DEWPOINT CONTROL AND PREVENTION OF HYDRATE FORMATION IN THE BRITISH GAS HIGH PRESSURE TRANSMISSION SYSTEM.

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Measures taken by British Gas to implement its policy of operating a dry high pressure natural gas transmission system are described. The importance of retrograde condensation in relation to the specification of dew points limits, and conditions under which hydrocarbon hydrates can form and the methods of inhibiting their formation are discussed. A description is given of the methanol swabbing procedure developed by British Gas to prevent the formation of hydrates during commissioning of new mains which have been hydraulically tested.

INTRODUCTION

The construction of the British Gas high pressure transmission system began in 1963, when a pipeline some 560 km in length and 450 mm diameter was laid from Canvey Island to Leeds for the distribution of 2.7 x $10^6 m^3$ per day of re-evaporated Algerian L.N.G., the importation of which began in October 1964. Since the first discovery of natural gas under the North Sea in 1965, the system has been rapidly extended until it can now handle 150 x $10^6 m^3$ per day, and further development is in hand to deal with gas from the more recently discovered fields in the northern part of the North Sea.

The presence of liquid hydrocarbons and or water in such a system can be a considerable hazard to security or supply, since it could result in damage to filters, malfunctioning of reducing values and reduction of the effective capacity of the system. Hydrocarbon hydrates, being solids, are even more likely to cause such problems if they are allowed to form.

To eliminate the risk of the occurrence of these problems, British Gas decided to implement a policy to operate a dry transmission system. To achieve this, the contracts with the suppliers require them to treat the gas so that it conforms to water and hydrocarbon dew point specifications that ensure that liquids will not condense at any temperature or pressure likely to be encountered anywhere in the system down stream of the reception terminals.

The greatest danger of the formation of hydrocarbon hydrates in large quantities is when new mains are commissioned which still contain water left after hydraulic pressure testing. Considerable quantities of water are left in mains even after swabbing and British Gas have developed a standard pigging procedure with methanol which not only displaces the bulk of the water, but leaves behind a mixture that is rich in methanol which gives a high degree of protection against hydrate formation.

HYDROCARBON HYDRATES

Formation Conditions

Natural gas hydrates are formed under pressure by combination between the lighter hydrocarbons and liquid water. In appearance they resemble wet snow or ice, but may be distinguished by inflammability and the crackling sound they emit on decompression. Hydrates are clathrate compounds in which water molecules are linked together to surround a molecule of hydrocarbon. Although they were initially investigated in Europe work on the aspects of their formation which effects natural gas production was carried out largely in the U.S.A., promoted by early mishaps in transmission.

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The complete phase diagram of a water/hydrocarbon system is complex, but the generalised and simplified diagram shown in Fig.1 illustrates the essential features which are characteristic of any system. Practically the problem is to predict the hydrate equilibrium line BE, and the well established method of doing this is that devised by Katz et al (1).

From the observation that on decomposition the behaviour of gas hydrates resembles that of solid solutions, it was postulated by analogy with vapour/liquid equilibrium that hydrate formation conditions could be calculated from empirically determined vapour/solid equilibrium constants. The accuracy of the method is said to decrease at pressures in excess of 7 MN/m^2. However, pressures in the British Gas transmission system are at present limited to this value, and we are satisfied that it gives sufficiently accurate predictions.

Some years ago London Research Station tested the accuracy of the method over a limited pressure range by experimentally determining the hydrate formation conditions for evaporated Algerian L.N.G. in a simple glass windowed high pressure cell. The good agreement found between experimental and calculated data as shown in Fig.2 In common with the experience of American workers, it was found in these experiments that hydrate formation was difficult to initiate. Conditions far more severe than equilibrium conditions were required to start hydrate formation.

The calculated formation conditions for typical North Sea gases are compared with that for Algerian L.N.G. in Fig.3. These curves illustrate the effect of gas composition on formation conditions; the larger proportion of ethane and propane in the Algerian gas significantly lowers formation pressure as compared with North Sea gases. The hydrate formation properties of individual North Sea gases do differ a little from those quoted, but this is of little importance since it would be unwise to attempt to operate at conditions which very closely approach the calculated limits.

Prevention of Hydrates

Once hydrate has formed in a transmission system it can be decomposed by lowering the pressure or by raising the temperature of the system, or by a combination of both. Whilst these methods are used in practice, their application is however generally limited to short lengths of main or individual items of pipeline equipment. Temporary heating is not always readily available and lowering the pressure could be a greater embarrassment than the already existing restrictions in supply caused by the hydrate.

The only practicable method of hydrate prevention and decomposition is by the introduction of a chemical as an inhibitor into the system. Among the most effective are ammonia and methanol, though the use of the former has obvious drawbacks. Salts such as sodium and calcium chlorides are almost as effective as methanol, but difficult to apply and leave behind solid residues. Glycols are used where continuous addition is necessary and recovery can be practiced.

Again, not surprisingly, the principle workers in the field have been Americans, and the information available in the literature on the suppression of hydrate formation is commonly derived from the work of Hammerschidt(2).

Methanol is used exclusively by British Gas for hydrate control, and the degree of suppression of formation temperature predicted from (2) by various amounts of methanol in the aqueous phase is given in Table 1. It is independent of pressure.

TABLE 1 - Depression of Hydrate Formation Temperatures by Methanol.

Methanol % w/w in Liquid	Temperature Depression,K
5	2
10	4
15	7
20	10
25	13
30	17

In practice the actual amounts of water present or the quantity of hydrates formed is unknown. It is therefore necessary to add methanol to the gas at a rate such that the gas phase concentration is in equilibrium with the necessary liquid phase concentration required to effect the desired depression of hydrate formation temperature. The necessary experimentally determined equilibrium data between methanol in the gas and liquid phases is presented graphically in (2).

Table 2, which is derived from this source shows the concentration of methanol in the aqueous liquid in equilibrium with four different concentrations of methanol in the gas, as a function of pressure at 278K.

TABLE 2 - Equilibrium of methanol between Gas and Water at 278K.

Methanol in gas, mg/m^3 (1 atm, 288K) -	200	300	400	500
Pressure, MN/m^2	Methanol in liquid, % w/w			
2	6	8	11	14
3	7	11	15	18
4	9	13	18	22
5	10	16	21	26
6	12	18	23	29
7	13	20	26	33

However, the information contained in Tables 1 and 2 and Fig. 3 are not in the most convenient form for use by the engineer in charge of operations. Knowing the pressure in the system and the minimum temperature likely to be attained, he requires to know the quantity of methanol to be added to the gas to prevent the formation of hydrates. It is on this basis that Table 3 has been constructed, which shows hydrate formation conditions for gas in contact with aqueous methanol in equilibrium with four different concentrations of methanol in the gas.

TABLE 3 - Hydrate Formations Conditions for North Sea Gas in the Presence of Aqueous Methanol.

