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EXPERIMENTAL INVESTIGATION OF THE REMOVAL OF KRYPTON AND XENON FROM CONTAMINATED GAS STREAMS BY SELECTIVE ABSORPTION IN FLUOROCARBON SOLVENTS:

PHASE I COMPLETION REPORT

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EXPERIMENTAL INVESTIGATION OF THE REMOVAL OF KRYPTON AND XENON FROM CONTAMINATED GAS STREAMS BY SELECTIVE ABSORPTION IN FLUOROCARBON SOLVENTS: PHASE I COMPLETION REPORT

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ABSTRACT

Substantial quantities of radioactive krypton and xenon isotopes are produced during the irradiation of nuclear fuel. In fuel reprocessing schemes; during normal operation of certain types of nuclear reactors; e.g., those with vented fuel elements; and in the possible event of cladding rupture or fuel meltdown, these fission gases are, at some point, released to the surrounding containment. Because of increasing concern about subsequent discharge of these active nuclides to the atmosphere, a development project was initiated at the Oak Ridge Gaseous Diffusion Plant to investigate and define a process to remove krypton and xenon from contaminated gas. The first phase of this work was successfully completed recently and is described in this report. The separation process is based on the selective absorption of the noble gases in a fluorocarbon solvent such as refrigerant-12 (dichlorodifluoromethane). A pilot plant was designed and built to evaluate overall process feasibility and to collect engineering performance data necessary for the design of plant-scale systems. In the first phase of this project, a total of 34 pilot plant tests, all employing refrigerant-12 as the process solvent, were conducted. Operating conditions and performance data, including correlations of mass transfer parameters, are presented and discussed. In the experiments, column decontamination factors as high as 1000 were measured, and the general performance of the pilot plant demonstrated that a continuous selective absorption process of the type studied has the capability of removing essentially all traces of krypton and xenon from a contaminated gas source. The second phase of the work, in which refrigerant-11 (trichloromonofluoromethane) is being evaluated as a process solvent, is now in progress.

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EXPERIMENTAL INVESTIGATION OF THE REMOVAL OF KRYPTON AND XENON FROM CONTAMINATED GAS STREAMS BY SELECTIVE ABSORPTION IN FLUOROCARBON SOLVENTS: PHASE I COMPLETION REPORT

Irradiation of nuclear fuel results in the production of substantial quantities of radioactive krypton and xenon isotopes. In normal fuel reprocessing schemes; during normal operation of certain types of nuclear reactors, e.g., those with vented fuel elements; and in the possible event of cladding rupture or fuel meltdown, these fission products are released to the surrounding containment. To eliminate the potential exposure hazard of subsequent discharge of these nuclides to the atmosphere, the Environmental and Sanitary Engineering Branch of the U. S. Atomic Energy Commission Division of Reactor Development and Technology initiated a development project at the Oak Ridge Gaseous Diffusion Plant to evaluate a process for collecting and concentrating krypton and xenon.

Several methods have been proposed for removing krypton and xenon from contaminated air streams[3,5]. One of the most direct techniques for dealing with these gases, however, is the selective absorption process being studied at the ORGDP. This process was conceived at the Brookhaven National Laboratory[15] and is based on the preferential dissolution of the noble gases in a fluorocarbon solvent, such as refrigerant-12 (dichlorodifluoromethane).

The ORGDP program is divided into three main areas: (1) pilot plant testing, (2) conceptual design studies, and (3) optimization studies. The objectives of the pilot plant tests are to evaluate the overall process feasibility and to collect engineering performance data necessary for the design of plant-scale systems. The conceptual design studies are directed toward the preparation of detailed equipment layouts and cost estimates for specific plant applications. Process optimization studies are being used to guide the efforts of the overall project by supplying estimates of system operating parameters which lead to the lowest cost plants.

A pilot plant for the selective absorption process was designed and built at the ORGDP. The first phase of the pilot plant testing program has been completed, using refrigerant-12 as the process solvent. The results of these experiments are presented and discussed in this report, following a discussion of process and equipment design details and a description of pilot plant operating procedures and observations. The second phase of the testing program, in which refrigerant-11 is used as the process solvent, is currently under way, and the results will be presented later in a separate report. The conceptual design and optimization studies are not summarized here, but details are available elsewhere[6,7,8,9,10].

SUMMARY

The removal of krypton and xenon from contaminated air can be accomplished by intimately contacting the bulk gas stream with a continuously flowing stream of fluorocarbon solvent in a packed absorber column at some relatively low temperature and high pressure. Because of differences in solubility, essentially all of the krypton and xenon, plus substantial amounts of oxygen, nitrogen, and argon, can be dissolved in the solvent. The off-gas leaving the absorber column is approximately free of the noble gas contaminants and can be safely vented. The loaded solvent, containing absorbed gases rich in krypton and xenon, is routed from the absorber to a fractionator system where most of the dissolved nitrogen, oxygen, and argon is driven off. Next the solvent is directed into a stripper system where a product gas concentrated in krypton and xenon is evolved. Also, pure solvent is regenerated in the stripper and recycled back to the absorber.

Sizing of equipment items for the pilot plant was based on the criterion of processing 15 scfm of air at absorber pressures as high as 40 atmospheres and absorber temperatures as low as minus 94°F. For design purposes with refrigerant-12, the operating pressure and temperature of the fractionator were taken as 44 psia and 32°F, respectively, with values of 24 psia and 2°F used for the stripper. The pilot plant equipment items were constructed primarily using stainless steel and were insulated with glass foam. An on-line process gas chromatograph was developed to analyze gas samples from the various sectors of the process.

From the standpoint of operational feasibility, the initial design of the plant required little modification. Generally, pilot plant startup was easy, and once in operation, little effort was needed to maintain system operation. The major problem encountered initially in the shakedown of the pilot plant was the accumulation of water as ice in the equipment, but the addition of desiccant traps at strategic locations completely eliminated this problem. Minor problems associated with the experimental nature of the work included process gas and solvent leaks around sample valve packing and gaskets, and occasional column flooding during the early part of the program. Radioactive isotopes of krypton were not used in the testing program. Also, xenon has not been used yet, since it is felt that a plant designed and operated to remove krypton from a process gas will remove proportionally more xenon because of the higher solubility of xenon in refrigerant-12.

In the first phase of the project, 34 pilot plant tests were conducted to define the operational characteristics and feasibility of the process. The absorber column was operated under pressures of 164 to 437 psia and at temperatures between minus 77 and minus 21°F. Feed gas flows to the absorber were varied from 9.5 to 22.3 scfm, while solvent flow rates varied from 0.75 to 1.25 gpm. Krypton concentrations in the absorber feed ranged from 42 to 8800 ppm, and krypton removals in the absorber varied between 71.52 and 99.9%. Column decontamination factors as high

as 1000 were achieved. Average absorber column key component stage heights ranged from 10.5 to 61.8 inches on an H_{OG} basis and from 6.9 to 39.8 inches on an HETP basis.

The overall performance of the pilot plant has demonstrated that a continuous selective absorption process of the type tested can be used confidently to remove most of the krypton and xenon from contaminated gas sources now envisioned as presenting gas cleaning problems during the next few years. Test results showed that efficient plant operation favors lower absorber operating temperatures, higher absorber pressures, and higher L/G ratios. Economic studies, however, have indicated that higher absorption temperatures, as well as higher pressures, are preferable. Based on the phase I data, it appears that a plant designed around an absorber with an operating temperature of minus 30°F and a pressure near 425 psia should give a good balance between economics and performance with refrigerant-12 as the solvent. The expected column decontamination factor under such conditions is between 300 and 400, and over 99.7% of the krypton in the absorber feed gas should be removed. Overall process decontamination factors can, in most instances, be made to approach the column decontamination factor as closely as desired by proper selection of auxiliary system operating conditions. Refrigerant-12 appears to be a satisfactory solvent, both from the standpoint of the separation data and from the standpoint of stability. However, since the refrigeration costs do constitute a large fraction of the investment costs of a plant using refrigerant-12 as the process solvent, Phase II of the development project was initiated to evaluate the performance of a plant utilizing a higher boiling solvent. Presently, pilot plant tests are being conducted with refrigerant-11 (trichloromonofluoromethane). The results of the Phase II testing program will be presented in another report after the completion of the scheduled tests.

PROCESS DESIGN

As shown in figure 1 and as previously noted, both krypton and xenon are substantially more soluble in refrigerant-12 (dichlorodifluoromethane) than argon, oxygen, and nitrogen, especially at lower temperatures. The separation process, as conceived, incorporates an absorption step at some relatively low temperature and high pressure, followed by an intermediate fractionating step at some higher temperature and lower pressure to concentrate the krypton and xenon in the absorbed gas, and ending with a gas stripping and product removal operation conducted at a slightly lower temperature and further reduced pressure than used for the fractionation step. The noble gas product is recovered from the overhead vapors of the stripper column. Detailed descriptions of the process and the specific purposes of the primary equipment items are given in this section.

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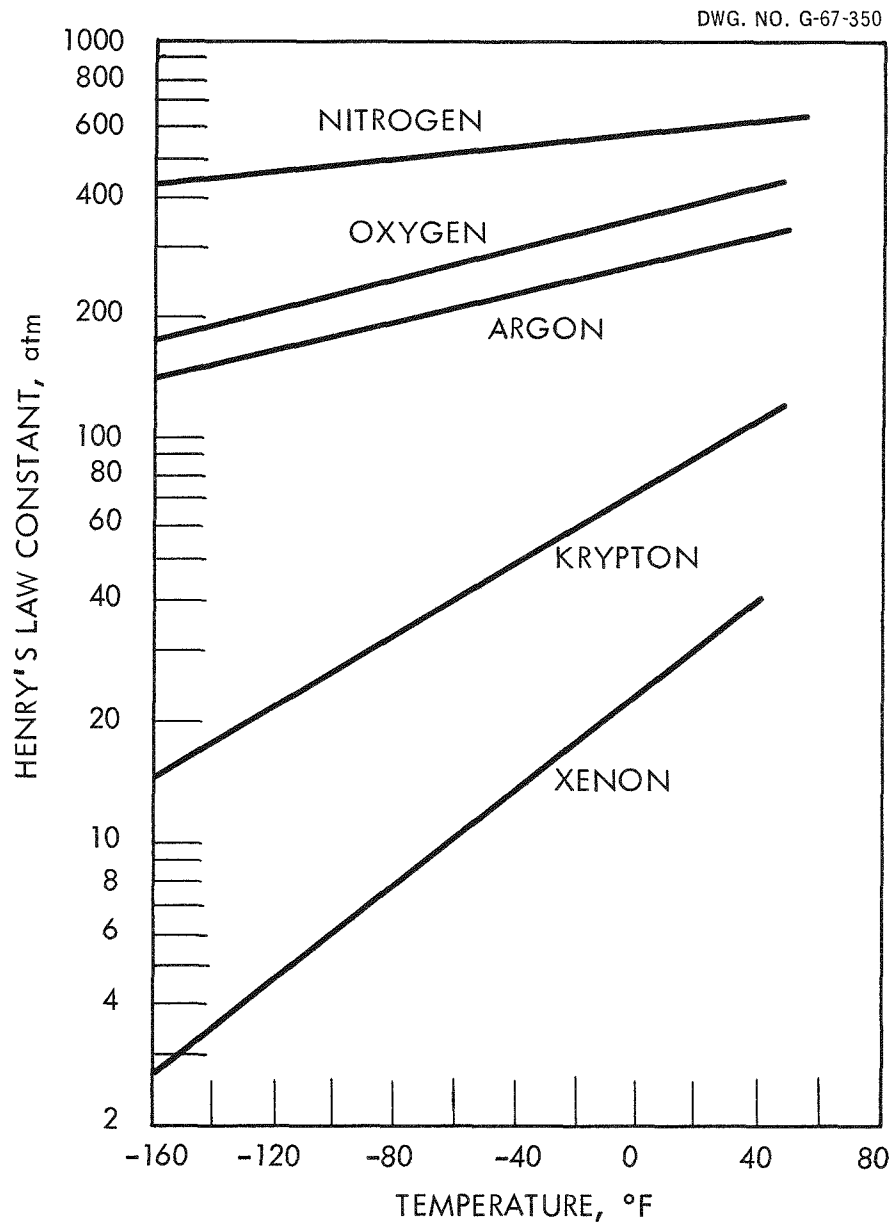
Figure 1

RELATIVE SOLUBILITIES OF GASES IN REFRIGERANT-12

Process Description

A schematic diagram of the absorption process is given in figure 2. The major equipment items in the process are three packed columns which function as intimate gas-liquid contactors. The absorption section of the process consists of a single packed column. The other two columns, each fitted with a reboiler, a flash drum, and an overhead condenser system, comprise the fractionator and stripper sections. The remainder of the process equipment includes gas and solvent heat exchange and refrigeration systems, desiccant traps, a gas compressor, a solvent pump, and solvent storage tanks.

The feed gas, contaminated with krypton and xenon, is first compressed to the absorber column operating pressure, passed through a fixed-bed desiccant to remove trace quantities of water and oil, and then cooled to the desired absorption temperature. The gas is next passed into the bottom of the absorber column and is contacted countercurrently with downflowing solvent. Under the proper operating conditions, essentially all of the krypton and xenon, plus a significant quantity of oxygen, nitrogen, and argon, is dissolved in the solvent. The cold process gas leaving the top of the absorber, depleted in contaminants, is used to cool the incoming feed and is then vented or, for convenience in pilot plant operation, recycled for feed makeup. Similarly, the liquid solvent containing absorbed gases passes from the bottom of the absorber column and is warmed by the incoming solvent feed before being fed, after some additional heating, to the fractionator flash drum. Because of the normal inefficiencies in heat transfer and the differences in stream flows, both the fresh solvent and contaminated feed gas require further cooling by auxiliary refrigeration equipment before being pumped into the absorber column. Interchange of heat between the absorber feed and discharge streams does, however, allow a considerable reduction in refrigeration requirements and, ultimately, in processing costs.

The fractionator is operated at a lower pressure and higher temperature than the absorber. Upon entering the flash drum of the fractionator, part of the solvent is vaporized and, along with a portion of the absorbed gases, passes into the fractionator overhead condensers. The remaining liquid is fed into the top of the packed fractionator column where it is contacted with upcoming vapor from the reboiler. Solvent vapor and a gas mixture consisting predominately of oxygen and nitrogen, with some argon, krypton, and xenon, pass out the top of the column and into the overhead condensers for solvent removal. The liquid solvent from the condenser system drains back to mix with the fractionator column feed liquid.

