Helium: Its Extraction and Purification

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Abstract

This paper discusses the extraction of helium from natural gas as practiced in existing helium plants. There are various sources of helium but natural gas is currently the only commercial source. Several phases of the helium extraction process, such as refrigeration systems and methods of carbon dioxide and water removal, are similar to those in natural gas processing. It is concluded that in cryogenic processes, solid desiccants are more suited than glycol for water removal, and that with proper plant design, natural gas containing small amounts of carbon dioxide can be processed cryogenically.

Discussed are (1) the relationship of processing pressure to the recovery method and equipment sizing, (2) various methods of developing required refrigeration for the cryogenic process and (3) the design, utilization and metallurgy of such items as compressor, heat exchangers, control valves, fractionating towers, dehydrators and insulation. Helium purification is examined as to methods of removing hydrogen, nitrogen and methane from the helium stream. Included are noncryogenic methods of purifying helium.

Introduction

The role of helium has shifted in recent years from its well known use as a lifting gas to many new, exciting and possibly more important applications. The quantity of helium used for lifting purposes has fallen behind that used for such other present-day purposes as pressurization, shielded arc welding, controlled atmosphere and research. Helium is valuable because as a gas it is odorless, tasteless, nontoxic, nonflammable, inert and light. As a liquid it is valuable because of its very low boiling point of −452F at atmospheric pressure. Because of these unique properties, it has other small but important uses such as purging, leak detection, cryogenics, chromatography and heat transfer.

Small concentrations of helium can be found in air and in certain minerals, and it was recovered from these sources for some early experimental work;[1] but because of the very low concentrations, these are not considered to be commercial sources. When helium was discovered in natural gas, all commercial recovery efforts quickly shifted to this new and exciting source. Some pioneer plants were built in the United States and Canada to extract helium from natural gas during World War I. These early plants, built before the advance of technology and under a wartime emergency atmosphere, were small and of uncertain design. From 1921 to 1925 the Linde Co. operated such a plant for the U. S. Navy near Fort Worth, Tex. In 1925 operation of this plant was assumed by U. S. Bureau of Mines. Great advances in technology resulted from the pioneering effort in the Fort Worth plant, contributing heavily to the establishment of an economically feasible method for extracting helium from natural gas by a low-temperature liquefaction process.[2] This new technology was used in the late 1920's when USBM erected a helium extraction plant near Amarillo, Tex., to process natural gas from the Cliffside field. At this time the plant at Fort Worth was closed down.

During World War II, USBM built four additional helium extraction plants and enlarged the one at Amarillo to provide helium for wartime use. These plants were built under extreme emergency conditions when time was not available to experiment with different designs; therefore, they were all quite similar to the Amarillo plant. In 1959 the government put its latest plant on stream at Keyes, Okla. This plant featured larger units and increased efficiency in helium recovery.

In the early 1960's the government started its farsighted conservation efforts for helium that resulted in construction of five new helium plants by private companies. In

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[1]References given at end of paper.

1868-1968 Helium Centennial

A helium centennial celebration began in October, both as a tribute to the discovery of helium and as a focusing point for the increased need of more effective conservation of all natural resources. The centennial is sponsored by government agencies, private companies and institutions that are interested in attracting public attention to the helium program as one successful example of conservation. Activities in the year-long celebration will include essay contests for students, a Helium Applications Symposium in Washington, D. C., and other related scientific meetings and conferences featuring exhibits and technical papers on helium applications.

As depicted on this month's cover, a Times Column monument is being erected in Amarillo, Tex., to commemorate the 100th anniversary of the discovery of helium. Time capsules forming the monument will be opened at 25-, 50-, 100- and 1,000-year intervals.

This and the following paper are published to orient the petroleum engineer in the production, uses and potential of this resource. The papers elaborate on the various helium extraction and purification techniques, upon government-industry cooperation in the use and conservation of helium, and upon future prospects for uses of helium and its distribution.

comparison with earlier plants, these five new plants are much larger, processing approximately ten times as much gas; they produce only crude helium (50 to 85 percent purity) while the older plants produce refined helium (99.995+ percent purity). The new conservation plants process natural gas streams containing considerably less helium. In addition to these five plants, four commercial plants producing refined helium have gone into operation since 1960. Three of these are in the U. S. and one is in Canada. Currently, two additional commercial plants are under construction, one in the U. S. and one in Canada.