Methanol in gas, mg/m^3 (1 atm, 288K) -	200	300	400	500
Pressure, MN/m^2	Hydrates form at temperatures K, less than:			
2	273	272	270	269
3	277	275	273	272
4	278	276	274	271
5	280	277	274	271
6	280	277	274	270
7	281	277	273	267

Hydrates in British Gas Mains

The occurrence of hydrates in the British Gas high pressure system has been confined to a few incidents during the early operations concerned with the distribution of re-evaporated Algerian L.N.G. from the Canvey Terminal.

The first cargo of L.N.G. arrived from Algeria on 12th October 1964, gassing-up the main to Leeds began on the following day, and hydrate was encountered within two weeks. No provision had been made to deal with this hazard since the gas was extremely dry and it had been intended to dry out the main before admitting natural gas.

After draining and pigging out the water used for hydraulic testing, this drying was attempted using nitrogen from the Coleshill Works, near Birmingham, (where it was produced as a by-product of oxygen production for the Lurgi plant there). Although it was estimated that about 4000 kg of water was removed in this way, calculations showed that more than 30,000 kg still remained in the pipeline.

It was thus appreciated at the start of operations that pressures would have to be kept at the lowest possible levels if hydrates were to be avoided. The hydrate formation curve in Fig.2 indicates the severe limiting pressures which this imposed. However, a steadily rising demand for gas resulting from additional offtakes coming into use, made increases in pressure inevitable.

To hasten the drying of the main, and thus ultimately to reduce the risk of problems with hydrates it was necessary to carry out pigging operations particularly on the northern sections of the main after the main was gassed. It was during these operations that hydrates were first encountered when it was found in front of a pig in a receiving pig trap. On the same day there was a short failure of supply at one offtake which appeared to be due to hydrate blocking a pilot governor on a pressure regulator. As a result of the latter incident the then Area Boards were asked to install as soon as possible means of methanol injection and to arrange for temporary heating of the above ground installations at Area reception points.

During further pigging operations, pigs twice became stuck by plugs of hydrate which built-up in front of them. The pigs were moved by a combination of local methanol injection, lowering of pressures and reversing differential pressures across the pigs. There were also two instances of partial blockage of exposed branch mains which were dealt with by local heating and methanol injection.

After these incidents pigging operations were suspended until continuous methanol injection into the gas could be arranged. The equipment was installed at Derby because dew point measurements indicated that the main line would soon be dry south of that location. At that time, the mean pressure in the main was a little less than 2 MN/M^2 and the minimum,temperature estimated as 278K. It was considered that a depression of hydrate formation temperature of 3.5K should give sufficient protection; this required the addition of methanol at a rate of 400 mg/m^3 as determined by the method outlined above. These methods were continued until dew point measurements indicated that there was no further risk of hydrates forming.

The discovery of natural gas under the North Sea followed closely after these early experiences, and by the time that extensions to the system had to be commissioned in 1967, methods and procedures to be adopted to prevent recurrence of such incidents had been defined, and there have been no further operational incidents attributable to hydrates.

Commissioning New Mains

To avoid the potential danger of the formation of hydrates from the residual water left in mains after hydraulic pressure testing, pigging with methanol was introduced as a mandatory part of the commissioning procedure.

An estimate of the amount of water likely to be present was obtained during the drying out of sections of the Canvey to Leeds main, when it was calculated from dew point measurements and the flowrate and pressure of the gas that the residual water was equivalent to 165 kg per km length of the 450 mm diameter pipe. Assuming that this water was left by the pigs,as an evenly distributed film over the inner surface of the pipe,then the expected residual water in any diameter main can be expressed as:

Water, kg = 0.37 x (pipe diameter mm) x (length, km)

This relationship was a useful guide for determining the quantity of methanol required to displace most of the water from the main and to leave behind a high concentration of methanol which would give adequate protection against hydrate for as long as possible during the drying out period. Very simplified calculations showed that a quantity of methanol equal to 2½ times the anticipated volume of water in the main should be capable of removing 85% of the water and leave behind a mixture containing well over 60% w/w of methanol. Such quantities of methanol, equivalent to 0.9 litre per mm diameter per km length of pipe were used in a number of swabbing operations as a single slug.

Some of the results did not meet the theoretical expectations, and since the results which can be accepted as indicating a successful operation are to some extent arbitary, the specified limits adopted were modified in the light of practical experience and it was agreed that the final liquid pigged out should contain not less than 60% w/w of methanol, and that the volume of the liquid recovered should exceed 80% of the volume of methanol used. Acceptance was later relaxed to include results which represented an approximately equivalent degree of water removal, but limited by stipulating a minimum liquid recovery of 60% of the methanol used, or containing not less than 50% w/w of methanol.

Later when some further actual data became available it was possible to calculate the amount of water initially present in the main, and this was found generally to exceed the previously estimated quantities. As a result in an attempt to ensure that a satisfactory result would be obtained in a single operation, the quantity of methanol used was increased by 50% to 1.4 litre per mm diameter per km length, and the total quantity divided into two slugs to increase further the efficiency of the operation.

In the combined methanol pigging, purging, and gassing procedure, the first slug of methanol contained between pigs is preceeded by a slug of nitrogen equal to 10% of the length of the section of main and separated from the second slug of methanol by a slug of nitrogen 800m long. The complete procedure is incorporated in a British Gas Code of Practice (3).

Although the liquid left in the main after these operations contains a percentage of methanol usually far in excess of that required to prevent hydrate formation, since methanol is more volatile than water, it will evaporate preferentially into the gas, leaving behind a continuously diluting solution of methanol. To monitor this situation, frequent determinations are made of the water dew point and methanol concentration in the gas downstream of newly commissioned mains, so that if necessary methanol can be added to the gas to maintain the necessary concentration in the liquid phase. This methanol is injected at the terminals where storage and pumps are permanently sited.

DEW POINT CONTROL

To ensure trouble free operation of a natural gas transmission system it is necessary to prevent the condensation of liquid water and hydrocarbons. Apart from the risk of hydrate formation, the free liquids can reduce the volumetric capacity of the system and interfere with the operation of equipment such as pressure regulators and filters. For these reasons British Gas specifies upper limits for both the water and hydrocarbon dew points of natural gas. The water dew point limits, which are specified at the delivery pressure at which the producers supply gas to British Gas are based on published minimum ground temperatures and allow a margin of safety.

However, the maximum hydrocarbon limits are specified as not to be exceeded at any pressure lower than the delivery pressure. This stipulation is required because of the retrograde dew point properties of the gas. In the very simplest terms this behaviour means that on reduction of the pressure from a high value, the hydrocarbon dew point will first of all increase to a maximum and then fall in the normal manner as pressure is further reduced.

The evaporated Algerian L.N.G. does not exhibit retrograde dew point behaviour below the maximum transmission pressure of 7 MN/m^2 (Fig.4) so that hydrocarbon condensate was not a problem whilst this gas was transmitted alone, and it was on the assumption that liquids would not enter the system except during pressure testing, that the system was designed without catch pots or drains.

