was from top to bottom. Thus, as the gas flowed through the bed, the molecular sieves at the bottom only adsorbed traces of water, which were not adsorbed at the top. This enabled the attainment of the required dew point or maximum parts per million (ppm) of water in the gas. Based on this, it was noted that the topmost layer of the molecular sieves got saturated first and with continuous flow of gas through the bed, the saturated layer of the molecular sieves moved gradually, with time to the bottom of the bed. This resulted in the formation of a saturation gradient across the height of the bed. Critical examination of the dehydration, regeneration and cooling processes of the beds revealed that for effective and optimum results, dehydration was done for approximately 1200mins, regeneration 410mins and cooling 150mins while De-pressurization and re-pressurization took 20mins.

Keywords: *Dew point, Molecular sieves, saturation gradient, dehydration, regeneration, cooling process.*

1. INTRODUCTION

It has been verified that a greater percentage of the water content of natural gas exist freely and physically i.e. they are not chemically bound to the hydrocarbon molecule, thus it can be removed by physical methods of separation. To achieve this, a material which has very high selective affinity for water molecules, but at the same time would not chemically react with water nor the hydrocarbon components of the natural gas, form the base for the dehydration material (desiccant). Apart from being chemically non-reactive, the desiccant material (solid or liquid) should not also adsorb/absorb much of the hydrocarbon components of the natural gas and should be easily regenerated for continuous re-use, thus making it economically suitable. The dehydrated gas is expected to withstand changing conditions of temperature and pressure depending on its intermediate or final application, without condensing out free water or hydrocarbon liquids.

The removal of water vapor which exists in solution in natural gas requires some form of complex treatment (Christensen, 2009). This treatment involves one of two processes: either absorption or adsorption.

- **Absorption** occurs when the water vapor is taken out by a dehydrating agent (liquid desiccant). Here, the water vapor becomes absorbed into the material (Huffmaster, 2004).

- **Adsorption** occurs when the water vapor is condensed and collected on the surface of the dehydrating agent (solid desiccant). In adsorption, the water molecule physically sticks to the surface of the solid material.

1.1 Adsorption by Activated Solid Desiccants

Solid desiccant dehydration is the primary form of dehydrating natural gas using adsorption, and it usually consists of two or more adsorption towers, which are filled with solid desiccants. The solid desiccants are characterized by internal porous structure that contains very large internal surface area (e.g 200-800m^2/g) with very small radii of curvature (0.001-0.2um); (Manning & Thompson, 1991). The equilibrium partial pressure of water vapor above such concave surfaces is much less than that above the plane surfaces and so solid desiccants exhibits a very great affinity for water. These desiccants exhibit capacities from 5 -15% on a weight basis and can dry natural gas to less than 0.1ppm of water or a dew point of -101^{o}C

There are various materials which are being used as solid desiccants and they have the physical characteristics to adsorb water from natural gas. Adsorbents in common commercial use include the following:

- Silica Gel; Silica-based beads; Activated alumina; Alumina-gel balls; Activated bauxite.
- Molecular sieves.

1.2 Molecular Sieves

This is the most versatile adsorbent because it can be manufactured for specific pore size, depending on the application. It is:

a) Capable of dehydration to less than 1ppm water content.

b) The overwhelming choice for dehydration prior to cryogenic processes.

c) Excellent for H_2S removal, CO_2, dehydration, high temperature dehydration, heavy hydrocarbon liquids, and highly selective removal.

d) More expensive than silica gel and alumina, but offers greater dehydration.

e) Requires higher temperature, for regeneration.

When very low dew points are required, solid-bed dehydration becomes the logical choice. It is based on fixed-bed adsorption of water vapor by a selected desiccant. A number of solid desiccants could be used such as silica gel, activated alumina, or molecular sieves. The selection of these solids depends on economics. The most important property is the capacity of the desiccant, which determines the loading design expressed as the percentage of water to be adsorbed by the bed. The capacity decreases as temperature increases (Julie and Henry, 2011).

The equipment and process flow arrangements for each of the adsorbents are essentially the same with the possible exception of molecular sieves which normally require higher regeneration temperatures. A typical plant for water vapor removal by adsorption will consist of two or more vessels filled with granular desiccant along with auxiliary equipment for desiccant regeneration.