A large fraction of the absorbed oxygen, nitrogen, and argon is liberated from the solvent in the fractionator and, correspondingly, the remaining dissolved gas becomes further enriched in krypton and xenon. However, since a perfect cut cannot be achieved, a measurable amount of krypton and xenon is also evolved during fractionation; therefore, the fraction-ator off-gas is recycled back to the absorber to mix with the fresh feed

PURIFIED
VENT GAS

CONCENTRATED PRODUCT
GAS FOR STORAGE

GAS RECYCLE

CONDENSER

CONDENSER

LIQUID
CHILLER

CONTAMINATED
GAS SOURCE

ABSORBER COLUMN

LOADED SOLVENT

FRACTIONATOR COLUMN

CONCENTRATED SOLVENT

STRIPPER COLUMN

GAS COOLER

GAS CHILLER

GAS COMPRESSOR

LIQUID COOLER

HEATED
REBOILER

HEATED
REBOILER

PURE SOLVENT
RECYCLE TO
ABSORBER

LIQUID
PUMP

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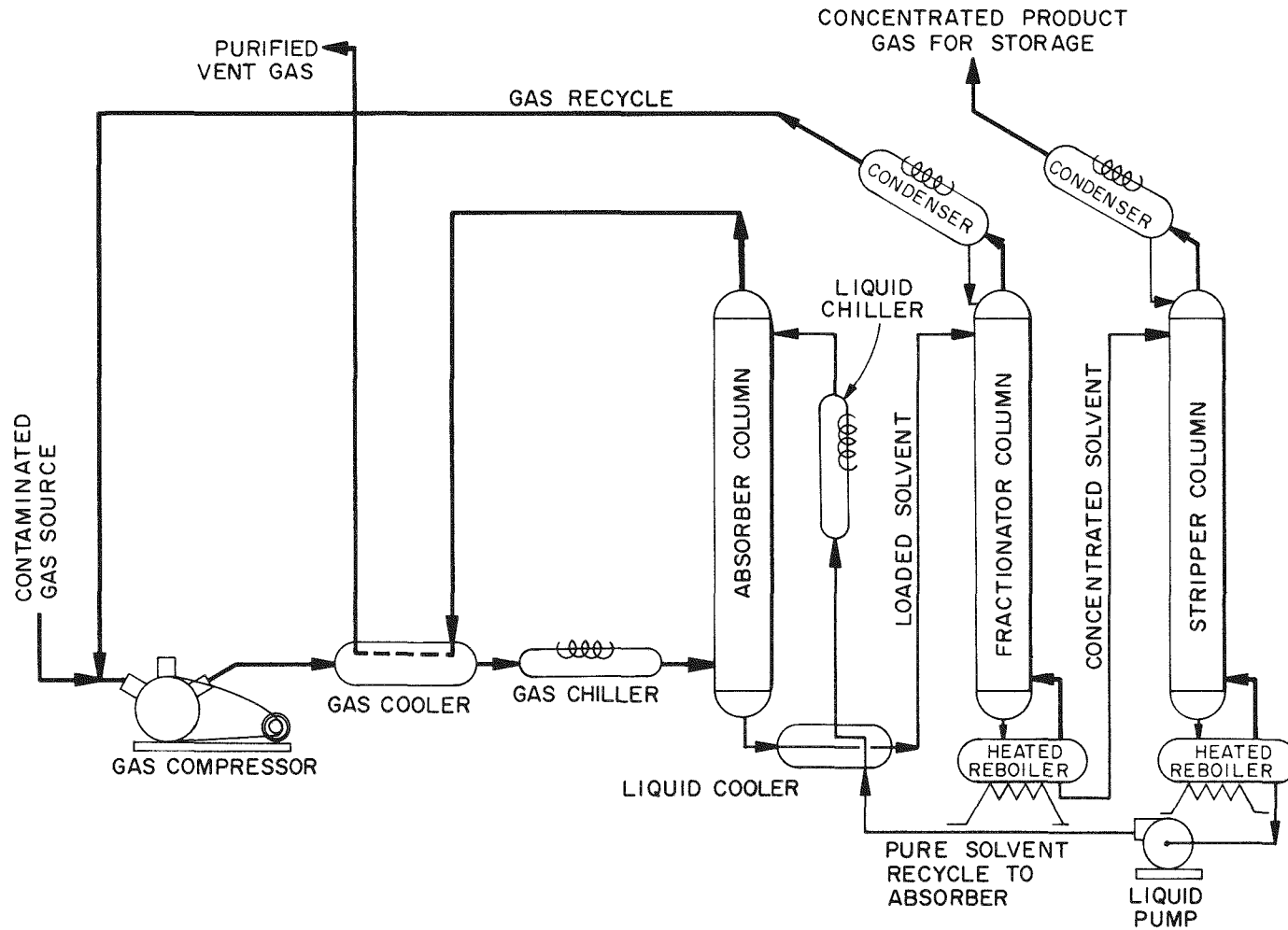
Figure 2

KRYPTON-XENON ABSORPTION PROCESS PILOT PLANT
SCHEMATIC FLOW DIAGRAM

at the suction of the process compressor. The amount of gas recycled and, hence, the concentration of the noble gas remaining in the solvent after fractionation depends upon the operating conditions of the fractionator; for example, lowering the operating pressure of the fractionator tends to increase the amount of recycle.

The solvent, containing absorbed gas enriched in krypton and xenon, is next routed from the reboiler of the fractionator to the stripper for noble gas recovery and solvent purification. The stripper section of the process is similar to the fractionator, and the action described for the fractionator is repeated in the stripper equipment. By operating the stripper at a different L/G ratio and under a lower pressure and, consequently, lower temperature than used previously in the fractionator, the remainder of the absorbed gases can be driven from the solvent. Essentially pure solvent flows from the reboiler of the stripper into a solvent storage tank prior to being pumped back to the absorber column for reuse. The composition and flow rate of the product gas stream leaving the stripper condensers depend upon the relative operating conditions of the fractionator and stripper.

In application, the stripper off-gas would be collected as product, but in the pilot plant testing program, the gas is recycled and mixed with the absorber off-gas to provide a simulated process feed.

PILOT PLANT DESIGN

A flow diagram of the pilot plant is given in figure 3. The design of the plant is flexible enough to permit extensive testing of the process over a broad range of operating conditions and also with considerable variation in operating schemes. Consequently, the pilot plant is intentionally more complex than may be necessary for some plant applications, and it is important to recognize that significant simplifications could perhaps be made for a specific plant application. The design criteria upon which the pilot plant was constructed and a detailed description of the major equipment items comprising the plant are given in this section.

Design Criteria

Basically, sizing of the pilot plant components was based on the criterion of processing 15 scfm of air at absorber pressures as high as 40 atmospheres and absorber temperatures as low as minus 94°F. The design flow rate for the refrigerant-12 solvent was between 0.75 and 1.50 gpm. The operating pressure and temperature of the fractionator were assumed to be 44.0 psia and 32°F, respectively, with values of 24.0 psia and 2°F used for the stripper. A computer program was written to model the absorption process and provide the component flow rate information needed for sizing the various equipment items.
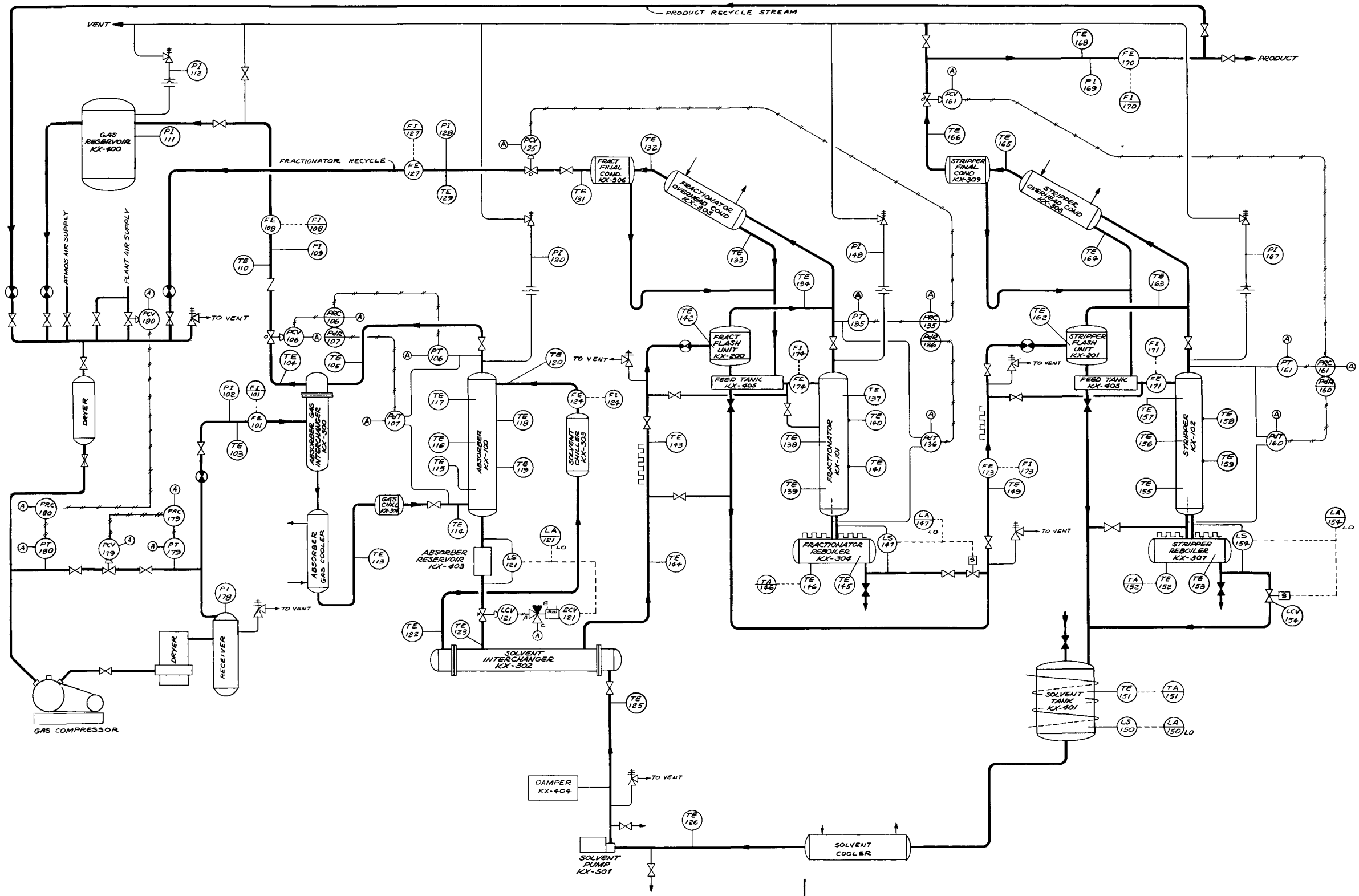
Figure 3
PILOT PLANT REFERENCE FLOW DIAGRAM

It should be noted at this point that many of the pilot plant equipment items except for the packed columns and the mechanical equipment, were chosen on the basis of the ease of adapting existing equipment not then in use to the noble gas process, in order to achieve time and cost savings. Consequently, some equipment items were not specially designed for this project and are somewhat oversized; more compact designs would clearly be possible in the case of a full-scale plant design effort. Thus, the specifications presented below should be viewed accordingly.

Absorber

The absorber column is a 3-inch-diameter stainless steel pipe, 10 feet high, with a 9-foot packed height. A photograph of the absorber column, along with the stripper and fractionator columns, is included as figure 4. There are three 3-foot-high sections of Goodloe column packing*, with intermediate gas sample and internal temperature points provided between the segments. Process gas feed and discharge lines are 1-inch-diameter stainless steel pipe, while solvent lines are 0.5-inch-diameter pipe.

Fractionator

The fractionator system consists of a packed column, reboiler, flash drum, and primary and secondary condensers. The fractionator packed column design is identical to that used for the absorber, except that provisions have been made for feeding between packed sections, if desired. This column is also pictured in figure 4.

The fractionator reboiler provides the heat necessary to generate a stripping vapor flow up the packed column. An enthalpy balance around the fractionator column and reboiler indicated a heating requirement of around 10,000 Btu/hr or 3 kw. To allow operating flexibility, a 5 kw electrical heater was strapped to the lower side of the reboiler. The reboiler, pictured in figure 4, is constructed from a 3-foot-long section of 8-inch stainless steel pipe and is connected to the column by a 1/2-inch pipe for downcoming liquid and by a 1-1/2-inch pipe for upflowing vapor. The liquid level in the reboiler is regulated by a liquid level controller which actuates a solenoid block valve. The liquid feed from the fractionator to the stripper passes through a 1/2-inch pipe welded to the bottom of the fractionator reboiler.

The fractionator flash drum, pictured in figure 5, is a 6-inch-diameter stainless steel cyclone, approximately 30 inches high and equipped with a tangential inlet, a liquid drain, a vapor discharge pipe, and a mist shield. The expanded bottom section of the unit serves as the fractionator column liquid feed tank. The design was based on limiting the peripheral gas velocity to 45 ft/sec under conditions where 100% of the liquid feed flashes.

Primary and final condenser systems remove solvent from the vapor streams leaving the flash drum and fractionator column. Most of the solvent

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* Product of the Packed Column Corporation, Springfield, New Jersey.
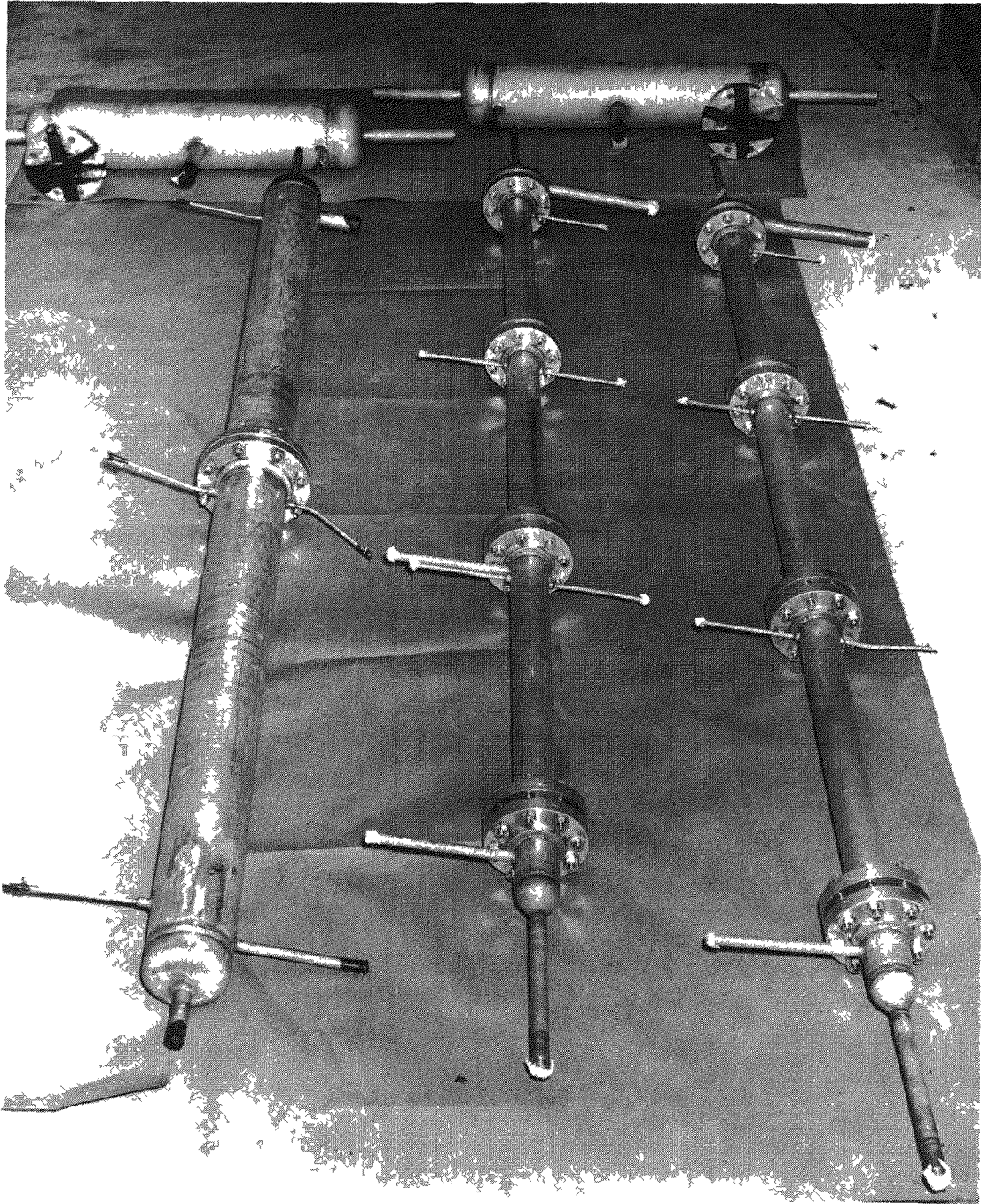
Figure 4