When natural gas was discovered in the British sector of the North Sea the transmission system was extended to accept this gas and the first delivery from the West Sole field took place in 1966. It was immediately apparent that retrograde condensation was occuring at pressures down to about 3 MN/m^2, and the extent of the retrograde condensation was determined experimentally by Cooper et al (4). Subsequently similar behaviour was demonstrated for other North Sea natural gas (Fig.4)

The measurements on the West Sole gas showed that without treatment to reduce the hydrocarbon dew point, this gas could deposit condensate at a rate of well over 1g per m^3 of gas on pressure reduction from 7 to 3 MN/m^2. In the event it was necessary to accept untreated gas from this field for some 4 years during which time it was necessary to pig the main regularly, and altogether during this period some 13,000 m^3 of condensate were recovered from the mains adjacent to the Easington terminal.

In contrast, all the gas transmitted from Bacton was treated for hydrocarbon dewpoint reduction from the start, and when the first feeder main from this terminal was pigged over 2 years after commissioning no hydrocarbon condensate was recovered at all.

Treatment of Gas to Meet Dew Point Specification

Under all the present contracts for the supply of North Sea gas, British Gas purchases pipeline quality gas, and so it is the producers who treat the gas to meet the desired dew point limits.

At present all the suppliers use the same methods of treatment, although the various plants can and do vary considerably in detail.

At the well head natural gas is generally saturated with water vapour and contains condensable hydrocarbons. The primary function of the offshore equipment is to remove water and a typical flow system is shown in Fig.5. After physical separation of liquid water, the gas is treated in glycol dehydration plant. The dew point may be lowered sufficiently so that no more water is removed onshore, or only to an extent which prevents condensation and hence hydrates in the sea-line. Liquid hydrocarbons which are also separated upstream of the driers are reinjected into the sea line, to come onshore with the gas. Two suppliers dispense with glycol drying and inject methanol to prevent hydrate formation in their sea-lines.

On shore all the present suppliers of natural gas, employ a refrigeration process for the control of hydrocarbon dewpoint, which may be used also for the simultaneous control of water dew point. A generalised flow diagram is shown in Fig.6. After removal of free liquids the gas passes through heat exchangers and is then chilled by evaporating refrigerant. The refrigerant may be propane or a freon, compressed in pumps driven by gas engines, electric motors or gas turbines. Individual units vary considerably in size from 2 x 10^6m^3 per day capacity to 14 x 10^6m^3 per day. Because of the retrograde behaviour of the gas, to comply with an upper hydrocarbon dewpoint limit of 272K at the maximum of the dew point curve, it is necessary to chill the gas to between 253 and 248K. The actual temperature achieved varies with the gas composition, and the efficiency of gas/liquid separation. If the water dewpoint of the gas is above this temperature, then glycol or methanol is injected into the plant to prevent hydrate formation. Where methanol is used, the gas passed to British Gas can contain up to 400 mg per m^3 of methanol, and this can at times be an advantage to British Gas in that it helps to maintain methanol concentrations in the aqueous liquid in new mains.

Dewpoint Measurements

First experiences of the measurement of the dew point of high pressure natural gas was gained during the drying out of the Canvey to Leeds main, where only the water dewpoint was of concern. This was carried out quite satisfactorily using the Foxboro Dewcel for continuous measurements and the UGC Dewscope for spot tests. However when the West Sole gas came ashore at Easington, the problem of measuring a water dewpoint in the presence of a higher hydrocarbon dewpoint was first encountered. The effect on the Dewcel was to cause it to indicate a high dewpoint, and with the Dewscope the large deposit of hydrocarbons on the mirror made it impossible to observe the water dewpoint satisfactorily.

The most reliable method available at that time was the chemical determination of water by Karl Fischer titration, but this was not suitable for routine use. However, it was then found that both the Dewcel and Dewscope instruments would work satisfactorily if the gas was first scrubbed to reduce the higher hydrocarbon content in a high pressure paraffin washer. The response of the instruments is slowed down, because it takes time for the water in the gas to come into equilibrium with the paraffin.

A recording instrument of the cooled mirror type made by Aqmel was also tried. This instrument was designed for the detection of the water dewpoint when the hydrocarbon dewpoint is higher, but only limited success was obtained, which can be attributed to this application being unsuitable for this instrument by virtue of the exceptionly high hydrocarbon dew point. Where gas is treated in a chilling plant, which now applies to all gases, measurement of the water dewpoint is usually of little consequence, because the low treatment temperature necessary to meet the retrograde hydrocarbon dewpoint requirements ensures that the water dewpoint specification is satisfied. The only time that this does not apply is when recently hydraulically tested equipment is used downstream of the producers treatment plant.

The hydrocarbon dewpoint is determined at 3MN/m^2 and at the line pressure of about 7MN/m^2, and it is usually sufficient to quote the water dewpoint as being less than that corresponding to the latter temperature. The hydrocarbon dewpoints in summer have a maximum of about 266K and in winter are less than 261K, both these being below the permitted water dewpoint at the time.

Aqmel continuously recording hydrocarbon dewpoint meters are installed at the terminals, but their performance has not been sufficiently reliable to enable us to dispense with spot measurements with the Dewscope. Measurements with Dewscopes are carried out at least twice per shift. Normally two instruments are permanently installed on each incoming gas stream. Gas is passed through the instruments continuously, with one at line pressure and the other adjusted to 3MN/m^2, so that checks can be carried out at anytime. These instruments are mounted in heated fibre glass huts which are sited as near as is practicable to the gas sampling points.

Dewpoint limits are sometimes exceeded, but for periods that are of insufficient duration to result in the formation of detectable quantities of condensates. There have been rare occasions when large volumes of condensate have been discharged by a supplier into British Gas mains.

Because of the absence of catch pots, this condensate has been found many kilometres along the mains and has sometimes resulted in minor incidents such as blocking and bursting of filters. It was therefore appreciated that when compressors were introduced into the system they would have to be protected by the provision of liquid separators at their inlets.

CONCLUSIONS

Operational problems arising from the presence of liquids and hydrates in the British Gas High Pressure Transmission System have been few, and except for the rare reception of slugs of condensate, have been confined to early operation.

Since the adoption of methanol swabbing of new mains and the addition of methanol to the gas whenever necessary there has been no evidence of the formation of hydrates.

The absence of any indication of the condensation of water or liquid hydrocarbons from treated gas has demonstrated the adequacy of the dew point specifications and the effectiveness of the monitoring of dew points at the terminals.