Natural Gas Processing: Pretreatment

The first step in processing natural gas for helium recovery usually is removal of certain objectionable impurities. Since all modern plants utilize the cryogenic process, the most undesirable impurities are water, carbon dioxide and hydrogen sulfide. Heavy hydrocarbons also can be a problem at cold temperatures.

When carbon dioxide and hydrogen sulfide occur in excessive quantities, they normally are removed by the use of amine systems. These systems are the typical water amine solution plants used for many years in plants processing gas for LPG recovery. The use of molecular sieves for removing carbon dioxide and hydrogen sulfide was studied and suggested; however, it has not been applied in any helium-extraction plants. One of the cryogenic-type plants can process streams containing as much as 0.25 percent carbon dioxide without removal facilities; it is probable that, with minor changes in design, higher concentrations of carbon dioxide could be processed.

Heavy hydrocarbons are being removed in various plants by different means. In some plants, the cryogenic section is preceded by a refrigeration system, an oil absorption cycle or a combination refrigeration-oil absorption process. These various methods have proven satisfactory. Typically, most of the propane and essentially all of the heavier fractions are removed before cooling the gas below −60F.

Successful plant operators have discovered that dehydrating gas in the best possible manner is important. Good removal of water insures trouble-free operation and extends the on-stream intervals between plant defrosts. Water removal by using glycols and solid desiccants has been practiced in existing plants. All current operators agree that dry desiccants are more suited for this application. Most operators strive for removal of water down to approximately 0.2 ppm or less. Even though it is difficult to measure water content this small, residuals of 0.1 or 0.2 ppm are indicated in some of the dehydration systems. At least one plant has operated 4 years without a complete defrost, which indicates that successful dehydration is being achieved.

Processing Pressures

Helium extraction plants generally have been built on existing pipeline systems; therefore, pressure available in the pipeline has dictated partially the operating pressure range of the plant. As gas compression is one of the main costs in operating helium extraction plants, all efforts are maintained to assure that gas pressure is not dissipated needlessly.

Using general terminology, present crude helium plants fall into two categories: high pressure and low pressure. The low-pressure plants normally use a flash system that utilizes a series of pressure drops and phase separations to achieve helium extraction. Some advantages claimed for this system are its simplicity and lower pressure ratings required for processing equipment. The lower pressure is a special advantage for heat exchangers in that the core or extended surface (Trane) type can be used, whereas under present manufacturing technology, the wound (Hampson) or shell-and-tube type might be required for higher pressures. Advantages claimed for the higher pressure process are smaller-sized equipment, better total heat transfer per square foot of heat exchanger surface and smaller piping and compressor equipment. One disadvantage is that a stripping phase is required. The system also has certain limitations as dictated by the critical pressure[3] of the natural gas being processed. A simplified illustration of a low-pressure flash system for recovery of crude helium is shown in Fig. 1.[4] A typical high-pressure process utilizing a stripping step is shown in Fig. 2. In a low-pressure process, pressures might range from 500 lb to as low as 100 lb, whereas in the high-pressure process the pressure range might be from 650 to 450 lb.

Refrigeration

The cryogenic process requires a great deal of refrigeration. Some temperatures in the cryogenic plants drop to −320F. Refrigeration normally is achieved by the use of one or more of three basic methods. Almost all plants use the auto-refrigeration method achieved by pressure drop on the gas stream itself. In addition, some closed-refrigeration cycles are used, and expansion engines also are utilized. Auto-refrigeration is accomplished by dropping the pressure on the main gas stream or by dropping the pres-