PILOT PLANT COLUMNS AND REBOILERS

Left to Right: Stripper Column and Reboiler, Fractionator Column
and Reboiler, and Absorber Column.
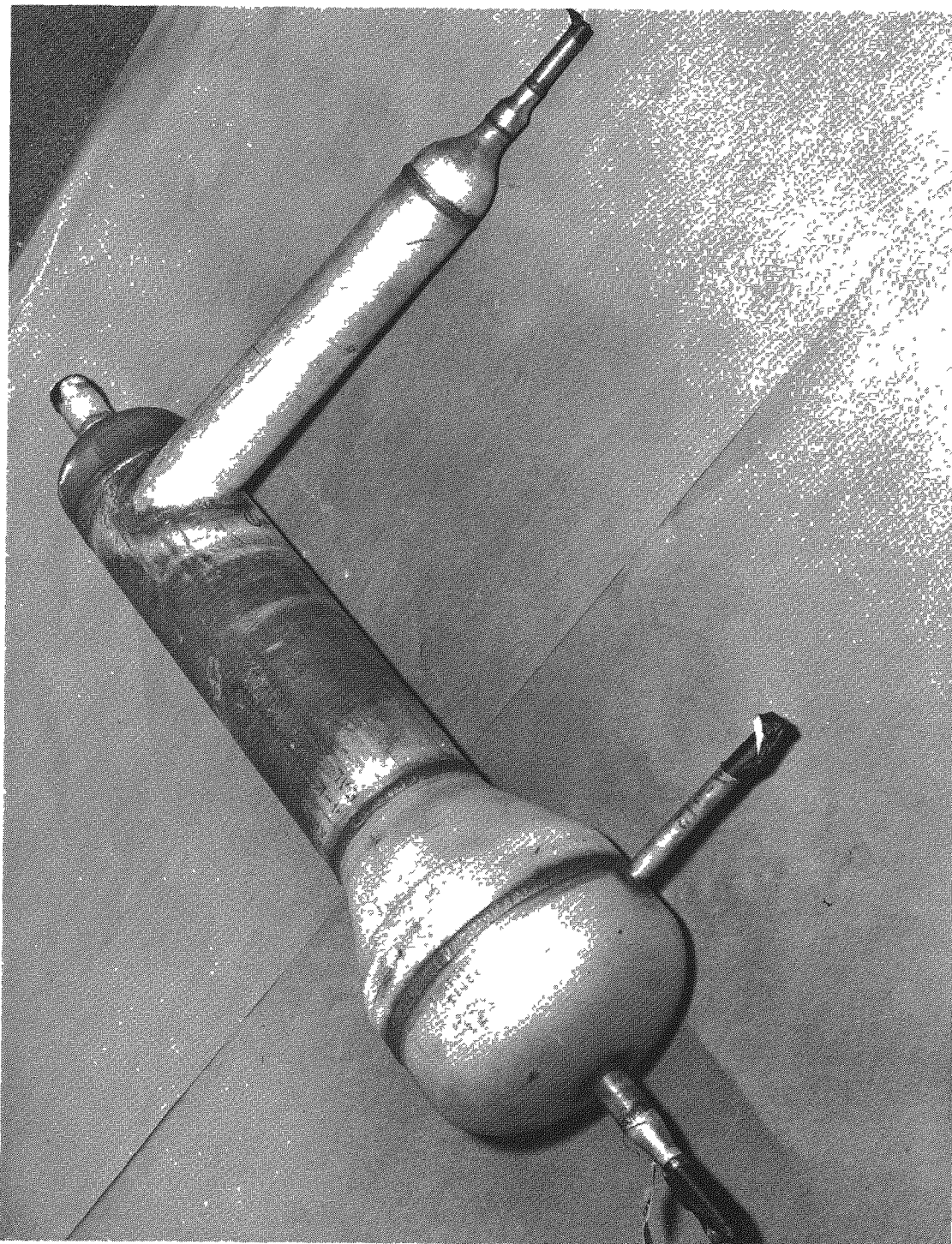
Figure 5
PILOT PLANT FLASH EVAPORATOR

condensation occurs in the primary condenser, which is a modified hairpin heat exchanger cooled by a recirculating low-temperature brine from an auxiliary refrigeration system. The shell is 70 inches long and is made from 4-1/2-inch-diameter heavy wall copper pipe. A 10-inch-diameter, 1-5/16-inch-thick copper flange is brazed to the shell at the tube sheet end, and the head-end is capped with 4-1/2-inch-diameter plate. The condensing surface consists of a 1-inch-diameter finned U-tube, each leg of which is 65 inches long. Both legs of the U-tube are brazed into the tube sheet, and there are twenty-one vertical baffles staggered regularly on the two sides of the tube. The condenser is inclined at an angle of about 15 degrees to the horizontal, with the vapor inlet at the lower head end and the gas outlet located on the shell next to the tube sheet. The condensate return line is connected to the lower side of the shell below the vapor inlet.

The final condenser consists of a tube bundle immersed in a refrigerated alcohol bath. The tube bundle is made up from thirteen, 42-inch-long, 1/4-inch-diameter, stainless steel tubes. The tubes are positioned by 1/4-inch-thick, 3-1/2-inch-diameter tube sheets, with 3-inch weld caps fastened to each end. The unit contains 2.3 square feet of condensing surface.

The primary condenser is designed to remove around 75% of the solvent contained in the fractionator column and flash drum off-gas streams. The bulk of the cooling load, therefore, falls on the mechanically re-frigerated primary condenser, with the low temperature final condenser relied upon for as little cooling as is necessary.

Stripper

In terms of associated equipment items, the stripper system is identical to that of the fractionator. There are, however, a few important depar-tures in design details. The column (figure 4) is constructed from 6-inch-diameter stainless steel pipe and contains 8 feet of Goodloe packing arranged in two sections. One intermediate sample and three internal temperature points are provided.

The stripper flash drum and reboiler are identical to those used with the fractionator. The nominal heat load to the stripper reboiler is 3.7 kw, and a 5 kw heater system is actually provided. The primary condenser system for the stripper consists of two hairpin heat exchangers, each identical to the one used for the fractionator primary condenser. The units are connected in parallel to handle the vapor flow from the stripper column and flash drum.

The stripper final condenser, like the fractionator final condenser, consists of a tube bundle and, in fact, is immersed in the same refrig-erated bath. The tube bundle is made up of thirty-seven, 42-inch-long, 1/4-inch stainless steel tubes positioned by two 1/4-inch-thick, 6-inch-diameter tube sheets, with a 6-inch weld cap located on each end.

Gas Compressor

An Ingersoll-Rand high-pressure type-30 compressor package* is used to compress the process gas to the operating pressure of the absorber. The unit consists of an Ingersoll-Rand Model 15T2, three-stage gas compressor, a General-Erie† aftercooler and air dryer, and an air receiver. The compressor is capable of delivering 15 scfm of air at 600 psia, with atmospheric suction. The compressed gas leaves the aftercooler at a temperature of 80°F.

The as-received compressor pressure regulator device consisted of a pressure-actuated flapper valve on the suction of the compressor. Each time the flapper valve was positioned, some amount of process gas was lost through venting of the control relief valve. The pressure limiting device was removed, therefore, and an automatic control valve was installed around the compressor to limit compressor discharge pressure by recycling excess inventory. The new setup allowed for better control and eliminated process gas losses. Obviously, recycle control would be essential for operations where radioactive materials were being handled.

Solvent Pump

A Milton Roy Model DMR1-97-70-SM Milroyal controlled volume pump§ is used to provide a metered flow of solvent to the process. The reciprocating, positive displacement pump is totally enclosed and features a diaphragm liquid end. The unit has a maximum capacity of 2.5 gpm and maximum discharge pressure of 600 psig. The stroke length is adjustable from 0 to 100% capacity variation while the pump is operating. The diaphragm is Teflon, while all other wetted parts are 316 stainless steel. A stainless steel surge chamber is provided to dampen the pulsations of the discharge.

Feed Gas Coolers

Before the process gas can be introduced into the absorber, it must be cooled to the operating temperature of the column. For the bulk of the cooling load, the otherwise wasted cooling capability of the gas leaving the absorber is utilized by passing the two gas streams countercurrently through a heat exchanger. The initial interchange of heat is accomplished using a series arrangement of two horizontal, hairpin, shell-and-fin tube heat exchangers. The shell of each exchanger consists of two parallel 76-1/2-inch lengths of 2-inch pipe welded to a return section. The return section is fabricated from 3/16-inch-thick plate and has a 5/16-inch-thick slip-on flange welded to it. The exchanger tube consists of 1-inch-diameter finned tubing, which enters the end of one of the shell pipes, makes a 180-degree bend within the return section, and

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* .Product of Intersoll-Rand, New York, New York.

† Product of General-Erie Corporation, Erie, Pennsylvania.

§ Product of Milton Roy Company, Philadelphia, Pennsylvania.

passes through the other shell pipe. The shell inlet and exit connections are made by standard couplings which are welded to the bottom of the lower shell and the top of the upper shell, respectively. All plate is SAE 1020 steel and pipe is seamless steel.

The remainder of the process gas cooling is accomplished in the absorber gas chiller. The chiller consists of three coils of 1-inch stainless steel tubing wound on a 9-3/4-inch radius, with the coils spaced 8 inches apart and immersed in a refrigerated bath.

A mechanically refrigerated gas cooler was installed in the process gas line between the interchanger and absorber gas chiller. The purpose of the added refrigeration capability was to decrease the process cool-down time during startup and to ensure adequate gas cooling during operation. Two heat exchangers, identical to the ones used as the fractionator and stripper primary condensers, were connected in series and operated with an evaporative refrigeration system to provide this auxiliary cooling.

Solvent Coolers

The function of the solvent interchanger is to facilitate an efficient transfer of heat between the solvent streams entering and leaving the absorber. The unit is a shell and tube heat exchanger; incoming solvent passes through the tube side, while solvent leaving the absorber column flows through the shell side. The tube bundle is composed of nineteen 1-inch stainless steel tubes, arranged on a 1-1/4-inch triangular pitch, welded to 1-1/2-inch-thick tube sheets. The shell is made from a 78-1/2-inch-long section of 8-inch stainless steel pipe. Segmental baffles are spaced 1 foot apart. The heads of the exchanger are 8-inch weld caps. The solvent interchanger contains 31 square feet of internal transfer area.

The solvent chiller completes the cooling of the incoming solvent to the absorber. The chiller unit consists of ten coils of 3/4-inch stainless steel tubing wound on a 3-5/8-inch radius, with coils spaced 2-3/4 inches apart, and immersed in the same refrigerated bath as the absorber gas chiller. The solvent chiller handles less than 10% of the total solvent cooling load.

In addition to the regular cooling equipment, a mechanically refrigerated heat exchanger was placed in the line between the solvent storage tank and the solvent pump. The precooler aids in the process startup by helping to prevent pump cavitation. The heat exchanger is identical to the ones used as primary condensers for the fractionator and stripper.

Solvent Storage Tank

The solvent storage tank is constructed from two 7-foot lengths of 10-inch-diameter steel pipe. The pipes are closed on each end with 10-inch weld caps and positioned side-by-side horizontally. The combined holding capacity of the tanks is just over 8.5 cubic feet. External

refrigeration coils are provided to cool the solvent and prevent boiling and pressure buildup.

Materials of Construction

Refrigerant-12, the process solvent, is thermodynamically stable and noncorrosive. For low temperature and high pressure service, the predominate materials of construction in the pilot plant are 304L stainless steel and copper. In most cases, standard low-carbon steel was not used in locations where the temperature could be lower than minus 20°F, because of embrittlement problems. It might be noted that the copper heat exchangers widely used in the pilot plant were obtained from another project.

Insulation

Glass foam is the major insulation material used in the pilot plant. A 4-inch-thick layer of insulation proved to be adequate around the absorber column, where temperatures as low as minus 75°F were eventually employed, and on the low temperature brine line, which was maintained near minus 110°F. Magnesia insulation was used around the reboilers.

Process Instrumentation

The temperature, pressure, and flow instrumentation provided for the pilot plant is illustrated in figure 3, with the identification of each instrument symbol and a further description given in the appendix. Much of the instrumentation shown would be desirable for plant-scale operation, although about half of the thermocouples could probably be eliminated.

Analytical Instrumentation

The pilot plant has many sample points on both the gas and liquid lines and a process gas chromatograph* was adapted for the determination of krypton, refrigerant-12, oxygen, and nitrogen in the gas streams. This analyzer provides automatic on-stream monitoring of the gas samples. The chromatographic separation of krypton and air constituents is accomplished on activated carbon and molecular sieves. The refrigerant-12 requires use of a third column, matched to the adsorptive characteristics of air, krypton, and refrigerant-12. The conditions of analyses are:

Temperature	250°F
Carrier	Helium, 44 cc/min
Column I	Silica Gel, 1/4-inch X 20 cm
Column II	Activated Carbon, 1/4-inch X 3 m
Column III	Molecular Sieve, 5A, 1/4-inch X 1-1/2 m

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* Model 26-212A, product of Process Analyzers, Inc., Houston, Texas.

By automatic valving, refrigerant-12 is diverted directly to the thermal
conductivity detector from column I, while krypton and air are stored in
column II. After the refrigerant is determined columns II and III are
automatically valved into the carrier stream for separation of oxygen,
nitrogen, and krypton. The total analytical cycle time is 15 minutes.
Sample pressure is set from atmospheric to several atmospheres by means
of a remotely actuated back-pressure regulator.

Calibrations for krypton over a range of 20 ppm to 0.74% indicate a limit
of detection of 5 to 10 ppm for samples of 10 cc. At 77 ppm, the stan-
dard deviation is ± 2 ppm and the limit of error for one determination
(95% confidence level) is ± 6% (relative). Calibrations for refrigerant-
12 were conducted over a range of 0.5 to 4.0%. At 1.84%, the standard
deviation is ± 0.06% (absolute), and the limit of error for one determi-
nation (95% confidence level) is 4% (relative).

PILOT PLANT OPERATION

The methods and procedures for pilot plant startup, operation, and shut-
down, developed during the course of process testing, are directly
adaptable to the operation of large-scale plants. On an overall basis,
performance was excellent during the phase I program, operation was
easy to maintain, and problems were easy to identify and remedy. An
account of the various operational procedures and a discussion of the
problems encountered during operation follow.

Pilot Plant Startup

During the course of this work, the pilot plant was operated on a 5-day
schedule, with routine shutdowns each week-end. Both initial and routine
startup of the plant were relatively easy, with a systematic startup
procedure employed satisfactorily.

Prior to beginning the phase I tests, refrigerant-12 was charged to the
pilot plant system as a vapor and condensed in the solvent storage tank.
This vapor was first dried by molecular sieves to remove possible traces
of residual water prior to condensing the solvent in the refrigerated
storage tank. After the solvent tank was filled, the mechanically refrig-
erated systems for the solvent and gas precooler and for the fractionator
and stripper primary condensers were turned on, and the chiller and con-
denser baths were cooled. Next, the gas compressor was started, and the
absorber column was valved in and pressurized with air to the desired
operating point. The absorber had to be cooled, at least to below the
boiling point of the solvent, prior to starting the solvent flow through
the column or else an unreasonable amount of solvent would have been
vaporized and carried back to the compressor. The absorber was cooled
by recycling gas in a closed loop from the compressor, through the
refrigerated heat exchangers (including the auxiliary units), up the
absorber column, and finally back to the compressor.

Once the desired operating pressure and temperature of the absorber were achieved, the solvent pump was valved to the absorber and liquid was pumped from the storage tank to the absorber. After the solvent was in motion through the absorber, the fractionator and stripper were valved to the process. With the pressure controllers set, gas liberated from the solvent quickly filled the two systems to their respective operating pressures. As cold liquid was introduced into the warm columns, much of the solvent was vaporized, and the overhead condensers were momentarily overloaded. Heat was supplied to the reboilers once the liquid and gas flows and the condenser temperatures leveled out. The reboiler heat was adjusted until the column pressure drops reached around 1.0 inch of water per foot of packing.

The time required for pilot plant startup varied to some extent with the operating temperature desired but was usually less than 4 hours.

Steady-State Operation

Once the plant was started up, little effort was required to maintain efficient operation. Small system fluctuations sometimes required occasional adjustment of reboiler temperatures using manual heater controllers. Dry ice had to be added to the refrigerated baths periodically to maintain the lower operating temperatures employed for some of the colder runs. Sampling losses necessitated periodic solvent makeup while the plant was in operation; in the pilot plant, solvent can be fed directly to the storage tank while normal operations are maintained, as long as the temporary pressure increase in the tank due to the vapor transfer does not exceed the working pressure of the stripper.

For the pilot plant testing program, once the plant reached steady operation, krypton was injected into the system at the suction of the compressor. Xenon was not used in the first phase of the project since it is felt that a plant designed and operated to remove krypton from the process gas will easily remove at least a comparable amount of xenon, since xenon is considerably more soluble than krypton in refrigerant-12 (figure 1). During pilot plant operation, the krypton feed mixture was internally regenerated, since all gas streams were recycled; thus, charging of fresh material for each run was not required.

Samples were withdrawn from various points of the process for either chromatographic or mass spectrographic analysis as soon as the plant achieved steady-state operation after the introduction of the krypton. Chromatograph samples were withdrawn through any one of several sample lines connected to the various sample points. In the normal sequence of operation, the chromatograph controller actuated a solenoid valve to purge the sampling line running to the selected sample point before introducing a sample into the analyzer. Occasionally, samples were taken manually from the various sample points for mass spectrographic analysis. The chromatograph was relied upon almost entirely for sample analysis, with mass spectrographic analysis used as a backup. With essentially instant results, the gas chromatograph enabled observation of runs as

they were being made and greatly reduced the time required to make the
necessary tests.