ACKNOWLEDGEMENT

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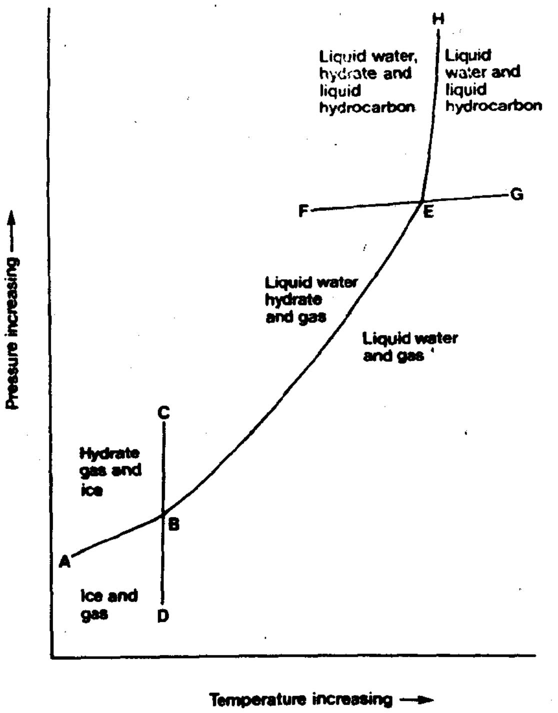

Figure 1. Simplified phase diagram of gas/water system.

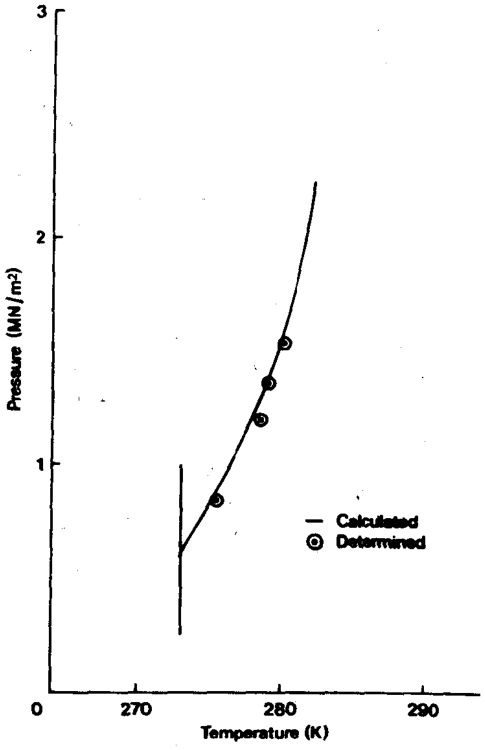

Figure 2. Comparison between determined and calculated hydrate formation conditions.

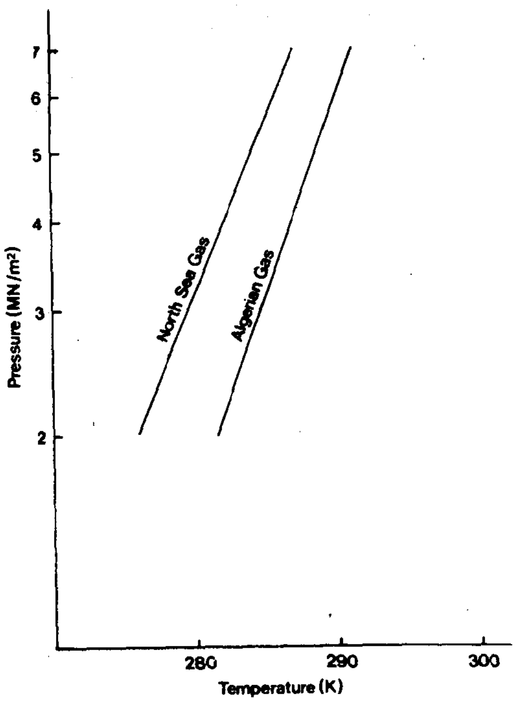

Figure 3. Hydrate formation conditions

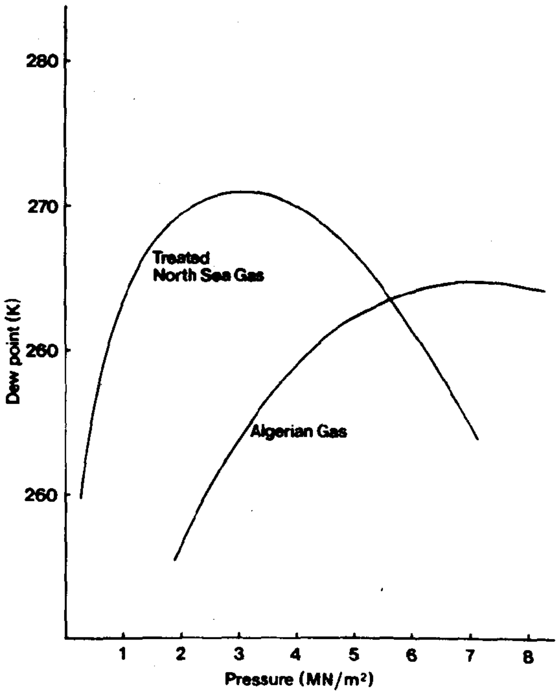

Figure 4. Hydrocarbon dew point curves.