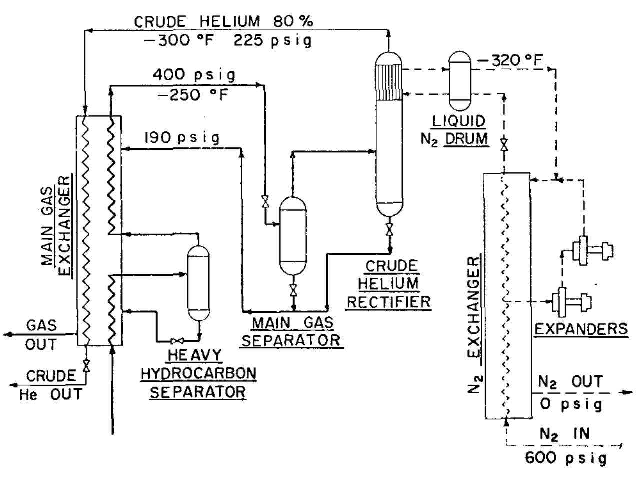

Fig. 1—*Crude helium separation cycle using low-pressure flash system.*

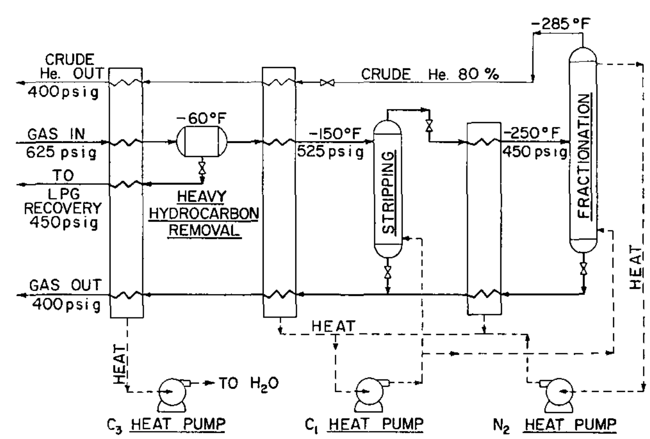

Fig. 2—*Crude helium extraction cycle using high-pressure stripping process with multiple cascade refrigeration systems.*

sure on a small side stream, or a combination of both. Some of the refrigerants used in closed loops are propane, propylene, methane, ethylene and nitrogen. In some cases where multiple closed cycles are used, one refrigerant is cascaded onto another. In other applications, refrigerant condensing is accomplished by utilizing the main gas stream itself. Fig. 2 illustrates a plant using propane, methane and nitrogen cycles. In this process the propane is condensed with cooling water, the methane is condensed on the process itself and the nitrogen is condensed on the methane circuit.

Equipment and Metallurgy

A great variety of equipment is utilized in the plants now in operation. It has been said that a helium extraction plant is nothing more than a collection of compressors and heat exchangers. This is very near the truth. All types of compressors can be found in the various plants. Some types typically used are electric motor-driven centrifugal, electric motor-driven reciprocating, gas engine-driven reciprocating, and steam turbine- and jet engine-driven centrifugal. Some plants have made economical use of steam turbines and jet engines in that a fuel with low heating value and high nitrogen content is used, which is a product of the process itself. This technique has the advantage of upgrading the heating value of the residue gas.

Heat exchangers in a helium plant take on many shapes and forms. The typical shell-and-tube type is found in the warmer sections of the plant, while in the cold sections the wound tube and the core (extended surface) types are utilized. Since some pressure limitations have been experienced with the extended surface exchangers, the larger plants generally have used the wound-type exchanger for the large heat exchange requirements.

A variety of materials have been used in manufacturing the heat exchangers, compressors, piping, valves, etc. For economic reasons, the metal is graduated from common carbon steels in the warmer sections of the plant to low-grade alloys, and finally to stainless, 9 percent nickel steel, and aluminum or copper for the coldest temperatures. For some intermediate temperatures, such materials as 3.5 percent nickel steel and killed steel have been used. Some economic advantages have been realized by using 9 percent nickel for large pieces of equipment. A recent change in the ASME code allows fabrication of 9 percent nickel steel without stress relieving. This has enhanced its value in the operating temperatures between −50 and −320F.

Materials selected for valves, piping, etc., also are dictated by the temperatures involved. Generally, soft-seated valves are used where tight shut-offs are required. Leaking cryogenic valves pose more problems than simply a waste of products in that they sometimes will cause undesirable icing or frosting of lines and equipment.