Pilot Plant Shutdown

The shutdown procedure for the pilot plant was relatively fast and simple.
In stopping operation, the first step was to turn off the reboiler heat
on both the fractionator and stripper. Next, after several minutes'
delay to allow some of the sensible heat to be carried away from the
columns, the solvent pump was stopped, and the block valves between the
three columns were closed. The gas compressor was then stopped and
valved out of the system. Last, the refrigeration systems were shut
down. The total time required to complete the pilot plant shutdown
operations was typically less than one hour.

Operational Comments and Problems

The absorption process is not a complex one, and as noted, the pilot
plant was fairly easy to operate. Nevertheless, minor design and opera-
tional difficulties were occasionally encountered in the course of the
plant shakedown and testing program which preceded the formal run series.

Off-on liquid level controllers were used to maintain reboiler inventories
and to control the solvent flow from the absorber column. In an actual
plant, the more expensive proportional control might be better, eliminat-
ing liquid surges from column to column; however, from a control stand-
point, the off-on controllers did perform satisfactorily. The pneumatic-
ally operated control valve used with the absorber leaked frequently
around the packing and had to be retightened routinely. Frost buildup
around the valve stem and exposed valve body interfered with valve
operation, and as a necessity, a small air blower was positioned to keep
the exposed surfaces of the valve dry. To fully insulate the valve would
have made it inaccessible for leak checking and periodic maintenance. In
view of this nuisance, bellows seal or other packless valves would be
preferred in an actual plant. Packless solenoid-operated refrigeration
valves were installed on the solvent lines leaving the fractionator and
stripper reboilers. These valves are relatively compact and were insu-
lated almost completely except for the solenoid coil. From a maintenance
standpoint, operation of the solenoid-operated valves was better by far
than that of the pneumatic valve.

The mass flowmeters monitoring the flow rates of feed gas and off-gas
from each of the three packed columns were practically indispensable to
plant operation. Performance and reliability of the meters were excellent.
In contrast, all of the turbine-type liquid flowmeters used initially in
the pilot plant could not be made to operate properly due to the effects
of pressure surges and small particles sometimes present in the solvent
lines. To trap particulates, fine mesh screens had been placed in front
of the meters, as suggested by the vendor, but both the screens and the
meters still demanded continual cleaning. These meters were eventually
removed from the process altogether. As a substitute, a magnetic-pickup

armored rotameter was installed in the solvent feed line to the absorber. Both operation and reliability of this instrument have been satisfactory.

As previously discussed, regenerated solvent from the stripper feeds by pressure difference into a refrigerated storage tank and from there to the solvent pump. During normal pilot plant operation, the temperature of the solvent storage tank was maintained near minus 10°F, under a refrigerant-12 vapor pressure of 19 psia.

Some operational problems were encountered because of the formation of ice in process lines during early shakedown tests with the pilot plant. After molecular sieve columns were installed to dry all new solvent and air being charged into the system, no further trouble was encountered.

Flooding was experienced occasionally in the fractionator and stripper columns, especially in the earlier stages of testing before operating techniques had been fully developed. In each case, flooding was attributed to excessive boilup from the reboiler. In normal service, the columns were maintained at 50 to 75% of flooding capacity. When operating outside this range at near-flood conditions, very small column pressure fluctuations sometimes resulted in a sharp increase in reboiler activity. Good pressure control with fast response is, therefore, important to the smooth operation of the process. In other cases, flooding resulted from too much heat on the reboiler, a situation mainly encountered during too rapid a startup. Most flooding conditions were arrested by simply decreasing the reboiler heat. In a few severe cases, however, the liquid pump had to be stopped or the flooded column isolated until it was brought under control. After each column excursion, the air compressor dryer and receiver tanks were blown down to remove possible traces of refrigerant-12.

Process gas leaks around gaskets and across the seats of sampling valves sometimes occurred. However, in actual plant applications, most joints would be seal-welded for containment of radioactive gases, the many sampling valves required for experimental work would not be required, and consequently, process gas leakage should not be a problem.

TEST RESULTS

The pilot plant experiments with refrigerant-12 as the solvent were conducted over a wide range of processing conditions. For the testing program, the absorber column was operated under pressures of 164 to 437 psia and at temperatures from minus 77 to minus 21°F. Process gas flows to the absorber were varied from 9.5 to 22.3 scfm while solvent flow rates varied from 0.75 to 1.25 gpm; the absorber feed L/G ratios were between 1.43 and 4.17, on a mole per mole basis. The fractionator was maintained at an operating pressure of about 44 psia, with reboiler temperatures of 32 to 35°F. The fractionator primary condenser was operated at about minus 60°F and the final condenser bath at minus 110°F. The flow of fractionator off-gas recycled to the absorber varied from 2

to 8 scfm. The stripper was maintained at a pressure of about 24 psia, with reboiler temperatures in the range of 1 to 5°F. The stripper primary condenser was operated at minus 25 to minus 30°F, and the final condenser bath at minus 110°F.

Before describing the experimental results, it should be emphasized that, for each test, the krypton concentration in the absorber feed was deliberately forced to a level high enough to yield at least a detectable quantity (5 to 10 ppm) of krypton in the off-gas. While krypton removals to below detectable limits are impressive and, in fact, sometimes resulted with low feed concentrations, such complete removals were purposely avoided in the formal tests, since the complete data analysis desired is impossible under these circumstances. In the testing program, inlet krypton concentrations ranged from 42 to 8800 ppm, with krypton removals in the absorber between 71.5 and 99.9%. Correspondingly, absorber decontamination factors as high as 1000 were achieved in the 9-foot-high column. Average absorber stage heights for the key component, krypton, varied from 10.5 to 61.8 inches on an H_{OG} basis and from 6.9 to 39.8 inches on an HETP basis. A summary of the test conditions and results is given in table I, with further discussion of the data presented in the following sections. First, some general comments about krypton absorption are made, and then, the stage height data and correlations are detailed.

Noble Gas Absorption

There are two related parameters which characterize the degree of noble gas cleanup in the absorber column; namely, the percentage of noble gas entering the bottom of the column which is absorbed in the solvent and the absorber column decontamination factor. Figure 6 can be used to indicate how these parameters are related to each other, as well as to other significant process performance indicators and operating constants.

In an absorption process operating at conditions where neither stream flow rates nor compositions change with time, and also where all of the absorber column off-gas is vented to the atmosphere, material balances around the absorber yield the following relationships between the percentage removal by absorption of a specified gas, e.g., krypton, and the absorber decontamination factor for that component:

$$\psi = \frac{100 \ D_A - 100}{D_A} \tag{1}$$

or

$$D_A = \frac{100}{100 - \psi} \tag{2}$$

where ψ = the percentage of a specified gas entering the bottom of the absorber which is dissolved in the solvent, and

D_A = the absorber column decontamination factor for that component.

TABLE I

PILOT PLANT TEST SUMMARY WITH REFRIGERANT-12 AS THE PROCESS SOLVENT

Run Number	Average Absorber Conditions Temperature, °F	Pressure, psia	Solvent Flow Rate, gpm	Absorber Feed Gas Flow Rate, scfm	Krypton Concentration, ppm	Absorber Off-Gas Flow Rate*, scfm	Krypton Concentration, ppm	Feed L/G Ratio, mole basis	Krypton Removal in Absorber %	Absorber Column Krypton Decontamination Factor
1	- 24	416	0.75	9.5	990	5.5	5	3.17	99.71	345
2	- 25	416	0.75	9.6	1670	6.1	5	3.16	99.81	526
3	- 30	416	0.75	15.1	125	9.4	5	2.00	97.51	40.2
4	- 32	416	0.75	15.0	305	8.5	8	2.04	98.51	67.1
5	- 31	416	0.75	20.6	60	14.7	21	1.47	75.02	4.00
6	- 26	416	1.0	15.2	1130	9.7	23	2.65	98.70	76.9
7	- 26	416	1.0	15.5	1070	9.2	15	2.62	99.17	120
8	- 24	437	1.0	15.0	3080	6.5	19	2.69	99.73	370
9	- 23	434	1.0	15.4	1640	7.1	8	2.62	99.78	455
10	- 23	338	1.0	14.9	8800	9.9	470	2.70	96.45	28.2
11	- 22	338	1.0	14.9	7700	9.7	400	2.70	96.62	29.6
12	- 25	338	1.25	15.0	690	9.8	16	3.36	98.48	65.8
13	- 26	260	1.0	14.4	8780	10.9	1360	2.81	88.28	8.53
14	- 26	260	1.0	14.9	8200	11.5	1680	2.71	84.19	6.33
15	- 26	260	1.0	14.6	5820	12.0	715	2.76	89.90	9.90
16	- 43	260	1.0	15.7	1620	12.0	272	2.62	87.17	7.79
17	- 45	260	1.0	15.5	6900	12.2	1260	2.65	85.63	6.96
18	- 41	260	1.0	15.8	5800	12.6	1060	2.59	85.01	6.67
19	- 53	260	1.25	15.3	1320	11.0	22	3.38	98.80	83.3
20	- 50	260	0.75	15.6	3820	12.7	1240	1.99	73.57	3.78
21	- 53	260	0.75	16.0	3480	13.0	1150	1.95	73.15	3.72
22	- 52	164	1.0	15.4	362	12.6	126	2.70	71.52	3.51
23	- 23	326	1.0	15.8	1950	11.1	262	2.54	90.56	10.6
24	- 21	326	1.0	15.1	1230	9.9	72	2.67	96.16	26.0
25	- 26	314	0.75	14.5	1150	10.5	222	2.09	86.02	7.15
26	- 27	314	0.75	14.8	1060	10.7	282	2.05	80.77	5.20
27	- 29	416	0.75	14.8	245	9.6	12	2.05	96.82	31.4
28	- 75	362	1.0	14.1	2370	7.8	16	3.01	99.63	270
29	- 77	164	1.0	15.9	140	12.9	26	2.67	84.93	6.64
30	- 74	266	1.0	15.1	420	10.4	5	2.81	99.18	122
31	- 73	266	1.0	10.2	2940	6.2	5	4.17	99.90	1000
32	- 71	266	1.0	10.1	2430	5.8	6	4.17	99.86	714
33	- 72	266	0.75	21.8	422	17.3	140	1.45	73.67	3.80
34	- 75	266	0.75	22.3	42	17.6	13	1.43	75.57	4.09

* The difference between the absorber feed gas flow rate and the off-gas flow rate yields the gas absorption rate.

33

RECYCLE GAS

R, y_R

PRODUCT
GAS

P, y_P

DECONTAMINATED
VENT GAS

V, y_V

S, x_S

RECYCLE
SOLVENT

ABSORBER SYSTEM

FRACTIONATOR SYSTEM

STRIPPER SYSTEM

CONTAMINATED
GAS FROM
NUCLEAR PROCESSING
SYSTEM

A, y_A

F, y_F

L, x_L

C, x_C

LOADED
SOLVENT
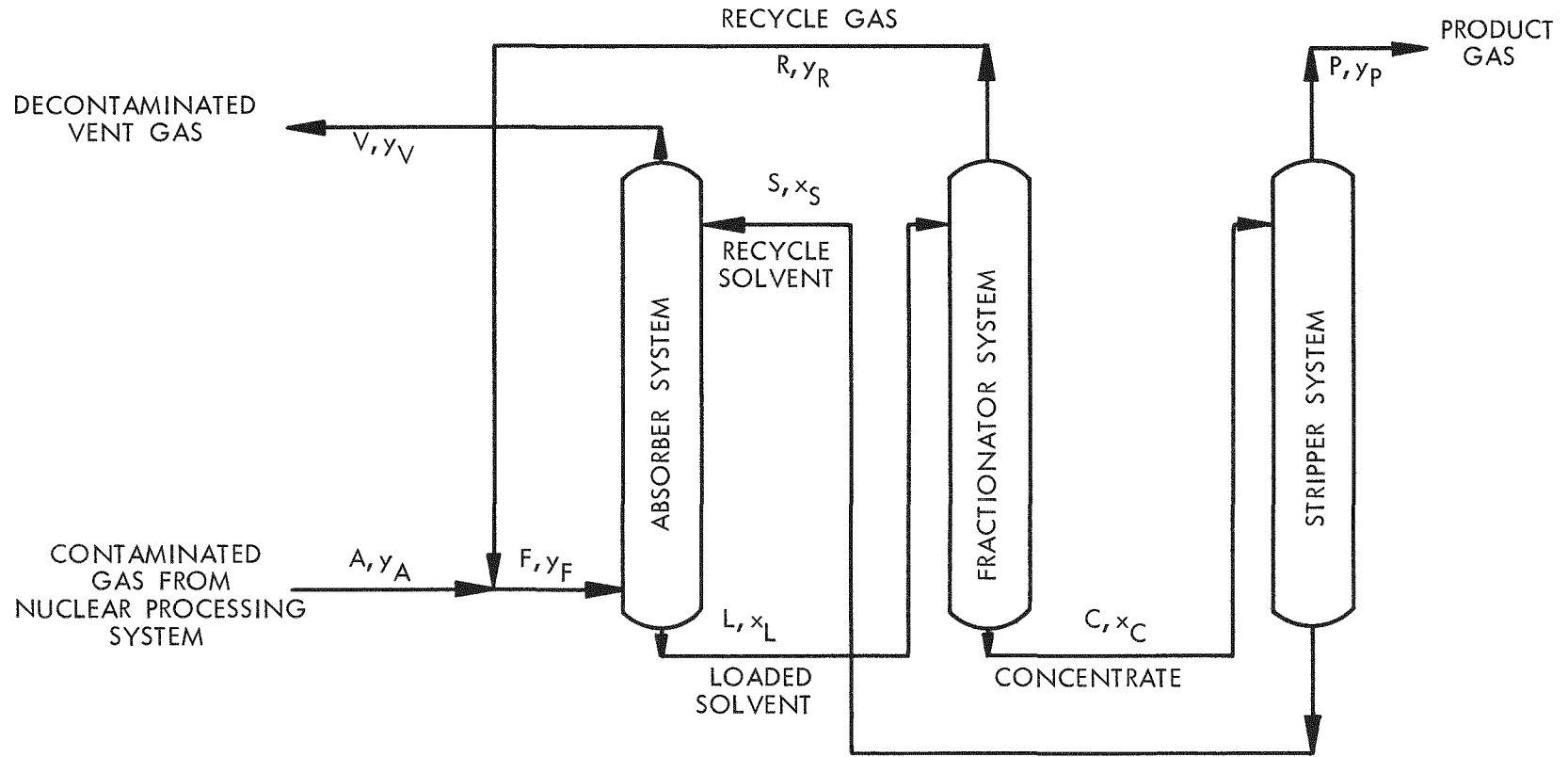
CONCENTRATE

Figure 6

ABSORPTION PROCESS SCHEMATIC FLOW DIAGRAM

Now, D_A is defined using stream flows as:

$$D_A \equiv \frac{Fy_F}{Vy_V} \qquad (3)$$

where F = total flow rate of feed gas, including recycle gas, entering the bottom of the ab~rber column;

y_F = concentration of specified gas component in F;

V = flow rate of gas leaving the top of the absorber column; and

y_V = concentration of specified gas component in V.

Related to D_A, but of more interest, of course, is the overall process decontamination factor, which is a method of expressing the gas cleanup required for safe venting. To ~rrive at relationships between the overall decontamination factor and D , however, two additional definitions are useful. First, the process ecovery efficiency can be represented by:

$$\varepsilon \equiv \frac{Py_P}{Ay_A} \qquad (4)$$

where ε = recovery efficiency, i.e., fraction of a specified gas component entering the process from outside which is collected in the product;

P = flow rate of gas product stream leaving the stripper system;

v_γ = concentration of specified gas component in P;

A = flow rate of contaminated gas from some ₙuclear reactor or processing system to the absorption system; and

y_A = concentration of specified gas component in A.

Next, an operating constant specifying the component internal recycle ratio, ρ, can be defined:

$$\rho \equiv \frac{Ry_R}{Ay_A} \qquad (5)$$

where ρ = ratio of the amount of specified gas component recycled to the absorber column from the fractionator system to the amount of specified gas component fed to the process from outside,

R = flow rate of gas stream recycled from the fractionator system to the absorber column, and

y_R = concentration of specified gas component in R.

With the above definitions, several additional relationships can be used to relate potential plant performance characteristics to the absorber parameters.