In the case of adsorption towers, the wet natural gas flow from the top of the tower and exit at the bottom (unlike that of the liquid absorption, in which the flow is from bottom to top). This is to prevent fluidization of the bed in the event of accidental increase in pressure in the wet natural gas. As the wet gas passes around the particles of the desiccant material, water is retained (adsorbed) on the surface of these desiccant particles. The desiccant material is properly placed inside the tower such that channeling (uneven flow-path inside the bed) is avoided, as this could hamper the efficiency of the adsorbent and subsequently, the whole dehydration process. Passing through the entire desiccant bed, almost all of the water is adsorbed onto the desiccant material, leaving the dry gas to exit at the bottom of the tower. In a system like this, two or more towers are required due to the fact that after a certain period of continuous adsorption, the desiccant in the tower becomes saturated with water, after which it can no longer adsorb water from the wet gas. At this point, the flow of the wet natural gas is diverted through a second tower in which the desiccants are fresh and ready for dehydration. At the same time, the first bed would require regeneration to remove the adsorbed moisture from the surface of the adsorbents.

1.3 Regeneration of Solid Desiccants

This involves the removal of water from the surface of the desiccant material. This is achieved by using a high temperature heater to heat up a gas stream called ***regeneration gas*** to a certain temperature depending on the desiccant material used for dehydration. The hot regeneration gas is then passed through the saturated desiccant bed to vaporize the water from the desiccant, leaving it dry and ready for another dehydration process. During regeneration, the hot regeneration gas flows through the bed from bottom to top (reverse of dehydration), thus driving off the water vapor from the surface of the desiccant in the direction of its flow.

The areas of application of dry desiccant processes include cases where essentially complete water removal is desired and installations in which the operating simplicity of the granular desiccant system makes it attractive (Kohl, 1985). Solid desiccant dehydration is generally specified if dew point depression consistently greater than 80^0F are required.

1.4 Thermal Swing Regeneration

The simplest and most common way of regenerating an adsorbent in industrial application is by heating. The vapor pressure exerted by the adsorbed phase increases with temperature, so that the molecules desorb until a new equilibrium with the fluid phase is established. An adsorption unit using thermal swing regeneration usually consists of two packed beds, one online, one regenerating. The desorption temperature depends on the properties of the adsorbent and the adsorbates. Exceeding the design temperature may accelerate the ageing processes which cause pores to coalesce and capacity to be reduced. A temperature which is too low could also result in incomplete regeneration so that the water content of the dry gas in subsequent adsorption will increase.

The relatively poor conductivity of a packed bed makes it difficult to get the heat of regeneration into the bed. This is easily achieved by preheating the regeneration gas. Even in the best conditions, it takes time for the temperature of the bed to rise to the required level. Thermal regeneration is normally associated with long cycle times. Such cycles require large beds and, since the adsorption wave occupies only a small part of the bed on-line, the utilization of the total adsorbent in the unit is low.

1.5 Pressure Swing Regeneration

An alternative to thermal swing regeneration is to use pressure rather than temperature as the thermodynamic variable to be changed with adsorption taking place at high pressure and desorption at low pressure- hence the description ***pressure swing adsorption.*** Because changes in pressure can be brought about more rapidly than changes in temperature, pressure swing regeneration can be used with shorter cycle times than was possible with thermal swing. This in turn allows smaller beds to be used and consequently a smaller inventory of adsorbent is needed in the system.

Pressure swing regeneration is useful when the stream to be treated is needed at pressures above atmospheric. Pressure swing units are compact and can be readily be made portable. When the process stream is at atmospheric pressure or below, then it is possible to regenerate using a partial vacuum.

2. OVERVIEW OF THE NATURAL GAS LIQUID (NGL) PLANT

This is a Natural Gas Liquid (NGL) extraction plant which functions primarily to extract NGL (propane plus) from the gas stream through adiabatic, turbo-expansion-liquefaction and fractionation processes. The plant is designed to handle a maximum of 600million standard cubic feet of natural gas per day, with the feed composition comprised mostly of methane, ethane, propane, butane, pentane and traces of water.