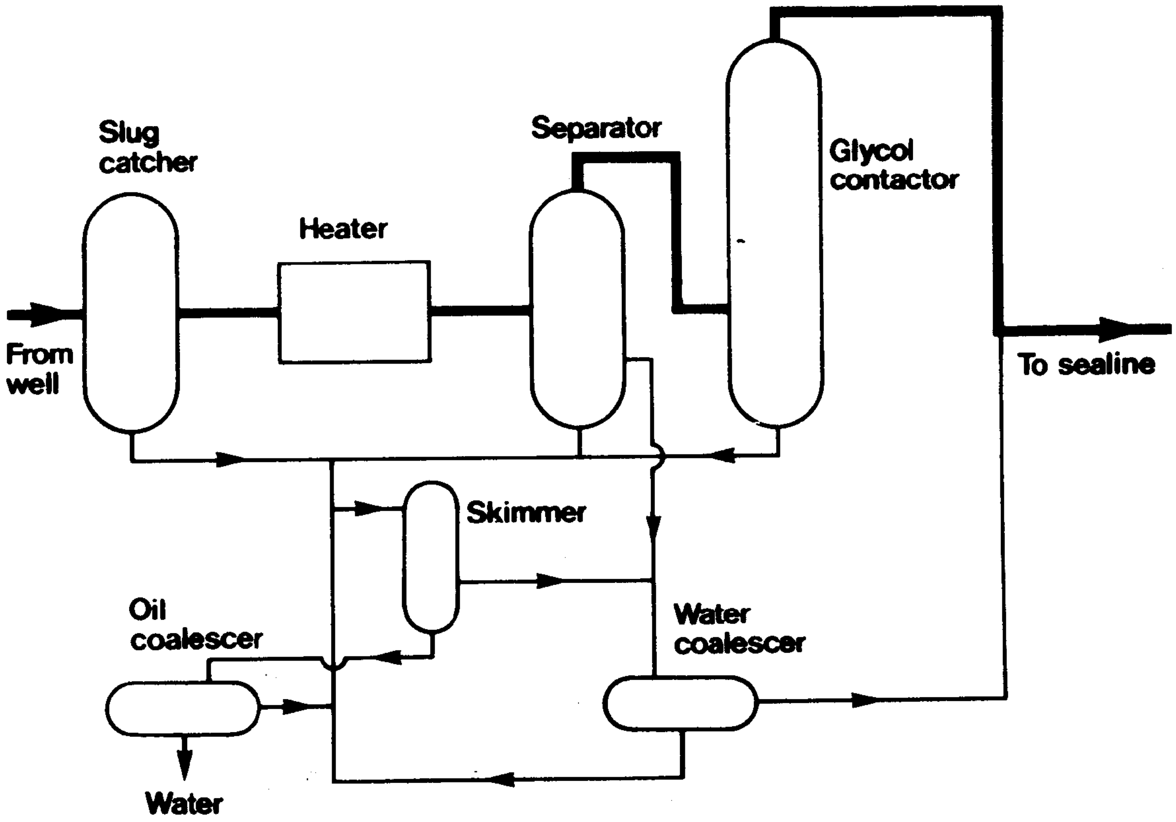

Figure 5. Offshore gas treatment plant.

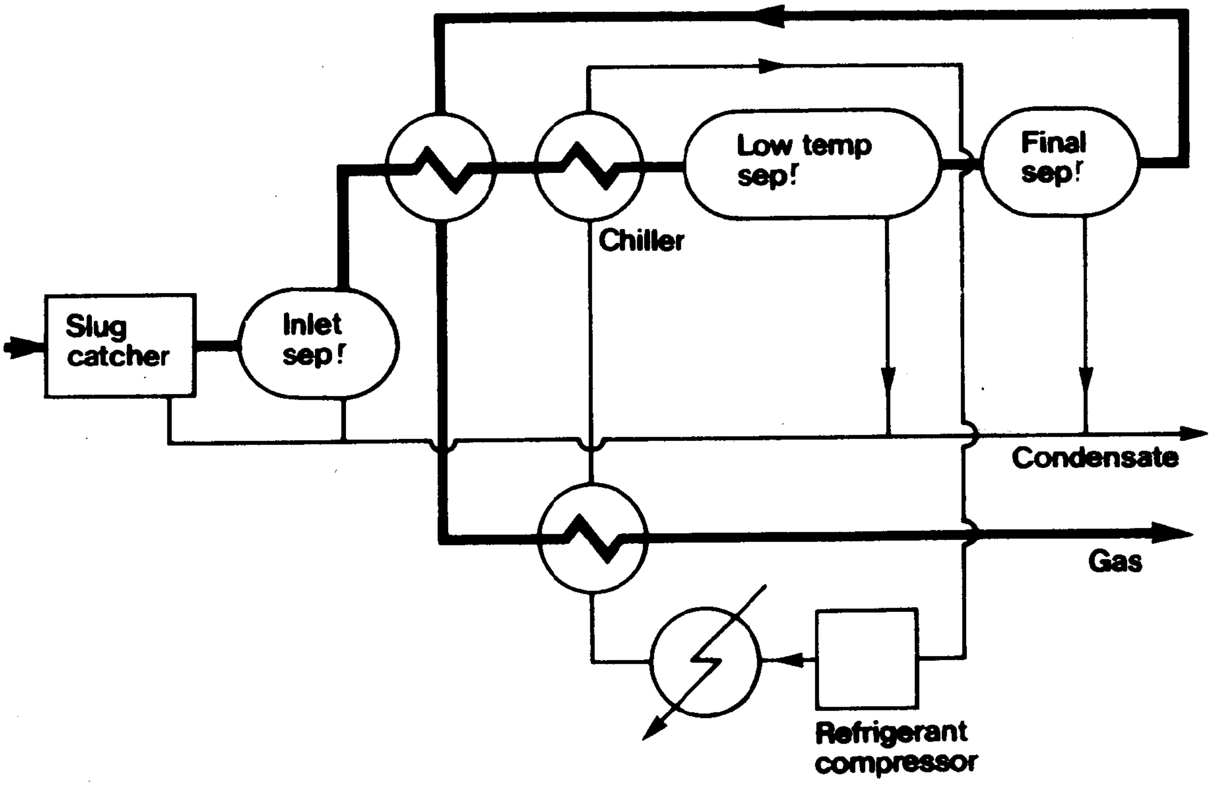

Figure 6. Onshore gas treatment plant.

MOLECULAR SIEVE PROCESSING IN THE NATURAL GAS INDUSTRY

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Molecular Sieve adsorption is a well established processing tool in the natural gas industry. The purpose of this paper is to review the range of Molecular Sieve purifications being routinely performed on a commercial scale in the world today and to provide an update on recent developments.

MOLECULAR SIEVES AND THE UNIT OPERATION OF ADSORPTION

Molecular Sieve adsorption is a well established processing tool in the natural gas industry (1,2). It is appropriate (a) to review the phenomenon of adsorption, (b) to describe adsorbents and especially Zeolite Molecular Sieves, and (c) to discuss the unit operation as practiced commercially for drying and purification.

(a) Adsorption is a phenomenon whereby molecules in a fluid phase spontaneously concentrate on a solid surface without undergoing any chemical change. Adsorption takes place due to unsatisfied forces in the surface which attract and hold the molecules of the fluid surrounding the surface. The energy of adsorption determines the strength with which any given molecule is adsorbed relative to other molecules in the system, and defines the separation efficiency that can be achieved. The range of separations practiced covers gases from gases, liquids from liquids, and solutes from solutions. The thermodynamics of adsorption systems have already been well defined along classical lines in many papers defining adsorption/desorption rate phenomena on a theoretical as well as a practical basis (3, 4, 5, 6, 7, 8, 9).

Adsorption is unique in a number of respects. In some cases, the separation performed involves the accomplishment of hundreds of theoretical mass transfer units. In others, the properties of the adsorbent allow the selective removal of one component from a mixture, based on selectivity of molecular size or shape configuration, that would be difficult to perform by any other means. In addition, removal of contaminents from fluid streams can be performed to leave virtually undetectable levels of the impurity in the product. Adsorption as a unit operation has undergone a major development in the last 15 to 20 years due to the advent of Molecular Sieves.

(b) Adsorbents commercially used for purification and separation processes all exhibit high surface areas per unit weight. This is to be expected since adsorption is a surface phenomenom. Typically, surface areas of 100 to 1000 square meters per gram are encountered in commercial adsorbents.

The commercial adsorbents which are generally used in separation processes include the activated carbons, activated clays, silica gel, activated alumina, and the crystalline alumino silicates (Molecular Sieves). The high surface area of the adsorbents is the result of countless fine pores within the solid which vary considerably in size from one adsorbent to another. Activated carbons, silica gel, and activated alumina are amorphous, and as such, the pores are non-uniform. The distribution of the pore diameters within these adsorbent particles may be narrow (20 to 50 Angstroms), or up to several thousand Angstroms, depending on the adsorbent. Hence, most molecular species with the exception of high molecular weight polymeric materials may enter the solid.