First, let D_P be the overall process decontamination factor, defined by:

$$D_P \equiv \frac{A y_A}{V y_V} \qquad (6)$$

Then, by manipulating the previous equations, several alternative forms can be obtained:

$$D_P = \frac{1}{1 - \epsilon} \qquad (7)$$

$$D_P = \frac{D_A}{1 + \rho} \qquad (8)$$

$$D_P = \frac{D_A - 1}{\rho + \epsilon} \qquad (9)$$

$$D_A = D_P(1 + \rho) \qquad (10)$$

$$D_A = \frac{1 + \rho}{1 - \epsilon} \qquad (11)$$

$$\epsilon = \frac{D_P - 1}{D_P} \qquad (12)$$

and

$$\rho = \frac{D_A - D_P}{D_P} \qquad (13)$$

To illustrate the use of the above equations, application to an example case might be helpful. In a typical process situation, the overall process decontamination factor, D_P, would be set by the cleanup job required of the absorption system. Therefore, the recovery efficiency, ϵ, would also be fixed (equation 12). The plant designer then would be free to select families of absorber decontamination factors, D_A, and recycle ratios, ρ, which would satisfy the removal criteria. Choice, within these families, of the particular D_A and ρ values used, and subsequent design of equipment and selection of processing parameters would then be done considering such factors as economics, ease of operation, and product specifications.

For example, suppose an overall krypton decontamination factor of 100 was required to ensure safe venting of a nuclear process off-gas. For this D_P, the corresponding recovery efficiency, ε, would be 0.99. In the pilot plant work, absorber decontamination factors between about 4 and 1000 were measured in the formal tests. Values in excess of 1000 were also observed in many cases where the krypton content of the off-gas stream was below the detectable limit; as was previously pointed out, however, complete data analysis for such situations is not possible, so these cases were excluded from the data summaries. In any event, absorber decontamination factors from 100 to 1000 should be easily attainable in a 9-foot packed height column similar to the pilot plant unit, as required.

For the example case, if the absorber were operated at conditions which resulted in a column decontamination factor, D_A, of 250, then the recycle ratio, ρ, could not exceed 1.5 (equation 13). For $D_A = 500$, the maximum ρ would be 4, and so on. A major factor in selecting a satisfactory combination of D_A and ρ would be product concentration and flow rate criteria. Another important point is that there would be considerable latitude in the plant design effort, permitting full consideration of economic factors. This is because the process appears to be versatile enough to perform most of the noble gas cleaning jobs envisioned for the next few years without placing undue restrictions on plant design.

Looking further at the absorption process and using the equations given above, some general trends and guidelines can also be noted:

1. With the restrictions noted previously for this development, the overall process decontamination factor, D_P, can be made to approach the absorber decontamination factor, D_A, by decreasing the recycle ratio, ρ (equation 8). Thus the absorber decontamination factor represents, in this case, an upper limit for the overall decontamination factor*.

2. The recycle ratio is the key fractionator design parameter. If this factor is zero (i.e., if a fractionator system as shown in figure 6 isn't even used), then the overall process decontamination factor is at its highest possible value; however, in this case, all of the gas components, such as oxygen, argon, and nitrogen, which are removed in the absorber column will end up in the product gas stream, and

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* Actually, if a portion of the absorber off-gas is recycled back through the absorber column rather than vented, then D_A is not an upper limit for D_P, which would in this case be defined on the basis of the atmospheric release stream instead of the absorber off-gas stream. However, as the amount of this recycle increases, the plant equipment item sizes generally increase as well. Such an operating scheme might nevertheless be employed in cases where the process gas load to the absorption system is variable, but where the operator prefers to maintain a constant feed flow rate to the absorber column by recycling portions of the vent gas as necessary to make up for decreases in the process feed rate.

the product dilution, which may be unwanted, is at its maximum. Such an arrangement might be feasible and even advantageous in some instances, however, such as cases in which the diluents in the low flow rate product gas stream can be dealt with in a practical manner chemically (oxygen or nitrogen) or else are present at low concentrations because of large separation factors (e.g., helium versus krypton).

The purpose of the fractionator, then, is seen to be to decrease the extent of noble gas product dilution to some point considered desirable by the plant designer.

3. Plant design studies can often be expedited using the above equations, since the overall plant can be relatively well defined without resorting to detailed column calculations for each parametric study case. That is, the column calculations can be limited to a relatively narrow range of cases consistent with choices of D_A and ρ.

In the pilot plant studies, krypton decontamination factors for the 9-foot-high absorber were measured for each of the tests. Since these values, as already noted, can represent overall plant performance limits which can be approached in an actual plant situation, it was felt that the trends noted even with respect to the fixed-design pilot plant column would be helpful in evaluating plant applications. Before discussion of these data, however, a few comments should be made to indicate why the reported testing range was chosen.

Steinberg[15] proposed operating the absorber column at minus 94°F and 206 psia, with an L/G ratio of 3.22 on a mole basis. The overall performance of the plant, of course, depends upon the operating temperatures, pressures, and gas and liquid flow rates in the various sectors of the process. Refrigeration costs associated with low temperature operation are typically high and for this process contribute significantly to the cost of a plant. Furthermore, use of low temperatures presents some potential operating problems. On the other hand, larger, more expensive process equipment is associated with higher pressure, higher flow operation. Economic studies performed at the ORGDP balancing equipment sizes, refrigeration requirements, and overall plant processing capabilities indicate that, for refrigerant-12, higher absorption pressures, around 425 psia, and warmer temperatures, around minus 30°F, are generally preferable to those originally recommended by Steinberg. Using the optimization studies as operational guidelines for the testing program, then, it was decided to place the major experimental effort on gathering absorber performance data in this preferred area. Less emphasis was, correspondingly, placed on operation at very low temperatures, as can be observed in table I.

The effect of the absorber feed L/G ratio upon process performance is clearly demonstrated in a comparison of runs 1 through 7 and again in a comparison of runs 30 through 34. In these sets, as the absorber feed L/G ratio was increased by a factor of 2 or 3, the absorber decontamination

factor increased almost two orders of magnitude, and the fraction of krypton removed in the absorber column increased from near 75% to more than 99%. On the other hand, in comparing run 3 with 27, 16 with 17, and 33 with 34, the average krypton concentration in the absorber feed gas stream appeared to have little, if any, effect upon the relative amount of krypton removed in the absorber.

The influence of absorber pressure upon plant performance is seen in a review of runs 6, 7, 10, 11, 13, 14, 15, 23, and 24. When the pressure was varied from 260 to 416 psia, with a temperature near minus 25°F and an approximate L/G ratio of 2.7, the absorber decontamination factor increased by about a factor of 10. Correspondingly, the fraction of krypton removed in the absorber increased from around 85% to near 99%.

The dependency of Henry's Law constants with temperature (figure 1) indicates that absorption temperature should play an important role in the total removal, as well as in the efficiency of the separation. Test runs 14, 16, and 17, runs 22 and 29, and runs 15 and 30 show that higher gas removals are found at lower absorber temperatures. For example, as can be seen from a comparison of run 15 with run 30, lowering the operating temperature from minus 26°F to minus 74°F had a substantial effect upon the fraction of krypton removed in the absorber, increasing the column decontamination factor by an order of magnitude. In addition to the data shown in table I, as the temperature was decreased the relative amounts of argon, oxygen, and nitrogen absorbed with krypton were also decreased.

The test results further show (by subtracting the absorber off-gas flows from the feed gas flows) that the total quantity of gas absorbed by the solvent in the absorber column is a relatively strong function of the solvent flow rate (comparing runs 19 and 20) and the operating pressure (runs 6, 9, 10, and 14). The bulk of the gas absorbed by the solvent in the absorber column is subsequently liberated in the fractionator, with the remaining amount released in the stripper. The processing requirements of the fractionating system vary, therefore, according to the operating parameters of the absorber, and, at a fixed temperature, absorber column performance is improved primarily at the expense of increased load requirements on the fractionator.

Mass Transfer Parameters

With the preceding general discussion of the effects of operating variables on krypton removal as a background, a more quantitative treatment of the pilot plant data can be presented. The major specific goal of this project, aside from establishing general feasibility, was to collect pilot plant data which would be needed for the design of mass transfer equipment in various plant applications of the process. Accordingly, stage heights for krypton separation were determined for each of the runs. Because each has some advantages, two approaches to this problem are described in the following sections, one based on film theory and one based on stage-wise concepts. In both cases, appropriate models were used with the run data to compute, for each test, the number of krypton

stages in the absorber column; these numbers of stages were next divided into the packing height, 9 feet, to obtain the stage heights. The stage height values were then correlated using operating conditions to form parameter groupings.

In a multicomponent absorption system, the number of stages, and hence, the stage height, is not required by any mass transfer model now in use to be the same for all dissolving gases. Thus, in principle, the stage heights chosen for use in design calculations may well depend on the particular gas for which the calculations are being made. To obtain a complete definition of column behavior, then, these design calculations must often be made for each gaseous component which is absorbing, and in the present system, all of the gases being considered are dissolved to a measurable extent in refrigerant-12. The absorber column design for this process is, however, simplified by the nature of the solubility data (figure 1) and the separation job. There is a substantial difference between the solubilities of the three nonradioactive gases, argon, oxygen, and nitrogen, and the two gases which will have active isotopes, krypton and xenon. The krypton and xenon are considerably more soluble than the other gases mentioned, and furthermore, xenon is more soluble than krypton. Consequently, for the absorber column, krypton can be logically selected as the key component for design purposes, and for this reason, krypton stage heights were the only ones determined for all runs for the pilot plant absorption step.

Differential Stage Approach. The most widely used packed gas absorber column calculation procedures are the ones based on writing a material balance for a differential column section, incorporating a film theory expression for the rate of diffusion of a gaseous component from the bulk gas phase to the bulk liquid phase, integrating the combined expression, and then rearranging terms. That is, an equation of the form

$$Z = (N_{OG})(H_{OG}) \tag{14}$$

is commonly employed for absorption column analysis and design work,

where Z = column height,

N_{OG} = the number of transfer units, defined by

$$N_{OG} = \int_{y_2}^{y_1} \frac{(1-y)_{lm}\,dy}{(1 - y)(y - y^*)} \tag{15}$$

and H_{OG} = the height of a transfer unit, defined by

$$H_{OG} = \frac{G}{K_y\,a(1 - y)_{lm}} \tag{16}$$

In equations (15) and (16), y is the bulk gas-phase mole fraction of some selected component, y* is a gas-phase mole fraction corresponding to equilibrium with the bulk liquid phase, G is a gas flow rate, K_y is a transfer coefficient, a is an interfacial transfer surface area, and the subscript "lm" is used to denote a log-mean quantity.

Perhaps the best known absorption column design equation based on this model is one presented by Colburn[4] and recommended by Steinberg[15] for the noble gas separation problem. The equation is essentially a simplified version of equation (15), whereby the integral portion can be evaluated after certain assumptions are made. These assumptions include (a) application of one equilibrium constant over the concentration region of interest, (b) a constant liquid-to-gas flow rate ratio, and (c) cancellation of the log-mean term and the (1 - y) term. The mathematical result of applying these assumptions is

$$N_{OG} = \frac{2.3}{1 - \frac{kG}{L}} \log\left[\left(\frac{y_1 - kx_2}{y_2 - kx_2}\right)\left(1 - \frac{kG}{L}\right) + \frac{kG}{L}\right] \qquad (17)$$

where k = gas-liquid equilibrium coefficient,

G = gas flow rate,

L = liquid flow rate,

y = gas phase mole fraction of a component,

x = liquid phase mole fraction of that component, and

subscripts 1 and 2 refer to the gas inlet and outlet ends of the column, respectively.

In considering the basic differential stage approach, it is seen that this column analysis technique, with its several variations, is characterized by an underlying family of assumptions, some of which are interrelated:

1. Film theory adequately describes the transfer process.

2. Equilibrium data are known and correct over a range sufficiently wide either to confirm the applicability of constant k values or to permit utilization of point-slope factors in certain versions of the model.

3. The concentration and flow parameters can be defined so that some type of reasonably straight operating line can be arrived at. Usually, the L/G ratio, or some equivalent, is taken as being constant.

4. Gases absorb independently.

Assumptions (1) and (4) are at the heart of this approach, so that while they may not in fact be true, they cannot be looked at from the standpoint of internally checking the validity of the model. Assumption (2) is difficult to correct if equilibrium data either are incorrect or else are not directly applicable to the particular design problem. For the present model, however, it was assumed that the Henry's Law constants for krypton, measured by Steinberg[15], were satisfactory as k-values for use in equation (17). These Henry's Law data are presented in table II, along with values for the other gases in the system, and in table III, correlating parameters are listed.

Assumption (3), however, which deals with the L/G ratio, is clearly not valid for this absorption process, since all of the gases are absorbed to some extent. The L/G ratio varies considerably over the column; consequently, before using the differential stage model to compute and then correlate the stage height data, it was decided that for design purposes it would be reasonable to use an arithmetic average L/G ratio.

The use of an average L/G ratio in the differential stage height model, while making the model more attractive for this particular system, does present some problems in the actual design of a column. This is because the known gas and liquid flows at the start of the design are the feed flows, and there is no a priori way to establish, in advance, what the average will be. For this reason, the first step in the pilot plant data analysis procedure was to correlate the feed-based and observed average L/G ratios, viz.;

$$\left(\frac{L}{G}\right)_{avg} = 0.313 \left(\frac{L}{G}\right)^{1.194}_{\substack{feed \\ basis}} \left(\frac{P}{14.7}\right)^{0.311} \tag{18}$$

where the liquid and gas flows are, in this equation, both on a weight basis and the pressure, P, is expressed in units of psia. The agreement between the actual average L/G ratios determined from pilot plant data and those computed using the above correlation is good, as can be seen in figure 7.

Using average L/G ratios (which were converted to a mole basis), equation (17) was applied to the krypton absorption data to establish the number of overall gas-phase transfer units, N_{OG}, for each run. These N_{OG} values were, in turn, divided into the 9-foot packing height to compute the corresponding krypton stage heights. The H_{OG} values, listed in table IV, ranged from 10.5 to 61.8 inches, and were correlated according to the following equation:

$$H_{OG} = 84.5 \left(\frac{L}{G}\right)^{-1.42}_{avg} (\alpha)^{0.885} \tag{19}$$

where H_{OG} = stage height, inches;

$\left(\frac{L}{G}\right)_{avg}$ = average L/G ratio, on a weight basis, as computed using equation (18) and measured feed flow rates, and

TABLE II

SOLUBILITY OF GASES IN REFRIGERANT-12*

Gas	Temperature, °F	H [Henry's Law Constant], atmospheres
Xenon	− 106.6	5.72
	32	37.0
Krypton	− 117.4	23.0
	− 112	25.2
	− 103.9	27.9
	− 20.2	57.1
	32	114
Argon	− 99.4	173
	− 50.8	250
	32	308
Oxygen	− 104.8	215
	− 32.8	351
	33.8	390
Nitrogen	− 103.9	485
	− 22	663
	37.4	578

* Steinberg, M., *The Recovery of Fission Product Xenon and Krypton by Absorption Processes*, Brookhaven National Laboratory, January 1959 (BNL-542).

TABLE III

CORRELATING PARAMETERS FOR GAS SOLUBILITIES

The data listed in table II were, for each gas, fitted to an equation of the form $H = \exp(A + BT)$. The units of H and T are atmospheres and °F, respectively; values for A and B are listed below for each gas.