Insulating cryogenic plants has always been a matter of engineering and operating concern. Care should be taken to insure the best job possible. In the typical cryogenic plant for extracting helium, each piece of equipment and piping that normally is warmer than −50F is insulated separately with foam glass. Below this temperature the typical procedure is to group the equipment into cold box construction. The most commonly used insulating materials for cold boxes are mineral wool and perlite. Mineral wool normally is chosen for areas where some repair and maintenance work is expected, and perlite has been used where little or no personnel entry requirements are expected. For obvious reasons, perlite is much easier to install but is more difficult to manage during repairs. Vacuum jacketing and liquid nitrogen shielding are used in the lower temperature ranges, and especially in plants producing liquid helium. Some of the newer multilayer super insulations also have been used in the plants handling liquid helium.

Instrumentation and Control

Many plant operators have experienced some instrumentation and control difficulties, at least initially, when bringing on a new plant. Most control problems arise from the large time delays in the control loops due to the thermal inertia of the equipment. The sensitivity of instruments normally must be reduced to prevent over-control, which tends to make over-all management of the process sluggish and unresponsive. Maintenance of instrumentation inside cold boxes has presented problems, and measuring levels in cryogenic fluids also is a challenge. The level instrument used most often is the simple differential pressure device. It has proven to be satisfactory for almost every requirement when applied properly and carefully. Most other instrumentation is typical of that used in natural gas processing plants except that greater accuracy occasionally is required in such applications as analyzing for impurities in refined helium.

Helium Purification

The extraction plants producing crude helium for storage under the government conservation program normally deliver helium in the purity range of 50 to 85 percent, whereas plants producing Grade A helium for sale must achieve a minimum purity of 99.995+ percent. To achieve such high purities, more sophisticated impurities-rejection equipment must be used, and lower temperatures are employed in the process.

The first step in purifying crude helium normally is hydrogen removal. Natural gas usually contains small quantities of hydrogen that become concentrated in the crude helium. This must be removed before Grade A purity can be achieved. Hydrogen removal is effected by catalytic oxidation, dehydration and finally low-temperature charcoal adsorption. In the oxidation step, all but a trace of the hydrogen is converted to water by introducing a slightly insufficient quantity of air. The water produced is removed by conventional adsorbents, and the trace quantity of hydrogen left over is removed by low-temperature charcoal adsorption along with trace quantities of other impurities in the final stage of the cryogenic purification process.

A typical cryogenic purification process is shown in Fig. 3.[5] This simplified drawing does not show the hydrogen oxidation step. In this process, crude helium is cooled (normally at high pressure) to temperatures at which the methane and nitrogen will condense and permit a phase separation. This phase separation normally takes place in two stages: the first stage at the temperature obtained with liquid nitrogen at atmospheric pressure, and the second stage of separation at a temperature obtained with liquid nitrogen under vacuum. The gaseous helium then is passed through charcoal, which also is held at liquid nitrogen temperature. The charcoal effectively removes the remaining contaminants, and the resulting helium (Grade A) generally contains less than 50 ppm of foreign material such as neon, hydrogen, nitrogen and methane.

At a newer plant the purification cycle is somewhat different in that crude helium is contacted with liquid methane, which "scrubs out" the nitrogen impurities and results in a helium purity near 99 percent. This helium then is purified further by the low-temperature charcoal adsorption step.

In the past, plants built to purify crude helium to Grade A all have used high-pressure design. The process pressures are great enough (in excess of 2,000 psig) that, after

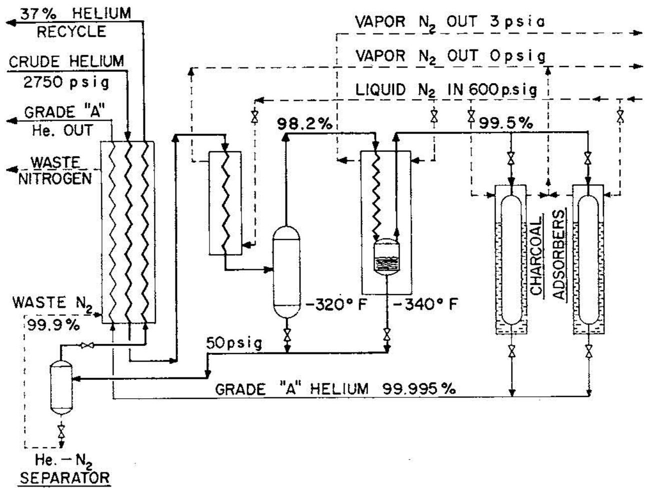

Fig. 3—*Helium purification cycle using low-temperature phase separation and charcoal adsorption.*