The NGL extraction process is cryogenic (-79^{o}C) in order to condense out propane-plus from the gas stream, after which the methane and ethane are removed in a de-ethanizer tower. Under this cryogenic condition, any traces of water molecules in the gas stream would result in hydrate formation which could pose serious operational inefficiencies for the plant. Thus, in order to inhibit this formation of hydrates, a dehydration unit is installed upstream of the cryogenic section of the process (Conder and King, 2004).

3. SPECIFICS OF DEHYDRATION SYSTEM UNDER STUDY

The system comprises three (3) solid desiccant beds, which are packed with molecular sieves and alumina balls. Each bed has a maximum design capacity of 300million standard cubic feet per day. The dehydrator beds are configured to operate under a timed-automated cycle, such that two (2) beds are always online while the third bed is undergoing regeneration. The feed gas stream flows through the two (2) beds online, from top to bottom, via a baffle placed at the top of the dehydrators. The baffle ensures a uniform spread of gas flow through the molecular sieve balls, thereby preventing ***channeling.*** As the gas flows through the beds, water molecules are adsorbed unto the surface of the molecular sieves, which have been specifically designed with pores to increase its surface area. The gas exits the dehydrators with a dew point of -101^{0}C. With the continuous adsorption of moisture from the feed gas stream, the molecular sieves gradually become saturated and thus require regeneration to prevent a carry-over of moisture (known as ***breakthrough***) into the cryogenic part of the process.

The regeneration system uses a dry residue gas (methane and ethane) separated from the NGL to drive moisture off the molecular sieves. The regeneration gas is heated by a waste heat recovery unit (turbine generator exhaust heat) from where it enters the bottom of the bed at a temperature of 266^{0}C and 2549.7KPa at a flow rate of 45mmscf/d. As the hot gas flows through the bed in counter-current direction, it vaporizes the water molecules adsorbed on the molecular sieve surface and it flows out from the top of the bed to a regeneration knock-out drum, via a cooler.

At the completion of the heating cycle, the cooling cycle begins. During cooling, the regeneration gas is not heated, but flows directly to the bed at a temperature of 37.7^{0}C. The pressure, flow rate and direction of flow remain the same with that of the heating period.

Table 1: Dehydration and regeneration parameters

EVENTS	PARAMETERS	INLET	OUTLET
Dehydration	Feed Pressure(Kpa)	8819.2	8715.9
	Feed Temperature(^{0}C)	40.5	40.5
	Feed Flow(MMscf/d)	300 max	300 max
	Dew Point(^{0}C)		-101.0
Regeneration	Heating Gas Pressure(Kpa)	2549.3	2411.5
	Heating Gas Temperature(^{0}C)	266.0	241 min
	Heating Gas Flow(MMscf/d)	45.0	45.0
	Cooling Gas Temperature(^{0}C)	37.7	40.5

4. ANALYSIS OF THE RESULTS AND DISCUSSIONS

4.1 Analysis of the Regeneration Process

The regeneration process is made up of four (4) different steps which are:

- **Depressurization-** This is the process of reducing the pressure in the bed from the feed pressure (8819.2KPa) to the regeneration gas pressure (2549.3KPa).
- **Heating-** It is the flowing of hot gas through the bed in a counter direction to the normal flow, in order to vaporize and drive off the adsorbed moisture from the surface of the molecular sieves.
- **Cooling-** After heating, the bed needs to be cooled down to its normal operating temperature prior to starting the drying cycle.
- **Re-pressurization-** This involves pressuring up the bed from the regeneration gas pressure to the feed gas pressure. Failure to do this could result in the disorientation/ destabilization of the molecular sieve and alumina balls in the bed.

During heating of the bed, the hot regeneration gas temperature is set to build up gradually, from 121^{0}C to 266^{0}C. This is to ensure a gradual introduction of heat into the bed, therefore preventing or reducing cracking or breakdown of the molecular sieve due to thermal shock. With the counter flow direction, the temperature of the bed gets steadily hotter from the bottom. This temperature gradient causes a *thermosyphon effect* and with the differential pressure across the bed, moisture is vaporized and driven-off from the top of the tower. At the initiation of the heating cycle, vaporization of water moisture from the bed does not take place, but rather the heat content of the hot regeneration gas is consumed through the latent heat of vaporization of water. The upward water drive through the bed starts from the bottom layer, therefore the molecular sieve at the bottom gets de-saturated first. The removal of water moisture from the surface of the molecular sieve with respect to time is graphically represented below.

