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MASTER

REMOVAL OF RADIOACTIVE KRYPTON AND XENON FROM CONTAMINATED OFF-GAS STREAMS*

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ABSTRACT

Radioactive isotopes of krypton and xenon are generated during the irradiation of nuclear fuels and, in a number of situations, subsequently contaminate various nuclear process off-gas streams. The Oak Ridge Gaseous Diffusion Plant is actively engaged in a development program to evaluate an absorption process for the removal and concentration of the noble gases from such contaminated gas streams. The separation process is based on the selective dissolution of krypton and xenon in a fluorocarbon solvent. A pilot plant capable of processing up to 20 scfm of gas was designed and built to establish process feasibility and to collect engineering data necessary for the design of plant-scale systems. During the first experimental phase of the project, a total of 34 pilot plant tests were conducted using refrigerant-12 as the process solvent. For the second phase, 40 tests were completed using refrigerant-11. Both sets of pilot plant experiments were conducted over wide ranges of operating conditions to define the process characteristics as completely as possible. Using an absorber column containing 9 feet of packing, column krypton decontamination factors as high as 1000 were measured, with 99.9% of the krypton in the contaminated feed removed. Stage height data were also measured and correlated using operating conditions to form parameter groupings. 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 reliability is essential.

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* This document is based on work performed at the Oak Ridge Gaseous Diffusion Plant operated by Union Carbide Corporation for the U. S. Atomic Energy Commission.

DISCLAIMER

INTRODUCTION

Two years ago, at the IAEA meeting held in conjunction with the Tenth AEC Air Cleaning Conference, we reported on the status of a new AEC development program being carried out at the Oak Ridge Gaseous Diffusion Plant, which was aimed at evaluating selective absorption as a method for removing krypton and xenon from contaminated gas streams[5]. At that time, we had just completed the design, construction, installation, and shakedown of an absorption pilot plant, and we were in the process of initiating a formal experimental program. Since then, we have successfully completed the two most important phases of this program and have found that the absorption process is reliable, efficient, and very versatile. Today, we would like to review our program, emphasizing the experimental results of the last two years and also mentioning our plans for future work and our views of different plant applications of the absorption technique.

To provide some background, it should perhaps be noted that there are several ways to remove krypton and xenon from gas streams which their radioactive isotopes contaminate. Because these noble gases are not ordinarily chemically reactive, the most practical separation processes are based mainly on physical considerations. Thus, it is possible to classify these processes in five main categories: (1) selective absorption; (2) distillation; (3) selective adsorption; (4) selective permeation of special membrane materials; and (5) special procedures, including underground injection into suitable rock formations and trapping of gas bubbles or individual gas molecules inside of hollow solid materials; e.g., clathration. Of the above, only the selective absorption, distillation, and selective adsorption processes have been tried on an engineering scale. Laboratory data for the selective permeation scheme indicate that it might be applicable on a larger scale, but the special procedures generally appear to be suited more for treatment of a concentrated noble gas product prepared by one of the other techniques than for initially stripping krypton and xenon from large volumes of gas.

Reviewing the three main processes further, some comparisons can be made. Selective absorption and distillation operations lend themselves well to continuous application, whereas selective adsorption processes are typically run batchwise. Also, if conducted at room temperature, the adsorption processes require relatively large traps in many cases; if conducted at low temperatures, the trap sizes are decreased considerably, but large amounts of refrigeration are required to maintain these temperatures, which are usually in the cryogenic region. Additionally, there are safety considerations which must be kept in mind.

Distillation processes for the separation of krypton and xenon are cryogenic operations, so again, refrigeration costs are substantial. Further, it is possible for ozone to form and concentrate when the condensed oxygen is subjected to irradiation by decaying krypton and xenon isotopes, so safety considerations are also important in this case.

Considering, then, ease of application and control, safety of operation, and cost factors, it appears that the selective absorption process offers many advantages over the other schemes mentioned. The absorption process relies on application of standard chemical engineering unit operations. The main disadvantage of the absorption route is that it has not, until recently, been demonstrated completely on an engineering scale, resulting in the absence of definitive design data for promising solvents until now.

The ORGDP program on noble gas absorption is being pursued along three lines--experimental testing in a pilot plant facility, conceptual plant design work, and optimization studies. In turn, the project is divided into five phases, each having a specific goal:

PHASE I - Evaluation of absorption process performance, using refrigerant-12 as the solvent, and collection of mass transfer data.

PHASE II - Same as Phase I, except using refrigerant-11 as the process solvent.

PHASE III - Determination of the effects on the absorption process of failures in upstream air cleaning systems which result in introduction of various impurities, such as iodine, methyl iodide, and nitrous oxide, to the absorption plant.

PHASE IV - Investigation of alternative methods for permanent storage of concentrated noble gases.

PHASE V - Further experimental investigation of special processing situations, possibly including argon-krypton or hydrogen-krypton separations and low concentration tracer work.

To date, Phases I and II have been successfully completed, and the results of these studies are presented in the following sections, after a brief description of the process and the ORGDP pilot plant. Work on the other program goals is now being initiated, and our plans in these areas are outlined near the end of the paper. For more information about the conceptual design and optimization study activities. reference can be made to the various project progress reports[4,6,7,8,9].

THE SELECTIVE ABSORPTION PROCESS

Steinberg[13] collected solubility data for various gases in dichlorodifluoromethane, i.e., refrigerant-12. Considering solvent capacities, separation factors, and thermal and radiation stabilities, as well as overall process safety and economic features, he first suggested utilizing an absorption process employing this solvent for stripping the noble gases, krypton and xenon, from contaminated air streams. Several other solvents, including carbon tetrachloride[3,16,17], kerosene-base liquids[11,12], liquid nitrogen[2], nitrous oxide[13], and trichloromonofluoromethane or refrigerant-11[5] have also been proposed.