Gas	A	B
Xenon	3.18266	0.0134913
Krypton	4.35078	0.0101965
Argon	5.63477	0.0041854
Oxygen	5.88359	0.0043413
Nitrogen	6.39020	0.0019443
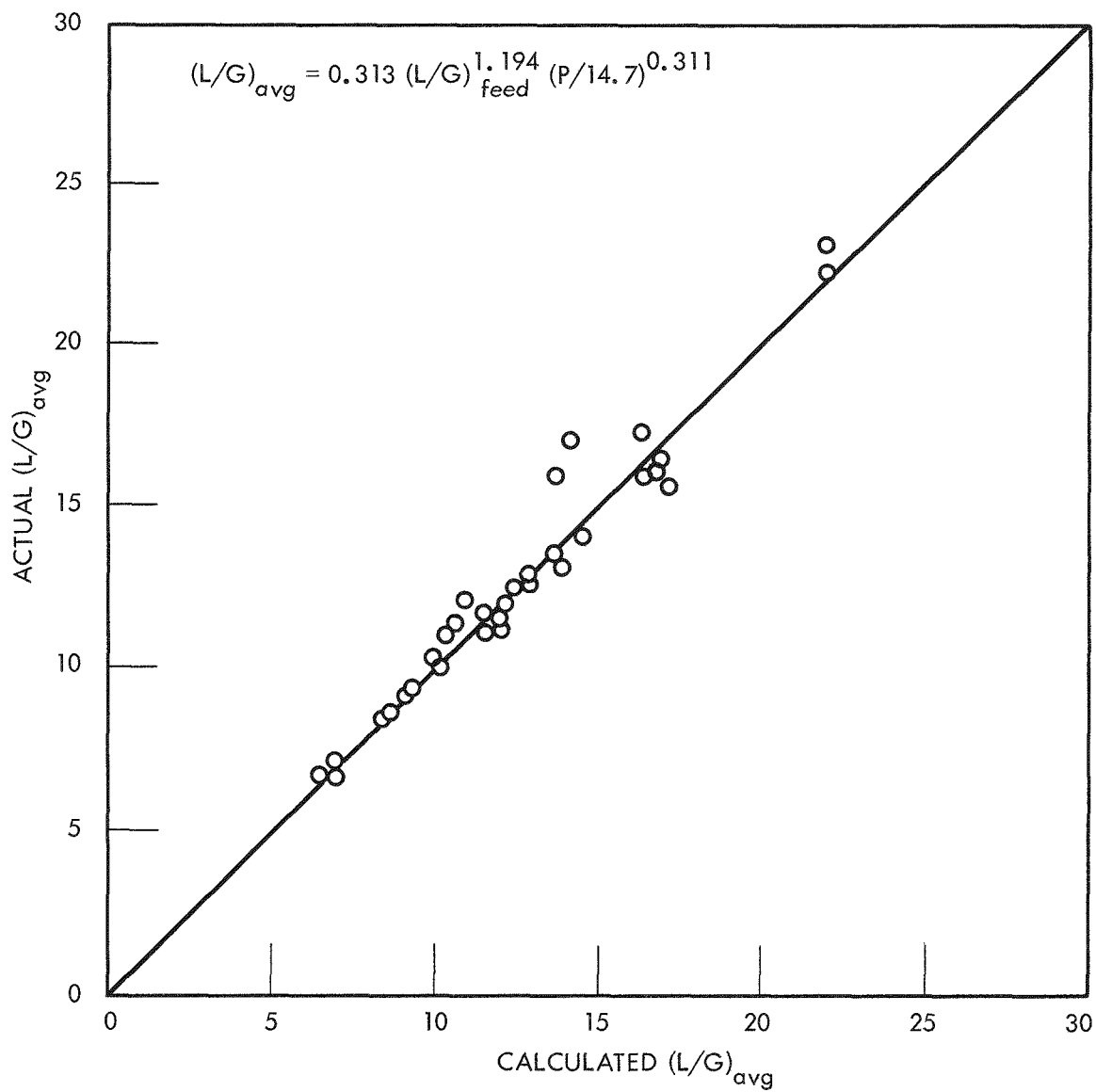
Figure 7

COMPARISON OF ACTUAL L/G DATA WITH CALCULATED VALUES

TABLE IV

ABSORBER COLUMN STAGE HEIGHTS

Run Number	Stage Height, inches	
	H_{OG}	HETP
1	12.2	14.1
2	10.5	11.9
3	14.9	15.0
4	14.4	15.3
5	55.6	33.8
6	14.7	15.3
7	13.6	14.8
8	13.5	16.7
9	12.2	14.9
10	15.9	14.9
11	15.7	14.9
12	15.3	15.7
13	20.0	15.0
14	25.5	17.9
15	11.0	6.9
16	26.9	21.0
17	29.7	22.5
18	20.2	27.4
19	13.2	13.9
20	44.8	27.7
21	46.4	28.6
22	37.1	22.0
23	23.6	19.3
24	15.1	14.1
25	22.7	17.0
26	35.2	23.9
27	15.9	15.4
28	15.8	20.8
29	22.5	17.5
30	15.0	17.4
31	11.7	15.4
32	12.6	17.0
33	61.8	39.8
34	49.6	32.6

α = ratio of Henry's Law constant for nitrogen to the Henry's Law constant for krypton*.

From the data given in table III, the parameter, α, can be seen to decrease with increasing temperature;

$$\alpha = \exp(2.03942 - 0.0082522\ T) \qquad (20)$$

where T is in °F.

Equation (19) was arrived at by starting with a modified form of the Murch equation[12] and then deleting those parameter groupings which did not affect the results of the correlation significantly at the 95% confidence level. The final results are illustrated in figure 8, where stage heights predicted from the correlation are compared with those determined using the experimental data.

Plate-to-Plate Approach. The problem which the existence of a varying L/G ratio caused in the above approach can be largely avoided in plate-to-plate calculations, but ordinarily, stage-to-stage calculations for a column with a varying L/G ratio do require that detailed enthalpy data be available. For the krypton-xenon work, however, advantage may be taken of the facts that the entire absorber column is operated approximately at constant temperature and pressure, and that the solvent constitutes a sizeable fraction of the liquid phase. Thus, the solvent composition in the vapor streams will remain virtually constant, from Raoult's Law coupled with the relatively constant column pressure. Examining the top of the column:

(Gas Out) V_1, y_1 L_0, x_0 (Solvent In)

} 1 theoretical stage

V_2, y_2 L_1, x_1
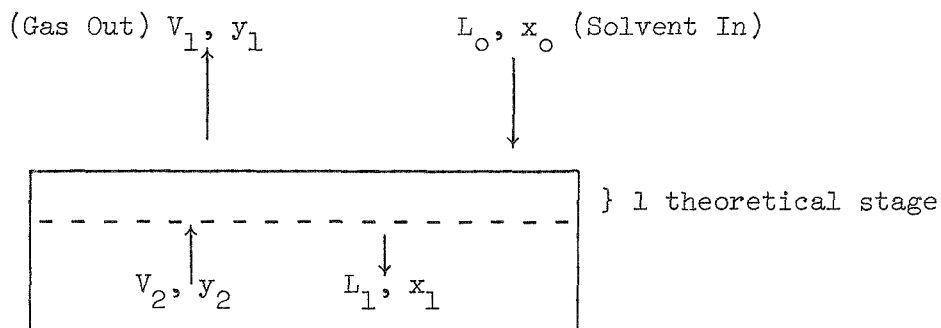
where V_1, L_0, all y_1 and all x_0 are known from pilot plant data.

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* In one sense, the use of α in this particular correlation limits it to systems where krypton and nitrogen are present. However, the α factor mainly provides for a convenient expression of temperature dependency which can be alternatively reflected using other system variables, such as density, viscosity, etc., to form the correlating group.
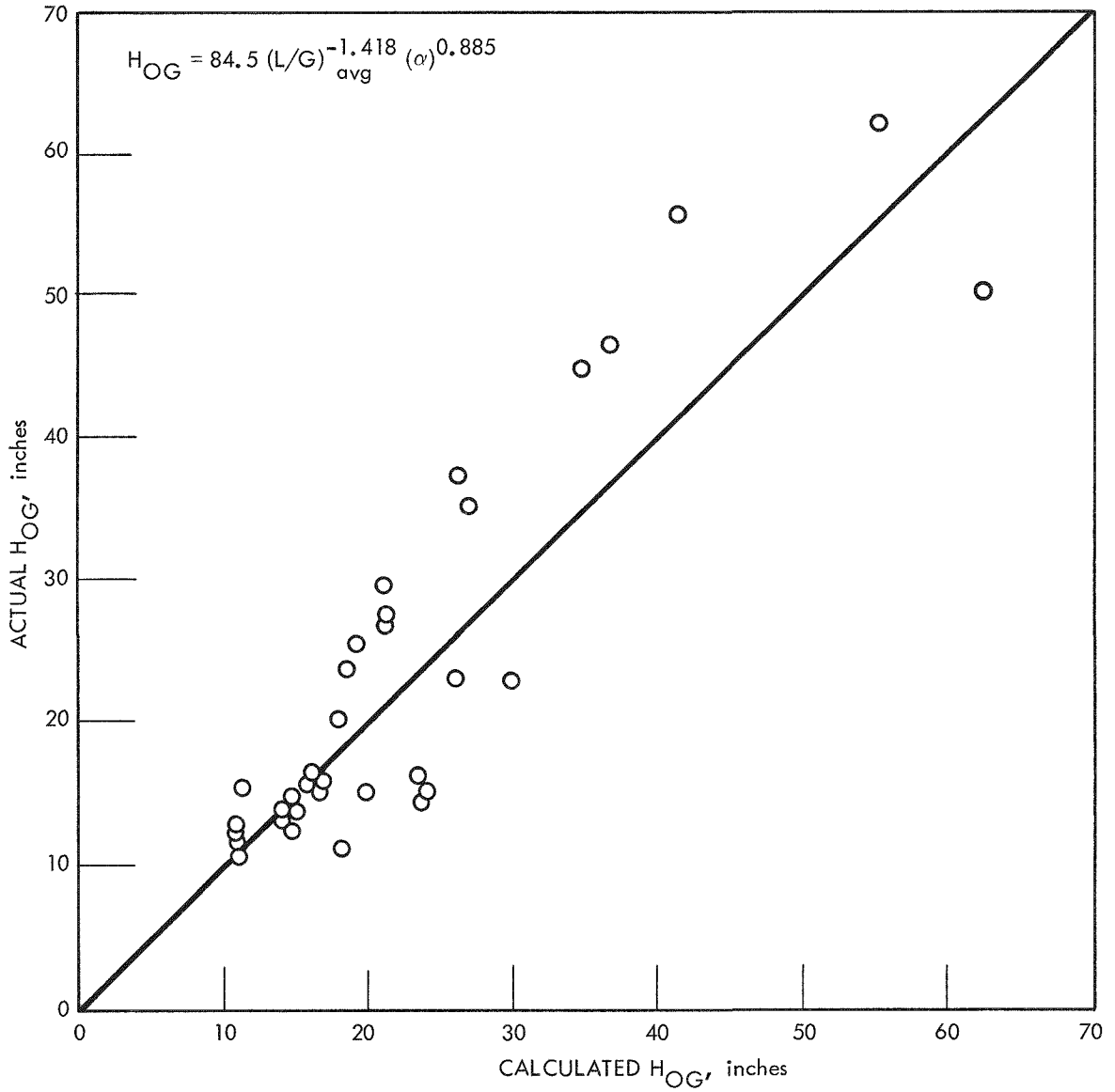
Figure 8

COMPARISON OF ACTUAL H_{OG} DATA WITH CALCULATED VALUES

The nonsolvent components in liquid stream 1 (L_1) may be obtained from equilibrium:

$$x_{1i} = y_{1i}/k_i \tag{21}$$

and the solvent in stream 1 is:

$$x_{1f} = 1 - \sum_{i \neq f} x_{1i} \tag{22}$$

where subscript f refers to solvent.

A solvent balance about the stage is:

$$V_1 y_{1f} + L_1 x_{1f} = V_2 y_{2f} + L_o x_{of} \tag{23}$$

and an overall balance shows that

$$L_1 = V_2 - V_1 + L_o \tag{24}$$

Thus:

$$V_2(y_{2f} - x_{1f}) = V_1(y_{1f} - x_{1f}) + L_o(x_{1f} - x_{of}) \tag{25}$$

or

$$V_2 = \frac{V_1(y_{1f} - x_{1f}) + L_o(x_{1f} - x_{of})}{(y_{2f} - x_{1f})} \tag{26}$$

Above, the assumption was made that $y_{1f} = y_{2f} = y_{3f} = \ldots$ Thus, V_2 may be calculated and $L_1 = V_2 - V_1 + L_o$. Finally, from a material balance,

$$y_{2i} = \frac{V_1 y_{1i} + L_1 x_{1i} - L_o x_{oi}}{V_2} \quad i \neq f \tag{27}$$

and streams V_2 and L_1 are completely known, so that the procedure now can be repeated down the column. The vapor stream entering the bottom of the column (V_b, y_b) is known, and eventually, the above procedure leads to the conditions that either

$$y_{j+1,i} < y_{bi} < y_{j,i} \tag{28}$$

or

$$y_{j+1,i} > y_{bi} > y_{j,i} \tag{29}$$

depending upon whether enrichment or depletion has taken place. When this happens, the number of stages for component i must lie between j and j+1, and a linear interpolation can be used to determine the fraction. For complete column analysis, stage height calculations are continued until the above is satisfied for all components, if possible, so that any variation can be detected.

The above procedure, which yields an NTP (number of theoretical plates), was also used to examine the pilot plant data. At first, all gaseous components were considered, and the k values were taken as the Henry's Law constants summarized in tables II and III. This approach did yield usable NTP numbers, but there were indications that it may be possible to obtain a set of k values that is more representative of this particular situation. After the second phase of the experimental program is completed, this problem will be looked at in more detail for both the refrigerant-11 and the refrigerant-12 data, so only the numbers for the key component, krypton, are presented here.

As with the N_{OG} values the NTP values obtained using the above model to analyze the krypton absorption data were divided into the column height to obtain HETP's for each run. The HETP's, which were found to be between 6.9 and 39.8 inches, are listed in table IV. Starting with the modified Murch equation and rejecting parameter groupings not significant at the 95% level, the same procedure applied to the H_{OG} values, resulted in the following correlation:

$$HETP = 16.8 (\frac{L}{G})_{avg}^{-0.706} (\alpha)^{0.778} \qquad (30)$$

where HETP = stage height, inches;

$(\frac{L}{G})_{avg}$ = average L/G ratio, on a weight basis, as computed using equation (18) and measured feed flow rates; and

α = Henry's Law constant ratio as determined using equation (20).

In figure 9, the HETP's obtained from the experimental results are compared with those predicted using equation (30). It is interesting to note that the same parameter groupings of the Murch equation were retained for both the H_{OG} and HETP correlations.

Comparison of Approaches. For quick absorber column calculations, the differential stage model is probably the easier to use of the two described. Once the feed conditions for the case are specified, an average L/G ratio can be estimated using equation (18). This value (converted to a mole basis for the N_{OG} calculation) can then be used with equations (17) and (19) to calculate the corresponding N_{OG} and H_{OG}. On the other hand, the plate-to-plate model is attractive because the use of a single L/G value is not required and also because it shows promise of consistent application to the other system gases. Furthermore, although calculation
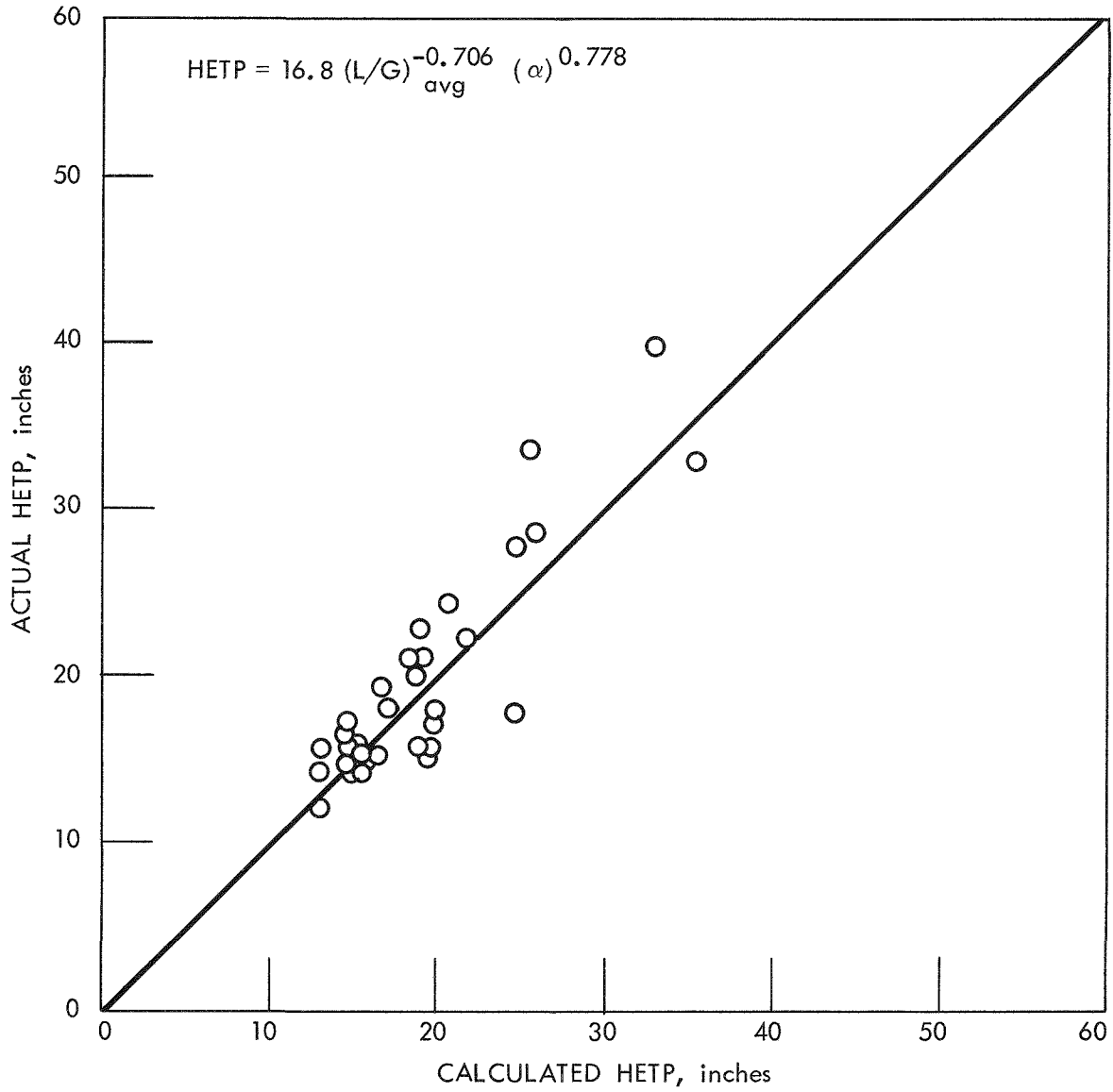
$$HETP = 16.8 \ (L/G)_{avg}^{-0.706} \ (\alpha)^{0.778}$$

Figure 9

COMPARISON OF ACTUAL HETP DATA WITH CALCULATED VALUES

of NTP perhaps requires more effort than calculation of N_{OG}, the correlation of HETP values appears to be better than the correlation of HTU's over the range investigated in these experiments.