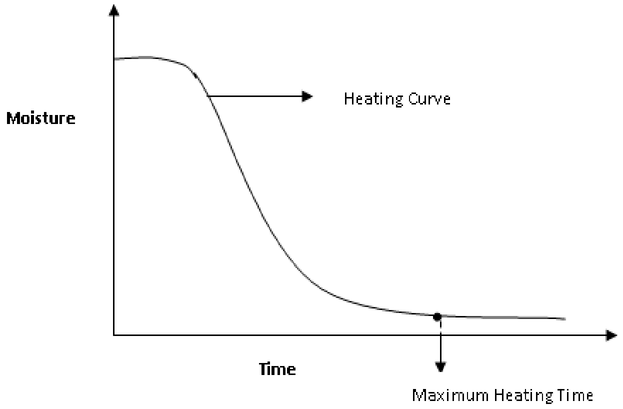

Fig 1: Graphical representation of moisture removal (Heating)

The evaluation of the rate of temperature change at each layer of the molecular sieve indicates a gradual increase in the temperature as more moisture is driven-off the layer. At complete de-saturation of the molecular sieve, the temperature increases rapidly until it reaches the temperature value of the hot gas at the inlet. At this point, the bed is considered fully regenerated and ready for cooling. The graphical representation of the temperature change with time is shown below.

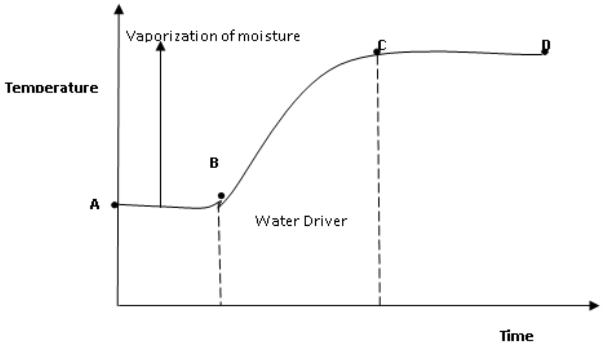

Fig. 2: Temperature profile during heating cycle

From the figure:

a) AB represents the moisture-vaporization phase, where the temperature of the molecular sieve remains relatively constant over a period of time, as a result of the heat energy being converted to latent heat of vaporization.

b) BC shows the actual water drive zone, in which the temperature of the molecular sieve rises gradually to a maximum (point C) where it equates with the regeneration gas temperature..

c) CD is another constant temperature zone at which the hot gas exiting the bed almost equals the one entering the bed. This is an indication that the water adsorbed by the molecular sieve has been completely removed, hence the bed de-saturated.