processing, the helium can go directly to fill shipping containers. This is an attractive method of handling the helium in that lubricated-type compression can be used because it is done before purification. Any compression after purification must be done non-lubricated to prevent contamination. Even though many non-lubricated types of compressors are available, they most often are less efficient and require more maintenance. Oil contamination resulting from preprocessing compression can be removed easily by suitable adsorbents.

Some newer plants that liquefy all or a sizeable percentage of their Grade A production are more likely to use lower processing pressures in the purification step because the higher pressures are not advantageous to the liquefying process.

Some problems in producing high-purity helium consistently have been reduced by the introduction of better methods to monitor and analyze the product. In the last few years on-stream chromatographic analyzers have been developed that can accurately measure trace contaminants. Some helium consumers are now requesting ultra-high purity, which sometimes presents a problem in that neon concentrations can often be too high. No special effort is being made at existing plants to remove neon, although it is partially removed by low-temperature charcoal adsorption.

Helium Liquefaction

Since helium has a gas-to-liquid volume ratio of 750:1, it is more economically transported as a liquid where long distances are involved, and large volumes of liquid helium presently are being transported not only across the nation but also by air across the oceans. Presently, three plants in the U. S. are performing the full cycle of extraction, purification and liquefaction. One liquefaction plant has an announced capacity of 900 liters/hour, which is considered to be the world's largest. There are many other liquefiers in operation ranging in size down to laboratory units.

The very low heat of helium vaporization (9 Btu/gal) imposes an extraordinary insulation and design problem upon the liquefaction process and transportation, storage and handling equipment.

Noncryogenic Separation

For a number of years there has been some research work conducted on noncryogenic methods of extracting helium from natural gas and on the purification of helium. Helium diffuses through glass tubing[6] and it is possible to extract and purify helium by this method. However, the diffusion rate is so low that this method has not yet been commercialized. Research work has been conducted with different diffusion membranes.[7] Schindler[8] reported that crude helium might be purified by absorption of the nitrogen in propane at relatively warm temperatures.

Future of Helium

Even though the demand for helium almost vanished between World Wars I and II, helium decidedly is here to stay and will be in demand in ever-increasing quantities. If the government's developmental uses are not curtailed, helium consumption could increase from the present rate of approximately 850 MMcf/year to 2 Bcf/year in 5 years. The extraction of helium from natural gas apparently will continue to be the only commercial source since it appears unlikely that more economical sources will be discovered.

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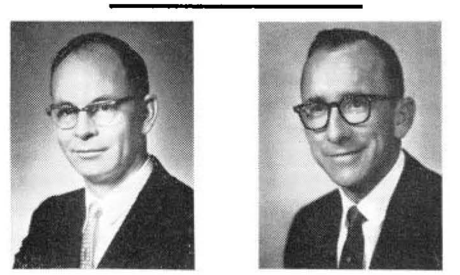

Ross W. Wilson *(left), executive vice-president of National Helium Corp., has some 20 years of experience in helium extraction. He started in 1946 with the U. S. Bureau of Mines' helium extraction plant at Amarillo, Tex., and in 1952 he joined Panhandle Eastern Pipe Line Co.— a co-owner of National Helium. Wilson received his BS degree from West Texas State College and an MS from the U. of Tennessee.* **H. R. Newsom** *(right) is president of the Sulphur & Industrial Chemicals Div. of Elcor Chemical Corp. in Midland, Tex. He was with National Helium from 1962-67 in various capacities, ending with vice-president of operations. An electrical engineering graduate of Texas A&M U., Newsom worked briefly with Sinclair Pipe Line Co. before joining Stanolind Oil & Gas Corp. During 13 years with Stanolind and other subsidiaries of Standard Oil Co. (Ind.), he held various positions, including plant superintendent.*