Absorber Pressure Drop

For column design, vendor literature provided pressure drop data for the Goodloe packing[1]. Prior to pilot plant startup, however, several bench-scale flow tests were performed to confirm these data, using air and water in a 3-inch-diameter glass column packed to a height of 2.5 feet. Gas and liquid flow rates covered the ranges expected for pilot plant operation. In general, it was found that the experimentally determined pressure drops agreed with those predicted by the manufacturer and that the absorber design gas and liquid flow rates could easily be achieved without flooding. During the pilot plant tests, the pressure drop in the absorber column was typically less than 0.3 inch of water per foot of packing.

Fractionator and Stripper Performance

During routine pilot plant operation, not only was the fractionator off-gas recycled back to the absorber, but also the stripper off-gas was mixed with the absorber off-gas to form a simulated process feed. Collectively, all three gas streams composed the absorber feed. For the refrigerant-12 studies, the fractionator and stripper were operated primarily as auxiliaries to the absorber. The operating conditions of each column and associated equipment were, therefore, maintained nearly constant throughout all the tests. The effect of individual column performances upon the overall process will be looked at in more detail as part of the scheduled pilot plant testing program with refrigerant-11.

As designed, both the fractionator and stripper columns performed satisfactorily. Both columns appeared to function best when column pressure drops were maintained near 1 inch of water per foot of packing.

RADIOLYTIC DECOMPOSITION OF REFRIGERANT-12

The extent of solvent degradation due to exposure to radioactive nuclides is always an important consideration in radiochemical process design. Accordingly, calculations aimed at estimating the magnitude of this problem for the krypton-xenon absorption process have been made. In another report[8], results of a literature survey[2,11,13,14] for data concerning the radiation stability of both refrigerant-11 and refrigerant-12 were presented; these data are also summarized in table V. In this section of the report, these G-values are used to illustrate procedures for predicting solvent degradation rates for possible plant cases.

TABLE V

SUMMARY OF G-VALUES FOR SOLVENT DEGRADATION*

Temperature, °F	G-Value, molecules solvent destroyed per 100 ev of absorbed energy†	
	Refrigerant-12	Refrigerant-11
- 94		0.78
32	3.58	3.82
95 to 100	3.6	4.6

The refrigerant-11 and -12 data, if taken together, can be approximated by the equation:

$$G = 120 \ e^{-\frac{3594}{RT}}$$

where T is in °R, and R = 1.987 Btu/lb mole-°R.

* Merriman, J. R., and Pashley, J. H., *Engineering Development of an Absorption Process for the Concentration and Collection of Krypton and Xenon, Third Summary Progress Report, January through June, 1968,* Union Carbide Corporation, Nuclear Division, Oak Ridge Gaseous Diffusion Plant, March 27, 1969 (K-1770).

† It is assumed here that one solvent molecule is destroyed for each halogen ion produced. This is a somewhat conservative assumption since it does not account for the possibility that more than one halogen ion may be removed from a single solvent molecule.

General Procedure for Estimating Solvent Degradation Rate

In a particular equipment item, the rate at which the refrigerant-12 solvent inventory will undergo radiolytic decomposition is:

$$D_P = \frac{(5.308)(10^{-3})(G_P)}{x_s} \left\{ \sum_j \left[x_j \left(\sum_i f_{ji} \ A_{ji} \ E_{ji} \ M_{ji} \right) \right] \right\} \tag{31}$$

where D_P = solvent degradation rate applicable to inventory in vessel P, percent of inventory decomposed per day;

G_P = G-value appropriate for vessel P's operating conditions, molecules solvent decomposed per 100 ev of absorbed energy;

x_s = solvent mole fraction in liquid phase;

x_j = average mole fraction of gaseous element j dissolved in liquid;

f_{ji} = fraction of element j which is radioactive isotope i;

A_{ji} = activity of species ji, curies per gram;

E_{ji} = effective energy release from species ji, Mev per disintegration; and

M_{ji} = molecular weight of isotope ji.

The average rate of solvent degradation for the entire plant, then, is attained by applying equation (31) to all equipment items used in the plant.

$$D_{TOT} = \frac{\sum\limits_{P} D_P I_P}{\sum\limits_{P} I_P} \qquad (32)$$

where D_{TOT} = overall average solvent degradation rate, percent per day, and

I_P = inventory of vessel P, any units.

Thus, for a given plant case, a vessel-by-vessel accounting is made of the extent of solvent decomposition, as follows:

1. Based on the operating temperature for the unit being considered, an appropriate G-value is obtained, considering the data summarized in table V.

2. From the operating conditions for the vessel and material balances, values of x_j for those gaseous elements which have radioactive isotopes are computed.

3. The nature of the gas cleaning job being accomplished determines which radioactive isotopes are present in significant quantities and their relative amounts. Accordingly, f_{ji} for all isotopes important for the particular case can be obtained.

4. Values of A_{ji} and E_{ji} for the isotopes being considered are readily available from any of several data compilations.

5. The operating solvent inventory of a particular equipment item can be computed based on sizing parameters.

6. Equation (31) can then be used systematically for each vessel, and its associated piping and hold volume, to provide an estimate of the solvent decomposition rate for each sector of the process. Finally, equation (32) provides the overall plant average solvent degradation rate.

As an absorption plant is being designed for some specific krypton-xenon removal situation, the procedure just outlined should be used to estimate the solvent degradation rate for that particular application of the process. In general, however, it is also possible to provide some upper limit estimates of the extent of solvent destruction without reference to any specific plant design. These estimates, described in the following sections, are made possible through the use of certain simplifying, yet still conservative, assumptions.

Simplified Procedures for Estimating Solvent Degradation Rate

Two separate cases can be looked at as typifying *best* and *worst* processing situations from the standpoint of solvent radiolytic decomposition. In the first of these, which might be represented by a light-water reactor fuel reprocessing plant off-gas treatment system, cooling times are large enough so that essentially all of the radioactive isotopes except krypton-85 have decayed away. The second case, on the other hand, might represent a situation where the absorption system feed gas is taken directly from a nuclear reactor blanket containing equilibrium production concentrations of several active krypton and xenon isotopes. Thus, in this case, other isotopes, primarily xenon-133, must also be considered. To assist in the following discussion of these cases, decay data for krypton-85 and xenon-133 are listed in table VI.

Now, some conservative assumptions can be made, as follows:

1. Since the degradation rate increases directly with the G-value, and since the G-value increases with increasing temperature, the number corresponding to the highest temperature occurring in the process can be assumed to apply to the entire plant inventory. (Because of the large differences between temperatures of the hottest and coldest portions of the plant, this assumption should be very conservative.) With refrigerant-12 as the solvent, the highest temperature, about 32°F, is the fractionator temperature; the reported G-value for this material at this temperature is 3.58.

2. From equation (31), the decomposition rate is also seen to increase directly with increasing average dissolved gas mole fraction, x_j. In turn, for each gas, this number increases with increasing pressure, increasing gas-phase mole fraction, and decreasing temperature. In the absorption process, the highest pressure, the largest mole fraction of radioactive isotopes in the gas phase, and the lowest

TABLE VI

DECAY DATA FOR KRYPTON-85 AND XENON-133

	Krypton-85	Xenon-133	Reference or Comments
Half-life	10.60 years	5.27 days	*
A_{ij}, Specific Activity, curies/gram	397	186,000	*
Gamma Releases, Mev/dis	0.41% @ 0.514	Taken as 99.3% @ 0.081	**
Maximum Beta Release, Mev/dis	0.67	0.346	**
E_{ij}, Total Energy Released to Solvent, Mev/dis	0.225	0.196	Average beta taken as one-third of endpoint, or maximum value

* Goldstein, G., and Reynolds, S. A., "Specific Activities and Half-Lives of Common Radionuclides", *Nuclear Data, A, 1,* 5, p. 435-452 (July, 1966).

** Lederer, C. M., et al., *Table of Isotopes,* Sixth Edition, John Wiley and Sons, New York, First Corrected Printing (March, 1968).

temperatures all occur at the inlet of the absorber column*. Further-
more, the average liquid phase dissolved gas mole fractions in the
absorber will not, in the case of krypton and xenon, exceed the values
which would correspond to equilibrium with this feed gas. Accordingly,
another conservative assumption is to take, as applicable to all of
the process inventory, dissolved gas mole fractions in equilibrium
with the absorber feed gas:

$$x_j = \frac{(y_j) \text{ absorber feed}}{(k_j) \text{ absorber column}} \tag{33}$$

where y_j = mole fraction of element j in the absorber column feed
gas†, and

k_j = equilibrium constant for element j at the absorber con-
ditions.

When it is realized that over one-half of the absorption process
inventory will probably be stripped solvent, held in the solvent
reservoirs and containing at most only trace amounts of krypton and
xenon, this assumption is, in particular, seen to be very conserva-
tive.

3. Additionally, it can be assumed that all of the gamma-plus-beta
   radiation emitted by the decaying isotopes is absorbed by the
   solvent.

4. As was noted in table V, it can be further assumed that one solvent
   molecule is destroyed for each halogen ion produced by the irradia-
   tion. That is, the possibility that more than one halogen ion might
   be removed from the same solvent molecule is ignored.

Using these assumptions of maximum G-value, maximum radioactive gas con-
tent, and maximum energy absorption, the two cases previously mentioned
can be studied further.

Long Cooling Time Case. For light-water reactor fuel, krypton-85 typi-
cally comprises about 7% of the total krypton produced during irradiation,
so that f_{ji} for this isotope is nearly equal to 0.07 in many cases.
Therefore, the degradation rate under the assumptions noted above reduces
to:

---

* This is true in all cases except for small portions of the fractionator
  and stripper final condensers which are about as cold as the absorber.
  In these units, the active gas mole fractions may considerably exceed
  the absorber column values at some point near the exits; however, the
  pressures are lower, and more important, the liquid solvent inventory
  at these points is essentially zero.

† The absorber feed is made up of fresh feed entering the process from
  some nuclear facility plus recycle gas from the fractionator.

$$D_{TOT} \doteq 10.2 \; \dot{x}_1 \doteq 10.2 \; \frac{\dot{y}_1}{k_1} \; .$$

Also, for krypton dissolved in refrigerant-12, the equilibrium constant, k_1, is 2.32 at 14 atmospheres and minus 94°F and about 2.7 at 30 atmospheres and minus 25°F[15]; therefore, a value of 2.5 should be representative of absorber conditions of most interest in refrigerant-12 based processes. Using this value, degradation rates are listed in table VII for various concentrations of krypton in the absorber feed gas stream. It can be seen that, for the concentrations most likely to be encountered in actual processing situations, the solvent degradation rate is negligible, less than 0.02% per day.

TABLE VII

ESTIMATED DEGRADATION RATES
FOR LONG COOLING TIME PROCESSING SITUATIONS

Krypton Concentration in Absorber Feed Gas, y_i, ppm	Estimated Solvent Degradation Rate, percent per day
50	0.0002
100	0.0004
500	0.002
1000	0.004
5000	0.02

Short Cooling Time Case. Prediction of degradation rates for this case is more difficult than for the long cooling time situation. This is due primarily to the fact that, for accurate calculations, several krypton and xenon isotopes need to be considered. To compute the concentrations of these isotopes entering the absorption system, not only must the irradiation conditions for the associated reactor be used to obtain equilibrium production quantities, but also the specific transport mechanisms and hold times associated with movement of each isotope first from its formation site in the fuel to the containment gas and then to the absorption process must be used to determine the extent of decay and

hence to provide a steady-state profile of the absorber feed*. Even then, in-process decay should also be accounted for in the case of some short half-life species. Based on some preliminary estimates for a few irradiation schemes, however, it appears that between 0.2 and 1% of the xenon will be radioactive and that the primary xenon isotope will be xenon-133. Thus, for these situations, f_{ji} for this isotope will be between 0.002 and 0.01. Following a development similar to that for the previous case, considering both krypton-85 and xenon-133 contributions†, and using a xenon equilibrium solubility constant of 0.7, degradation rates for both values of f_{ji} were computed. Presented in table VIII, these rates do not appear to be too significant except when a relatively large fraction of the xenon processed is radioactive and when the xenon content of the of the absorption system feed gas is appreciable. In such instances, the rigorous procedure discussed earlier should be used to predict a more accurate value without making the many conservative assumptions made here, in order to determine whether in-line solvent purification equipment is necessary or if other adjustments are required.

TABLE VIII

ESTIMATED DEGRADATION RATES
FOR SHORT COOLING TIME PROCESSING SITUATIONS

Xenon Concentration in Absorber Feed Gas*, y_2, ppm	Estimated Solvent Degradation Rate, percent per day	
	$f_{21} = 0.002$	$f_{21} = 0.01$
50	0.015	0.068
100	0.028	0.13
500	0.13	0.66
1000	0.26	1.3
5000	1.3	6.6

* The krypton concentration was taken at 500 ppm, and the solvent degradation rate corresponding to this value was added to the xenon contribution.

* For example, in a molten salt reactor system, fission product gases are formed in the salt and then diffuse, or are carried by bubbles, etc., to the blanket gas. This requires some finite time, during which decay occurs.

† Actually, in some cases krypton-85 may not be the most significant krypton isotope. However, it appears that, in general, the xenon-133 contribution to degradation is the most important one by a wide margin.

In summary, even when using some very conservative assumptions to esti-
mate solvent radiolytic decomposition rates, solvent degradation does
not appear to be a significant problem in most of the cases felt to
represent future absorption process applications. It should be noted
again, however, that it would certainly be appropriate to include an
item-by-item estimate of the degradation rate for each specific plant
case as a part of the plant design effort, to be sure that there are no
unusual problems.

CONCLUSIONS

The overall performance of the pilot plant demonstrated that a continuous
selective absorption process of the type described in this report can be
used confidently to remove essentially all traces of krypton and xenon
from contaminated air sources. The design, construction, and operation
of the plant are relatively straightforward. Consequently, the process
lends itself well to nuclear applications where a high degree of relia-
bility is essential. Actual operational problems encountered in the
course of the formal pilot plant testing program were minor and were
mainly associated with the experimental nature of the setup.