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Zeolite Molecular Sieves, however, possess an ordered crystal structure, resulting in a uniform pore size, determined by the unique structure and chemistry of the crystal. These pores will completely exclude molecules which are larger than their critical diameter. The zeolites available have pore sizes which cover the range from 3 to 10 Angstroms. The adsorption on Molecular Sieves is internal; that is, the pore openings lead to an internal three-dimensional cage network, on the surface of which the adsorption takes place. This is contrary to the amorphous adsorbents which adsorb on their external surface. In some cases, molecules which are small enough to pass through these pores can be separated from larger molecules, which are too large to enter -- hence, the name Molecular Sieves. Molecular Sieves have a strong affinity for polar or polarizable molecules. Furthermore, the basic zeolite can be altered by ion exchange to provide a nearly limitless variety of products and potential uses.

(c) The unit operation of adsorption is concerned with the separation of components from mixed systems.

Adsorbents have been developed for a wide variety of separations. Commercial materials are usually provided as pellets, granules or beads, although powders are occasionally used. The adsorbent may be used once and discarded, or, as is more common, it is employed on a regenerative basis and used for many cycles. They are generally used in cylindrical vessels through which the stream to be treated is passed. In this regenerative mode, two or more beds are usually employed with suitable valving, etc., with at least one bed being in regeneration to allow for continuous processing. Regeneration can be carried out by means of a thermal cycle, a pressure swing cycle, displacement purge cycle, an inert purge stripping cycle or combinations of these. An understanding of the unit operation of adsorption and the selection of the appropriate regeneration cycle is necessary for the successful design of any system (7). Adsorbents are used in a wide variety of applications requiring from a few ounces to over a million pounds in one plant.

Drying of Natural Gas

One of the first industry accepted gas purification applications for Molecular Sieves was dehydration of natural gas. Because of their high adsorption selectivity and high capacity at low water partial pressures, Molecular Sieves were an obvious processing choice for total front-end water removal for cryogenic extraction of helium from natural gas.

The process design aspects of dry bed Molecular Sieve dehydration were easily adapted to existing silica gel and activated alumina systems. In fact, many systems originally designed around other adsorbents were converted to Molecular Sieves for increased drying efficiencies when Molecular Sieves were first made commercially available in the late 1950's. Today, all of the major helium recovery plants in the United States use Molecular Sieves to dehydrate a total of over 3.5 billion SCFD of natural gas.

Total dehydration for cryogenic natural gas processing continues to be a major application for Molecular Sieves today. Molecular Sieve dehydration is now used almost exclusively in the cryogenic production of liquified natural gas (LNG), for both the relatively small peak demand type storage facilities found throughout the United States and Europe and the giant base load facilities around the world (11). Molecular Sieves dehydrate over 2 billion cubic feet of natural gas per day prior to liquifaction at this time with additional plants under construction which will treble this figure.

The trend toward deep ethane recovery from natural gas, using the cryogenic turboexpander process, has necessitated extremely low dew point dehydration of the feed gas. While some of the earlier plants have used methanol injection, high efficiency glycol systems or dry bed silica gel, Molecular Sieves have proven to be the most popular and effective dehydration route. It is expected that the majority of all future cryogenic ethane recovery plants will be designed with front-end Molecular Sieve dehydration.

A valuable application which is somewhat specific, but which demonstrates the unique features of Molecular Sieves as dehydration agents, is the removal of water from natural gas streams containing high percentages of acid gases (i.e., hydrogen sulfide and carbon dioxide). While other dry bed adsorbents degrade rapidly or produce undesirable side effects which complicate downstream processing, special acid-resistant Molecular Sieves have been developed which maintain their dehydration capacities over long periods of on-stream use without undesirable side effects. Two major acid-gas dehydration units are located in Canada (12) and Iran. With the increasing value of natural gas, many previously uneconomical acid gas fields are now attractive to produce acid resistant Molecular Sieves offer similar dehydration benefits for these high acid gas streams as standard Molecular Sieves do for the more typical natural gases.

In addition to the advantages of low pressure drop, low operating cost, and simple dry bed operation, another advantage of Molecular Sieves for gas drying is not commonly appreciated. That is, the ability of Molecular Sieves to attain extremely low dew points at high operating temperatures, e.g., up to 150°F., with ease. Before this point is reached -- say 100° to 120°F., the amorphous adsorbents rapidly lose both capacity and dew point depression capability. Likewise, glycol dehydrators become limited at these elevated temperatures. Thus, when a gas at an elevated temperature needs to be dried for either pipeline or liquids recovery operations necessitating moderate dew points, Molecular Sieves are attractive since no precooling is required.

In summary, the technology has been developed and commercially proven to allow the design of gas dehydrators employing Molecular Sieves to provide product gas streams containing less than 0.1 ppm(v) water. Applicable pressure ranges are from sub-atmospheric to several thousand psi and temperature ranges from below zero to 200°F. Design technology includes mass transfer rate information as a function of temperature, pressure, mass flow rate, viscosity, water content, and carrier composition.

Sulfur Removal from Natural Gas

Molecular Sieves have a high affinity for sulfur compounds and they are employed for the removal of sulfur compounds from a wide variety of hydrocarbon streams. A prime example is wellhead natural gas sweetening for selective removal of hydrogen sulfide and mercaptans. This application has matured (13) to the extent that well over 2 billion SCF of natural gas is now sweetened daily via Molecular Sieves and an additional facility is scheduled for start-up in the near future processing over 2 billion SCFD of North Sea gas.

Unlike most of the conventional liquid scrubbing processes, Molecular Sieves remove the sulfur compounds, but by design do not remove carbon dioxide. As a result, Molecular Sieve based processes for selective sulfur compound removal are possible. One of the major advantages of Molecular Sieve natural gas sweetening over liquid scrubbing processes lies in the simultaneous dehydration and desulfurization without removal of the carbon dioxide. There are Molecular Sieve units in operation today which sweeten natural gases with as little as 0.1% or as much as 50% carbon dioxide and with hydrogen sulfide levels ranging from <1 grain/100 SCF to over 400 grains/100 SCF. All units provide pipeline quality natural gas with less than 1/4 grain H_2S/100 SCF.

The operation of a Molecular Sieve natural gas desulfurizer is somewhat different from drying. Specifically, the regeneration gas must be processed since in essence, the Molecular Sieve process has provided a concentrating device -- that is, the sulfur compounds have been concentrated in the regeneration gas stream but have not been rejected from the system. Thus, the Molecular Sieve system is usually integrated with a liquid scrubbing system to clean up the regeneration gas unless the regeneration gas is to be reinjected or in some cases, directed to the fuel supply. The tail gas from the amine scrubber is a suitable feed for a Claus unit for ultimate sulfur rejection.

Natural gas desulfurization technology employing Molecular Sieves has been extended to the desulfurization of de-ethanizer overhead streams. More examples of this application are being encountered as process routes for natural gas liquids recovery evolve.