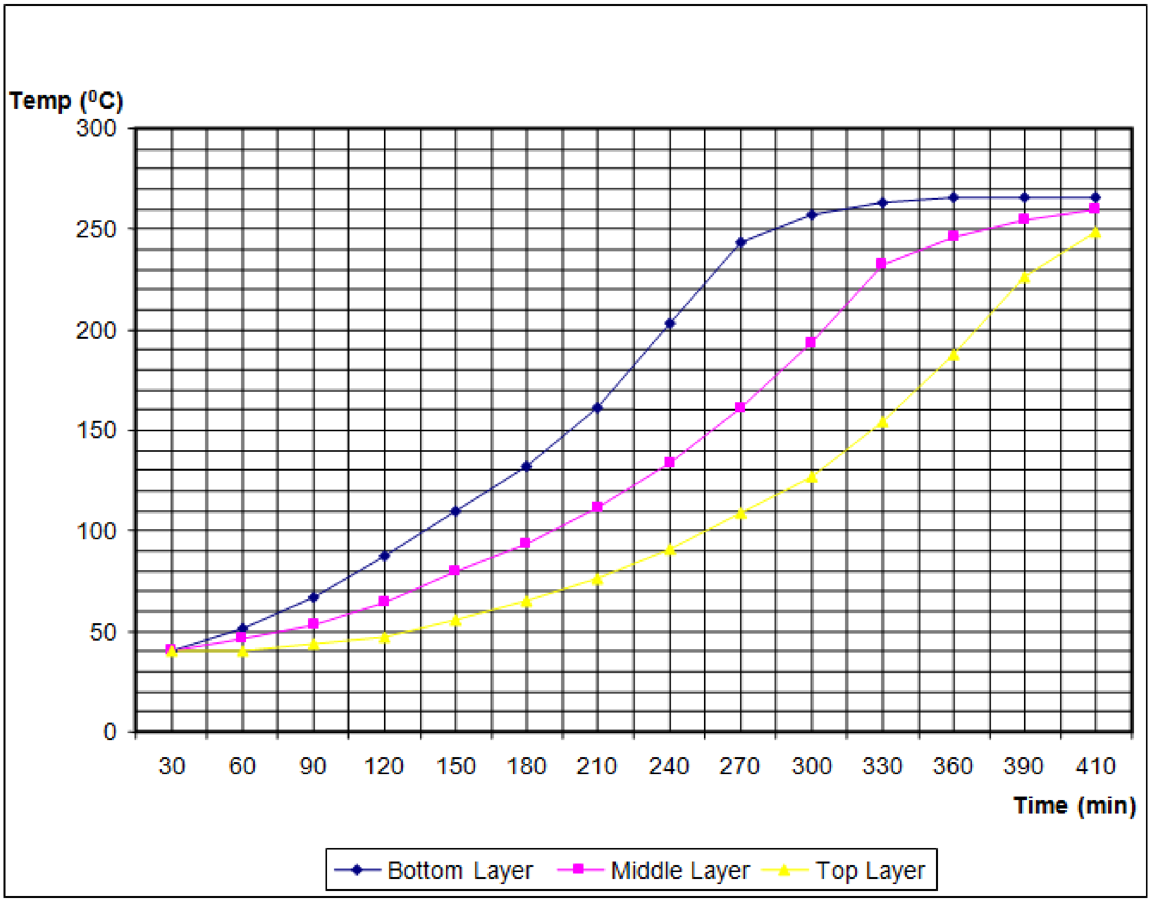

Fig. 3: A Temperature Profile of bed plotted against time during heating cycle

Further assessment of the regeneration process, using the level control system of the regeneration knockout drum revealed a trend that represents the heating process. The final control element (level valve) in the level control loop is meant to maintain a constant level set-point in the vessel. A study of the operation and functionality of this control valve showed that; at the beginning of heating, the valve remained in a closed position, but starts opening as the water drive begin. The opening increased correspondingly as more moisture is driven-off the molecular sieve bed. The opening of the valve is in response to the gradual increase in liquid level in the knockout drum. At the end of the water drive, the liquid level in the vessel started to drop thus reducing the opening on the valve. This is reflected in the figure below.