Test results showed that efficient plant operation favors low absorber
operating temperatures, relatively high absorption pressures, and high
L/G ratios. Economic studies, however, indicate that higher tempera-
tures, compensated for by higher pressures and L/G ratios, are preferable
because of significant reductions in refrigeration costs. With
refrigerant-12, a plant designed around an absorber with an operating
temperature of minus 30°F and a pressure of 425 psia should give a good
balance between economics and performance. With a feed L/G ratio of 3
to 3.5, pilot plant test results indicate that an absorber decontamina-
tion factor of 300 to 400 can be expected with only 9 feet of Goodloe
packing, corresponding to over 99.7% removal of the krypton. Under these
conditions, the H_{OG} will be about 12 inches, and the HETP about 14 inches.
Calculations show that solvent radiolytic decomposition rates will not
be high enough to affect system operability, at least for the cases
studied.

Additional experimental work with the pilot plant includes a formal test-
ing program (currently under way) using refrigerant-11 as the process
solvent. Actual separation performance is not expected to be better than
that experienced with refrigerant-12, but the use of the higher tempera-
ture solvent might offer further substantial economic gains. Variation
of operating parameters for these tests will be similar to that in the
refrigerant-12 work, except for the fact that the principal absorption
temperature for the new test series will probably be plus 25°F, as
opposed to minus 25°F in the work described in this report.

ACKNOWLEDGEMENT

LIST OF REFERENCES

1. Bragg, L. B., Packed Column Corporation, Springfield, New Jersey, Personal Communication.

2. Brock, C. M., "Freon" Products Laboratory, E. I. du Pont de Nemours and Company, Inc., Wilmington, Delaware, Personal Communication.

3. Browning, W. E., Jr., "Removal of Fission Product Activity from Gases", Nuclear Safety, *1*, 37-53 (1960).

4. Colburn, A. P., "Simplified Calculation of Diffusional Processes", Ind. Eng. Chem., *33*, 459-467 (1941).

5. Keilholtz, G. W., "Removal of Radioactive Noble Gases from Off-Gas Streams", Nuclear Safety, *8*, 155-160 (Winter, 1966-67).

6. Merriman, J. R., Pashley, J. H., and Smiley, S. H., *Engineering Development of an Absorption Process for the Concentration and Collection of Krypton and Xenon, Summary of Progress through July 1, 1967*, Union Carbide Corporation, Nuclear Division, Oak Ridge Gaseous Diffusion Plant, December 19, 1967 (K-1725).

7. Merriman, J. R., and Pashley, J. H., *Engineering Development of an Absorption Process for the Concentration and Collection of Krypton and Xenon, Second Summary Progress Report, July through December, 1967*, Union Carbide Corporation, Nuclear Division, Oak Ridge Gaseous Diffusion Plant, August 19, 1968 (K-1745).

8. Merriman, J. R., and Pashley, J. H., *Engineering Development of an Absorption Process for the Concentration and Collection of Krypton and Xenon, Third Summary Progress Report, January through June, 1968*, Union Carbide Corporation, Nuclear Division, Oak Ridge Gaseous Diffusion Plant, March 27, 1969 (K-1770).

9. Merriman, J. R., and Pashley, J. H., *Engineering Development of an Absorption Process for the Concentration and Collection of Krypton and Xenon, Fourth Summary Progress Report, July through December, 1968*, Union Carbide Corporation, Nuclear Division, Oak Ridge Gaseous Diffusion Plant, April 1, 1970 (K-1786).

10. Merriman, J. R., and Pashley, J. H., *Engineering Development of an Absorption Process for the Concentration and Collection of Krypton and Xenon, Fifth Summary Progress Report, January through June, 1968*, Union Carbide Corporation, Nuclear Division, Oak Ridge Gaseous Diffusion Plant, April 1, 1970 (K-1787).

11. Michelson, C., Union Carbide Corporation, Nuclear Division, Oak Ridge National Laboratory, Personal Communication.

12. Perry, R. H., et al., *Chemical Engineers' Handbook*, Fourth Edition, McGraw-Hill Book Company, Inc., New York (1963).

13. Silverman, M. D., et al., "Radiation Damage to Freon-11, CCl_3F, Nuc. Sci. Eng., *15*:217-8 (February 1963).

14. Steidlitz, M. E., et al., "Ionization of Fluorocarbon Gases by U-234 Particles", J. of Phys. Chem., *56*, 1010 (1952).

15. Steinberg, M., *The Recovery of Fission Product Xenon and Krypton by Absorption Processes*, Brookhaven National Laboratory, January 1959 (BNL-542).

APPENDIX

PILOT PLANT INSTRUMENTATION DESCRIPTION

Identification and description of the pilot plant instrumentation is given in table IX, corresponding to the symbols shown in the pilot plant reference flow diagram, figure 3. A description of each component and its function is listed along with the input and output ranges of the instrument, where applicable.

TABLE IX

KEY TO INSTRUMENTATION DIAGRAM

Symbol	Service	Description	Input Range	Output Range
FE-101	Flow to Absorber Gas Interchanger	Mass Flow Meter	0 to 25 scfm	
FI-101	Flow to Absorber Gas Interchanger	Mass Flow Indicator		
PI-102	Absorber Gas Interchanger Inlet Pressure	Pressure Gauge	0 to 600 psig	
TE-103	Temperature, Gas from Compressor to Absorber Gas Interchanger	Copper-Constantan Thermocouple		
TE-104	Temperature, Absorber Off-Gas from Absorber Interchanger	Copper-Constantan Thermocouple		
TE-105	Temperature, Absorber Off-Gas to Absorber Interchanger	Copper-Constantan Thermocouple		
PT-106	Absorber Gas Pressure	Pressure Transmitter	0 to 600 psig	3 to 18 psi
PRC-106	Absorber Gas Pressure Control	Pressure Recorder-Controller	3 to 18 psi	3 to 18 psi
PCV-106	Absorber Gas Pressure Control	Control Valve Size 1/4-inch, CV = 0.25	3 to 18 psi	
PdT-107	Pressure Drop Across Absorber	Differential Pressure Transmitter	0 to 1 psi	3 to 18 psi
PdR-107	Pressure Drop Across Absorber	Pressure Recorder	3 to 18 psi	
FE-108	Flow to Gas Reservoir	Mass Flow Meter	0 to 25 scfm	
FI-108	Flow to Gas Reservoir	Mass Flow Indicator		
PI-109	Pressure, Gas to Gas Reservoir	Pressure Gauge	0 to 600 psig	
TE-110	Temperature, Gas to Gas Reservoir	Copper-Constantan Thermocouple		

TABLE IX

(Continued)

KEY TO INSTRUMENTATION DIAGRAM

Symbol	Service	Description	Input Range	Output Range
PI-111	Gas Reservoir Pressure	Pressure Gauge	0 to 100 psig	
PI-112	Gas Reservoir Rupture Disc Pressure	Pressure Gauge	0 to 100 psig	
TE-113	Temperature, Inlet to Gas Chiller	Copper-Constantan Thermocouple		
TE-114	Temperature, Gas from Chiller to Absorber	Copper-Constantan Thermocouple		
TE-115	Lower Internal Temperature Absorber	Copper-Constantan Thermocouple		
TE-116	Center Internal Temperature Absorber	Copper-Constantan Thermocouple		
TE-117	Upper Internal Temperature Absorber	Copper-Constantan Thermocouple		
TE-118	Upper Skin Temperature Absorber	Copper-Constantan Thermocouple		
TE-119	Lower Skin Temperature Absorber	Copper-Constantan Thermocouple		
TE-120	Temperature, Fluid from Solvent Chiller to Absorber	Copper-Constantan Thermocouple		
LS-121	Absorber Reservoir Level	Level Switch		
LA-121	Absorber Reservoir Low Level Alarm	Alarm		
ECV-121	Absorber Reservoir Level Control	Three-Way Solenoid Valve		
LCV-121	Absorber Reservoir Level Control	Air-Operated Block Valve		

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TABLE IX
(Continued)

KEY TO INSTRUMENTATION DIAGRAM

Symbol	Service	Description	Input Range	Output Range
TE-122	Temperature, Fluid to Solvent Chiller	Copper-Constantan Thermocouple		
TE-123	Temperature, Fluid from Absorber to Solvent Interchanger	Copper-Constantan Thermocouple		
FE-124	Solvent Flow to Solvent Interchanger	Turbine Flow Meter	0 to 2.5 gpm	
FI-124	Solvent Flow to Solvent Interchanger	Turbine Meter Flow Indicator		
TE-125	Temperature, Solvent to Solvent Interchanger	Copper-Constantan Thermocouple		
TE-126	Solvent Pump Inlet Temperature	Copper-Constantan Thermocouple		
FE-127	Flow from Fractionator Final Condenser to Compressor	Mass Flow Meter	0 to 10 scfm	
FI-127	Flow from Fractionator Final Condenser to Compressor	Mass Flow Indicator		
PI-128	Outlet Gas Pressure, Fractionator Final Condenser	Pressure Gauge	0 to 200 psig	
TE-129	Outlet Gas Temperature, Fractionator Final Condenser	Copper-Constantan Thermocouple		
PI-130	Absorber Rupture Disc Pressure	Pressure Gauge	0 to 600 psig	
TE-131	Fractionator Final Condenser Outlet Gas Temperature	Copper-Constantan Thermocouple		

TABLE IX
(Continued)

KEY TO INSTRUMENTATION DIAGRAM

Symbol	Service	Description	Input Range	Output Range
TE-132	Fractionator Overhead Condenser Outlet Gas Temperature	Copper-Constantan Thermocouple		
TE-133	Fractionator Overhead Condenser Condensate Temperature	Copper-Constantan Thermocouple		
TE-134	Fractionator Flash Unit Outlet Temperature	Copper-Constantan Thermocouple		
PT-135	Fractionator Gas Pressure	Pressure Transmitter	0 to 200 psig	3 to 18 psi
PCV-135	Fractionator Gas Pressure Control	Control Valve Size 1/4-inch, CV = 0.10	3 to 18 psig	
PRC-135	Fractionator Gas Pressure Control	Pressure Recorder-Controller	3 to 18 psig	3 to 18 psig
PdT-136	Fractionator Pressure Drop	Differential Pressure Transmitter	0 to 1 psi	3 to 18 psi
PdR-136	Fractionator Pressure Drop	Pressure Recorder	3 to 18 psig	
TE-137	Fractionator Upper Internal Temperature	Copper-Constantan Thermocouple		
TE-138	Fractionator Center Internal Temperature	Copper-Constantan Thermocouple		
TE-139	Fractionator Lower Internal Temperature	Copper-Constantan Thermocouple		
TE-140	Fractionator Upper Skin Temperature	Copper-Constantan Thermocouple		

TABLE IX
(Continued)

KEY TO INSTRUMENTATION DIAGRAM

Symbol	Service	Description	Input Range	Output Range
TE-141	Fractionator Lower Skin Temperature	Copper-Constantan Thermocouple		
TE-142	Fractionator Flash Unit Internal Temperature	Copper-Constantan Thermocouple		
TE-143	Temperature, Fluid From Solvent Interchanger to Fractionator Flash Unit	Copper-Constantan Thermocouple		
TE-144	Temperature, Fluid From Solvent Interchanger to Fractionator Flash Unit	Copper-Constantan Thermocouple		
TE-145	Fractionator Reboiler Internal Temperature	Copper-Constantan Thermocouple		
TE-146	Fractionator Reboiler Skin Temperature	Copper-Constantan Thermocouple		
TA-146	Fractionator Reboiler Skin Temperature Alarm	Alarm Indicator		
LS-147	Fractionator Reboiler Level	Level Switch		
LA-147	Fractionator Reboiler Low Level Alarm	Alarm Indicator		
LCV-147	Fractionator Reboiler Level Control	Solenoid-Operated Block Valve		
PI-148	Fractionator Rupture Disc Pressure	Pressure Gauge	0 to 200 psig	

TABLE IX
(Continued)

KEY TO INSTRUMENTATION DIAGRAM

Symbol	Service	Description	Input Range	Output Range
TE-149	Temperature, Fluid to Stripper Flash Unit	Copper-Constantan Thermocouple		
LS-150	Solvent Tank Low Level	Level Switch		
LA-150	Solvent Tank Low Level Alarm	Alarm Indicator		
TE-151	Solvent Tank Internal Temperature	Copper-Constantan Thermocouple		
TA-151	Solvent Tank Internal Temperature Alarm	Alarm Indicator		
TE-153	Stripper Reboiler Internal Temperature	Copper-Constantan Thermocouple		
LS-154	Stripper Reboiler Level	Level Switch		
LA-154	Stripper Reboiler Low Level Alarm	Alarm Indicator		
LCV-154	Stripper Reboiler Level Control	Solenoid-Operated Block Valve		
TE-155	Stripper Lower Internal Temperature	Copper-Constantan Thermocouple		
TE-156	Stripper Center Internal Temperature	Copper-Constantan Thermocouple		
TE-157	Stripper Upper Internal Temperature	Copper-Constantan Thermocouple		
TE-158	Stripper Upper Skin Temperature	Copper-Constantan Thermocouple		
TE-159	Stripper Lower Skin Temperature	Copper-Constantan Thermocouple		

TABLE IX
(Continued)

KEY TO INSTRUMENTATION DIAGRAM

Symbol	Service	Description	Input Range	Output Range
PdT-160	Stripper Pressure Drop	Differential Pressure Transmitter	0 to 1 psi	3 to 18 psi
PdR-160	Stripper Pressure Drop	Pressure Recorder	3 to 18 psi	
PT-161	Stripper Gas Pressure	Pressure Transmitter	0 to 200 psig	3 to 18 psi
PRC-161	Stripper Gas Pressure Control	Pressure Recorder-Controller	3 to 18 psig	3 to 18 psig
PCV-161	Stripper Gas Pressure Control	Control Valve Size 1/4-inch, CV = 0.25	3 to 18 psig	
TE-162	Stripper Flash Unit Internal Temperature	Copper-Constantan Thermocouple		
TE-163	Stripper Flash Unit Outlet Gas Temperature	Copper-Constantan Thermocouple		
TE-164	Stripper Overhead Condenser Outlet Liquid Temperature	Copper-Constantan Thermocouple		
TE-165	Stripper Overhead Condenser Outlet Gas Temperature	Copper-Constantan Thermocouple		
TE-166	Stripper Final Condenser Outlet Gas Temperature	Copper-Constantan Thermocouple		
PI-167	Stripper Rupture Disc Pressure	Pressure Gauge	0 to 200 psig	
TE-168	Product Temperature	Copper-Constantan Thermocouple		
PI-169	Product Pressure	Pressure Gauge	0 to 200 psig	
FE-170	Product Flow	Mass Flow Meter	0 to 4000 sccm	

TABLE IX
(Continued)

KEY TO INSTRUMENTATION DIAGRAM

Symbol	Service	Description	Input Range	Output Range
FI-170	Product Flow	Mass Flow Indicator		
FE-171	Liquid Flow to Stripper	Turbine Flowmeter	0 to 2.5 gpm	
FI-171	Liquid Flow to Stripper	Indicator		
FE-173	Liquid Flow to Stripper Flash Unit	Turbine Flowmeter	0 to 2.5 gpm	
FI-173	Liquid Flow to Stripper Flash Unit	Indicator		
FE-174	Liquid Flow to Fractionator	Turbine Flowmeter	0 to 2.5 gpm	
FI-174	Liquid Flow to Fractionator	Indicator		
TR-176	System Temperatures	24-point Temperature Recorder for Copper-Constantan Thermocouples	-120 to +230°F	
TR-177	System Temperatures	24-point Temperature Recorder for Copper-Constantan Thermocouples	-120 to +230°F	
PI-178	Air Compressor Gas Receiver Pressure	Pressure Gauge	0 to 600 psig	
PT-179	Air Compressor Gas Recycle Pressure	Pressure Transmitter	0 to 600 psig	3 to 18 psi
PRC-179	Air Compressor Gas Recycle Control	Pressure Recorder-Controller	3 to 18 psi	3 to 18 psi

TABLE IX
(Continued)

KEY TO INSTRUMENTATION DIAGRAM

Symbol	Service	Description	Input Range	Output Range
PCV-179	Air Compressor Gas Recycle Control	Control Valve Size 1/4-inch, CV = 0.25	3 to 18 psi	
PT-180	Air Compressor Gas Make-Up Pressure	Pressure Transmitter	0 to 100 psig	3 to 18 psi
PRC-180	Air Compressor Gas Make-Up Control	Pressure Recorder-Controller	3 to 18 psi	3 to 18 psi
PCV-180	Air Compressor Gas Make-Up Control	Control Valve Size 1/4-inch, CV = 0.25	3 to 18 psi	

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