This same technology is used for Molecular Sieve based processes for total desulfurization of natural gas where the natural gas is used as feed for steam-methane reforming for ammonia synthesis. In this application, commercial experience has demonstrated that Molecular Sieves are effective in removing the trace quantities of sulfur compounds such as mercaptans, carbonyl sulfide and organic sulfides which are present in almost all natural gas feedstocks. Historically, activated carbons have been used in this service. However, studies have shown carbons to be inadequate for effective total removal of all sulfur contaminants. Noticeable improvement in the life of sulfur sensitive low temperature shift catalysts has been demonstrated when Molecular Sieves are employed for front-end feed purification (14). Currently, three ammonia plants are prepurifying the pipeline natural gas with Molecular Sieves. In this application, the regeneration gas goes directly to the plant fuel system.

A recent development in the sweetening of natural gas containing small amounts of hydrogen sulfide has been the utilization of the unique properties of custom manufactured proprietary Molecular Sieves. Specifically, these Molecular Sieves offer a combination of adsorptive removal of a pre-specified amount of the hydrogen sulfide coupled with a controlled conversion of the remaining hydrogen sulfide to non-corrosive COS via the following reaction:

$$H_2S + CO_2 \rightleftarrows COS + H_2O$$

For those cases involving low levels of hydrogen sulfide to be removed, this method of treating offers significant investment and operating cost savings.

In summary, the technology and proven commercial performance has been established for the removal of a wide range of sulfur compounds from natural gas. Purifications to exacting specifications can be achieved even with extremely sour feed streams. The regeneration technology is established and the means of the integration of the regeneration gas with sulfur disposal systems is available (15).

Carbon Dioxide Removal from Natural Gas

Molecular Sieves are commonly used to purify gas streams containing carbon dioxide in cryogenic applications where freeze-out of carbon dioxide would cause fouling of low temperature equipment. The unique adsorption features of Molecular Sieves are exploited by using one front-end purifier unit for simultaneous removal of both water and carbon dioxide. Product gas purities of less than 50 ppm carbon dioxide and 1 ppm water have been easily attained using a properly designed Molecular Sieve system.

Peakshaving natural gas liquefaction plants utilize Molecular Sieve for front-end feed purification for both water and carbon dioxide removal. Carbon dioxide in its free state forms a solid at ≈-109°F. It is only slightly soluble in liquid methane and must, therefore, be removed to low levels to prevent crystallization and plugging. Inlet natural gas typically contains from .05 to 2 volume percent carbon dioxide in addition to up to 10 pounds of water per million standard cubic feet. Safe operating practice requires carbon dioxide removal to below 50 parts per million by volume. Of the over 40 LNG peakshaving plants operating or under construction, nearly all utilize Molecular Sieve for feed purification.

An extension of this technology has been the selection of Molecular Sieves to simultaneously remove water and 1.5% carbon dioxide from the feed gas to a large turboexpander plant installed for deep ethane recovery. The alternate route would have required both a liquid system for the carbon dioxide removal and a Molecular Sieve system for the dehydration. The Molecular Sieve system is designed to provide <0.1 ppm water and <10 ppm carbon dioxide in the product gas. The application of Molecular Sieves for combined dehydration and carbon dioxide removal is easily extended to base load LNG plants. One such unit is currently in the engineering stage.

Closely related to natural gas purification, Molecular Sieves have been employed to remove carbon dioxide from ethane-propane mix. There are currently six Molecular Sieve units in commercial operation. Carbon dioxide levels are reduced from a range of 0.5 to 1.0 mole percent down to below a 1000 ppm(v) specification following extraction and fractionation of the ethane/propane from natural gas. The product is sold as a premium cracking feed to olefins producers who enjoy improved compression train efficiencies when the feed gas has low carbon dioxide concentrations. Even lower impurity specifications of the product can be attained if desired.

In summary, the design capability and proven commercial performance has been established for the removal of carbon dioxide from natural gas and light hydrocarbon streams over a wide range of operating conditions and feedstock compositions.

Natural Gas Containing Oxygen

The safety hazard of large quantities of oxygen in natural gas is well known but the presence and effects of trace amounts of oxygen has previously been considered unimportant.

Union Carbide's first encountered trace oxygen in a Molecular Sieve dryer/purifier the front end of a LNG peakshaving plant in 1972 (14).

While the system was designed to remove carbon dioxide to an effluent level of less than 50 ppm(v), plant operating data indicated that this level of purification could not be met at design conditions. An extensive performance evaluation by Union Carbide's field service engineering group eliminated the possibility of mechanical malfunctions such as valve leakage, valve sequencing, and gas flow distribution. Laboratory analysis of Molecular Sieve samples obtained from the beds showed no apparent deterioration of the Molecular Sieves. A subsequent material balance around the entire Molecular Sieve system using on-stream water and carbon dioxide analyzers, indicated unexplained levels of water and carbon dioxide at points in the process where essentially no impurities should be present. When the data from the material balance study were analyzed it was concluded that some form of combustion was occurring in the regeneration gas heater forming water and carbon dioxide. Proceeding on the assumption of a combustion phenomenon, the oxygen in the feed gas was measured using a portable oxygen analyzer. Oxygen concentrations of 5 to 25 ppm were detected in the feed gas. Additionally, oxygen measurements in the regeneration gas heater feed and effluent showed reduced oxygen levels in the heater effluent, adding support to the combustion theory.

Formation of oxidation products varies to a great degree depending on oxygen concentration, temperature, and hydrocarbon composition. The oxidation reaction may also be influenced by the presence of an active surface and the contact time. For example, it was observed that even low molecular weight hydrocarbons oxidize in the presence of steel surfaces at skin temperatures in the range of 600°F.

Oxygen which reacts to form water during the regeneration cycle can have varying effects on the performance of a unit. Molecular Sieve dryers can tolerate various amounts of water in the regeneration gas depending on operating temeprature, operating pressure, and the desired water specification of the treated gas.

For cryogenic processes, however, requiring ultra low water content, it is critical that low residual moisture levels be maintained in the mass transfer section of the Molecular Sieve bed. If the regeneration gas contains water from an oxygen reaction, this water can deposit on the Molecular Sieve bed during regeneration, effectively reducing the bed's capacity for processing feed gas. In the case of LNG peakshaving plants, carbon dioxide removal capacity will also be reduced by the coadsorption effects of residual water.

Since the conversion of oxygen to water is a chemical reaction, it is sensitive to temperature. There are threshold temperatures at which this reaction is minimized and in some cases eliminated. The concept of regenerating below a threshold reaction temperature has been used to optimize the operation of three Molecular Sieve units which were designed and started up before it was known that oxygen was present in the feed to the plant.

Experience has shown that some process modification should be considered if the oxygen content of the regeneration gas exceeds 5 to 10 ppm(v). Molecular Sieve units treating natural gas containing oxygen must be considered as a more severe service than natural gas without oxygen.