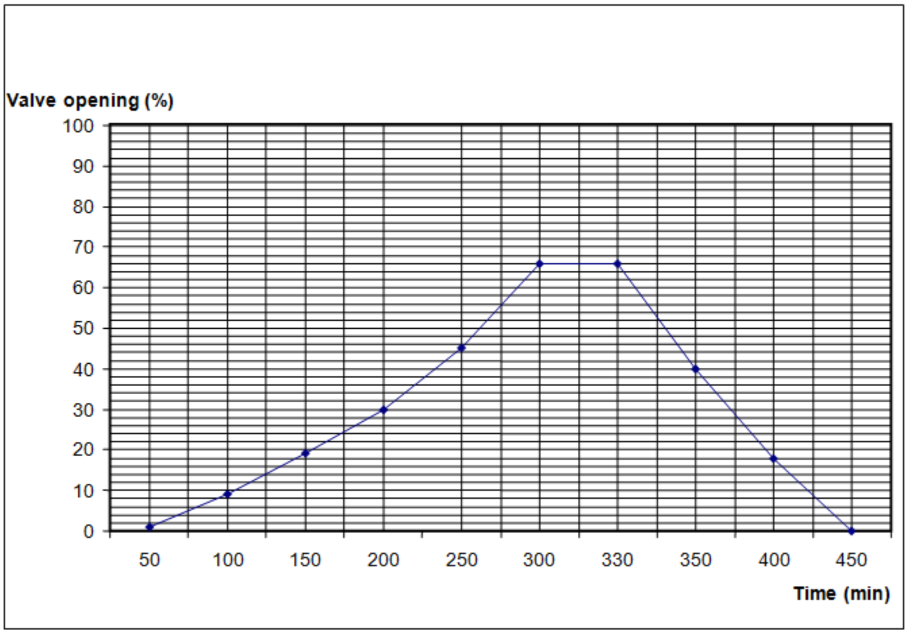

Fig. 4: Level valve reaction in the regeneration liquid knockout drum

4.2 Cooling Cycle

The re-introduction of feed gas into the molecular sieve bed after heating would cause a pressure surge as the feed gas would expand drastically at such high temperature and could result in over-pressuring and/or explosion of the column. In order to avoid this, the molecular sieve needs to be brought back to its normal operating conditions. This is achieved by the cooling process in which the regeneration gas from the blower flows directly to the bottom of the column. The cooling gas, which flows through the bed in the same direction as heating, absorbs heat from the molecular sieve, thus cooling the bed.

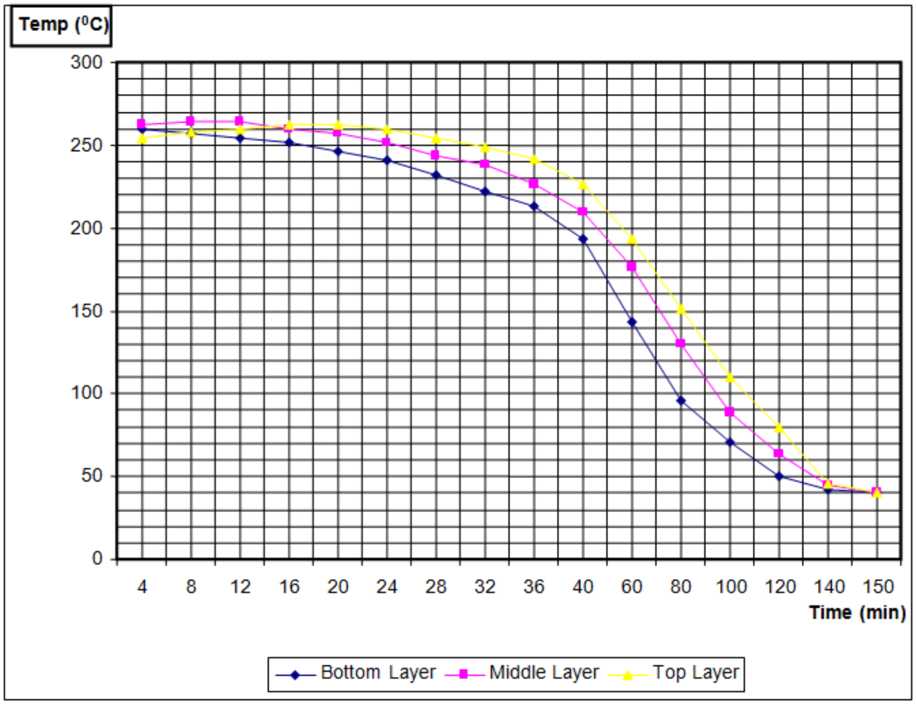

Fig 5. Graphical representation of the cooling cycle

With continuous dehydration and regeneration of the beds, the effectiveness of the molecular sieves begins to deteriorate over time and it gets saturated quickly, thereby reducing the online time of the bed. Also, over-saturation and ineffective regeneration of the bed could result in **caking**, a phenomenon in which the molecular sieves melt and come together to form a single solid structure. This is a very unhealthy situation in the solid desiccant dehydration because it gets to a point in which total replacement of the molecular sieve becomes very necessary and critical.

At the initial stage, a gas composition analysis is carried out to determine the components of the natural gas stream and the water (moisture) content (ppm) of the gas to be processed.

In the solid/liquid dehydration system, the desiccant must be properly regenerated to facilitate continuous and effective dehydration of the gas. The regeneration temperature should be set such that, water would be vaporized from the desiccant at the operating pressure. This is because the vaporization of any liquid is a function of the temperature and pressure the liquid is subjected to.

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