Since early 1973, Union Carbide's Molecular Sieve Department has provided designs with performance assurances for 13 plants treating over one billion SCFD natural gas for both dehydration and simultaneous removal of water and carbon dioxide, by combining the concept of regeneration threshold temperature with other process and product considerations (16).

If increasingly higher oxygen concentration levels are detected in natural gas streams (and this can be expected in the years ahead), additional treating technology will be required. While Union Carbide has found that oxygen can effect the performance of Molecular Sieve treating systems, pipeline and process metallurgy, liquid scrubbing processes, and other natural gas treating operations.

In the course of developing oxygen treating technology, an extensive effort into the development of catalytic oxygen removal systems was undertaken. This deoxygenation catalyst technology is now available through Union Carbide.

Sulfur Removal from Propane, Butane, and LPG

One of the most widely practiced uses of Molecular Sieves in the natural gas industry is LPG liquid sweetening. There are well over 200 Molecular Sieve installations processing propane, butane and mixed LPG streams to provide low sulfur content products (1A Copper Strip). The problems associated with handling and disposal of caustic solutions via conventional scrubbing processes are avoided. Additionally, Molecular Sieve treating combines removal of hydrogen sulfide, carbonyl sulfide, mercaptans and water in one unit, eliminating the need for separate equipment for each step of a multistage process.

The regeneration medium is typically a natural gas which is often consumed in the fuel system or can be scrubbed with amine systems, if necessary, for subsequent sulfur rejection. In some cases, a slip stream of product LPG is used for the regeneration step. Either system is satisfactory and both are successfully being used commercially. The product specification is related to the regeneration gas quality. Recently, demethanizer of deethanizer overhead streams have been employed as the regeneration gas medium. In these cases, the relationship between regeneration gas quality and product specification is of prime importance in determining the overall process route. In liquids treating as described, not only water and mercaptans are removed, but sulfides, disulfides and carbonyl sulfide can also be removed with Molecular Sieves when so desired by the proper selection of Molecular Sieve adsorbent and process design.

Units are in operation today treating from a few hundred to 35,000 barrels per day per train. Projects currently in the design stage extend this range of flowrate to over 50,000 barrels per day of propane per train and over 30,000 barrels per day of butane per train.

A recent development in the United States has been the desulfurization of ethane-propane mixtures. This has come about due to the deep ethane recovery being practiced as mentioned previously. The desulfurization process is liquid phase and carried out in the same fashion as the conventional LPG treaters except that due consideration must be paid to the inevitable carbon dioxide content of the ethane-propane mix.

A final point, often overlooked, is the advantage of Molecular Sieves for LPG or propane drying. In this application, the chance of the hydrolysis of COS to H_2S, with subsequent product fouling, must be recognized. Dehydration with Molecular Sieves can overcome this problem through proper product selection.

Analytical Aids

This paper would be incomplete without a review of current analytical capability. The laboratory analytical techniques available for trace determination of all of the contaminants previously discussed are plentiful. These techniques are essential for the process development work required. However, as a necessary adjunct to the laboratory techniques is the need for portable, accurate field methods.

The development of thise methods has been an on-going task for those involved in the development of adsorption technology. Furthermore, due to the dynamic nature of adsorption units, the analytical technique should be continuous or at the very least, rapid enough to allow repetitive, accurate analysis on the order of 10-minute intervals.

Union Carbide's current portable field analytical capability is as follows:

1) Water/gas: <0.1 ppm(v)
2) CO_2/gas or vaporized liquid: to 0.1 ppm(v)
3) S/gas or vaporized liquid: to <1 ppm(v) on all "S" compounds
4) Hg/gas: to 10 ppb(v)
5) O_2/natural gas: to 1 ppm(v)

The Design of Molecular Sieve Systems

With the growth and acceptance of Molecular Sieve adsorption as a valuable processing tool (e.g., from 5 billion SCFD in 1965 to 30 billion SCFD of natural gas treated in 1975), the size and complexity of the units also grew. The design of the optimum Molecular Sieve adsorption system requires judgement and insight in a unit operation not widely understood. It is appropriate to review some of the more important considerations. Obviously, in most cases, a balance is involved in the definition of the optimum system.

Cycle time is an obvious starting point. The longer the cycle time, the larger the vessels and inventory -- but, the efficiency of Molecular Sieve usage goes up and operating costs go down. As cycle time is reduced, the equipment gets smaller but the need to automate gets larger. For example, on a 24 hour cycle basis, Molecular Sieve adsorption units are usually run on a manual basis. However, by the time the cycle is reduced to 8 or 12 hours, most units have been automated -- thus, the vessel and adsorbent inventory savings may have been consumed by instrumentation and automatic valves.

Train size/vessel size are interrelated. Vessel size is often a function of the maximum diameter that can be shop fabricated. This can result in a considerable savings over the costs of field erection. This varies with manufacturers, codes and geography, but is usually in the realm of 11 to 13 feet. Furthermore, as opposed to one larger vessel, it is often more economical to employ two smaller diameter vessels in parallel. Also the wall thickness requirements, and subsequent vessel weight increase as the diameter increases. The train size can be adjusted to suit the size of the hardware. However, in most natural gas processing units, the limit on flow per train is more often limited by compressors, expanders, etc., than by Molecular Sieve adsorption design considerations. The throughput of adsorption systems can easily be expanded by the addition of parallel beds.

The integration of different systems in large processing complexes, e.g., those with natural gas dehydration, fractionation and liquids treating, requires that due care be exercised. The Molecular Sieve adsorbent engineer should be consulted at the earliest possible date. The fact that a total system is to be considered must be clearly defined, rather than simply assuming that the sum of the parts equals the whole. The impact of any upstream unit on the downstream units can be considerable. For example, presuppose a natural gas dehydrator/desulfurizer followed by fractionation to recover separate propane and butane cuts. The design of the liquid treaters will be dependent upon the degree of desulfurization achieved in the gas treater. Thus, a base case must be designed and appropriate variations must also be evaluated to achieve the most economical system, from both a capital and operating cost basis. In addition, the disposal of regeneration gases must be considered. If these gases are to be processed, the selection of the liquids unit can be important. Likewise, if the sour gas is to be reinjected, as is often the case, the regeneration pressure employed must be considered. Lower pressures favor efficient regeneration at the expense of increased recompression costs -- while high regeneration pressures may require larger heater sizes and higher gas flowrates.

Early communication between the contractor/end-user and the Molecular Sieve adsorption engineer is vital for the overall design of the most efficient processing unit.

CAPSULE SUMMARY

The use of Molecular Sieve adsorbents as a highly versatile means of purifying natural gas streams and related products has become firmly established in the industry. The ability to tailor Molecular Sieve adsorbents to provide a limitless variety of product performance characteristics promises the continued development and extension of natural gas applications. The importance of early contact with the Molecular Sieve adsorbent engineer to help define the most efficient and economical system is stressed.

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