As shown in figure 1, with refrigerant-12, krypton and xenon are markedly more soluble than argon, oxygen, and nitrogen, especially at temperatures below 32°F; the separation factor between these two elements and the other gases shown increases considerably with decreasing temperature. Coupled with an essentially direct pressure dependency for the solubilities, these temperature relationships allow a considerable latitude in the choice of processing conditions required to achieve a given separation. Conceptually, then, an efficient absorption process can be devised using the solubility data by specifying an absorption step at some relatively low temperature and high pressure to maximize both total noble gas absorption and separation, followed by a stripping operation conducted at a higher temperature and lower pressure to reclaim the noble gases as a product stream. Also, in some cases, an intermediate fractionating step may be desired to allow further concentration of the krypton and xenon in the absorbed gas prior to recovery as product.

PILOT PLANT

A pilot plant was designed and built at the Oak Ridge Gaseous Diffusion Plant to investigate the absorption process experimentally and to provide basic engineering scale-up data. The pilot plant was designed on the basis of processing up to 20 scfm of air at absorption pressures as high as 40 atmospheres, absorption temperatures as low as minus 94°F, and with a solvent flow of 0.75 to 1.50 gpm.

Plant Description

A schematic flow diagram of the pilot plant is shown in figure 2. A detailed flow diagram and description of the specific components, including instrumentation, are given in the Phase I completion report[14]. The plant can be logically divided into three functional sections: (1) the absorber, (2) the fractionator, and (3) the stripper. The absorber system is composed of a single packed column. Associated or support equipment items include gas and liquid heat exchangers, a gas compressor, and a solvent pump. The initial or main separation of gas constituents occurs in the absorber. Physically, the absorber column is 3 inches in diameter and 10 feet tall and contains three 3-foot-high sections of Goodloe column packing*. The fractionator system consists of another packed column, a reboiler, a flash drum, and an overhead condenser system. The purpose of the fractionator is to enrich the gas dissolved in the

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

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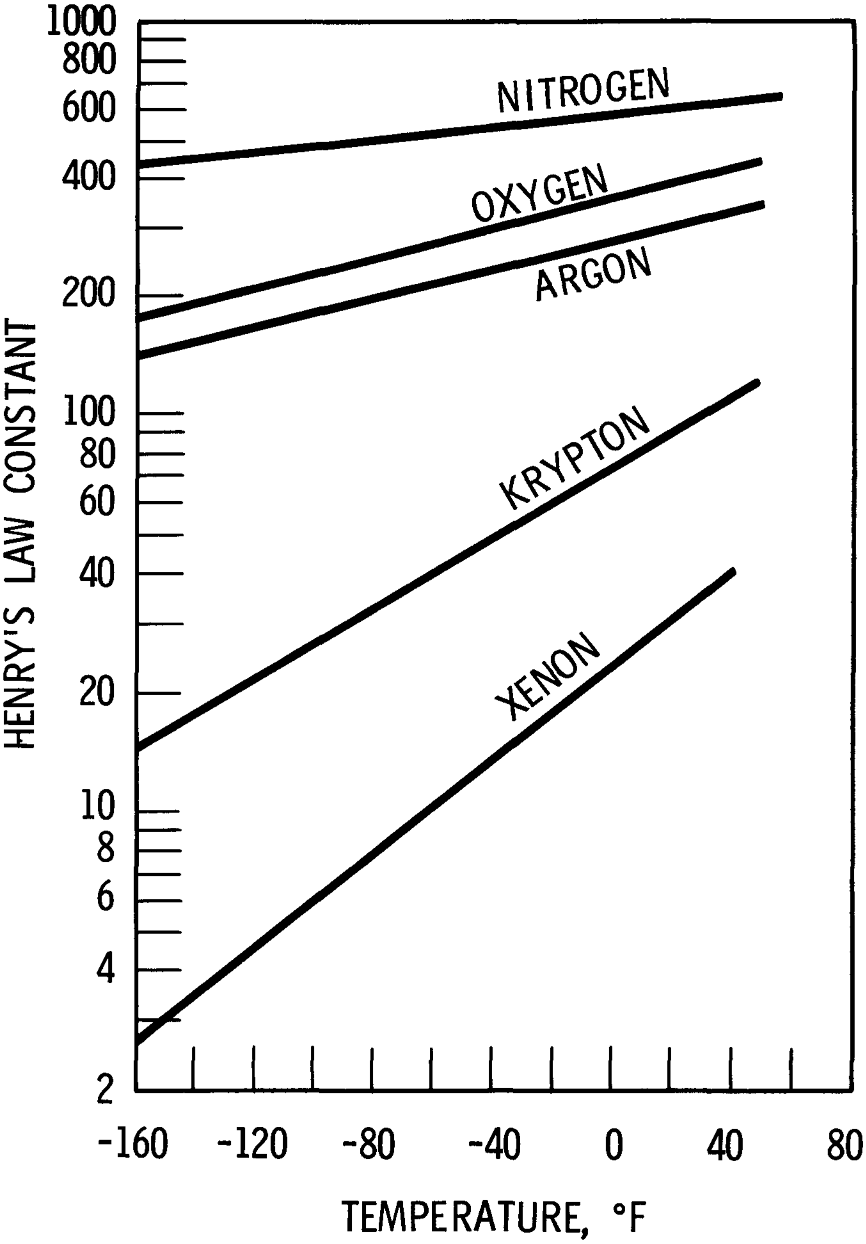

Figure 1

RELATIVE SOLUBILITIES OF
GASES IN REFRIGERANT-12

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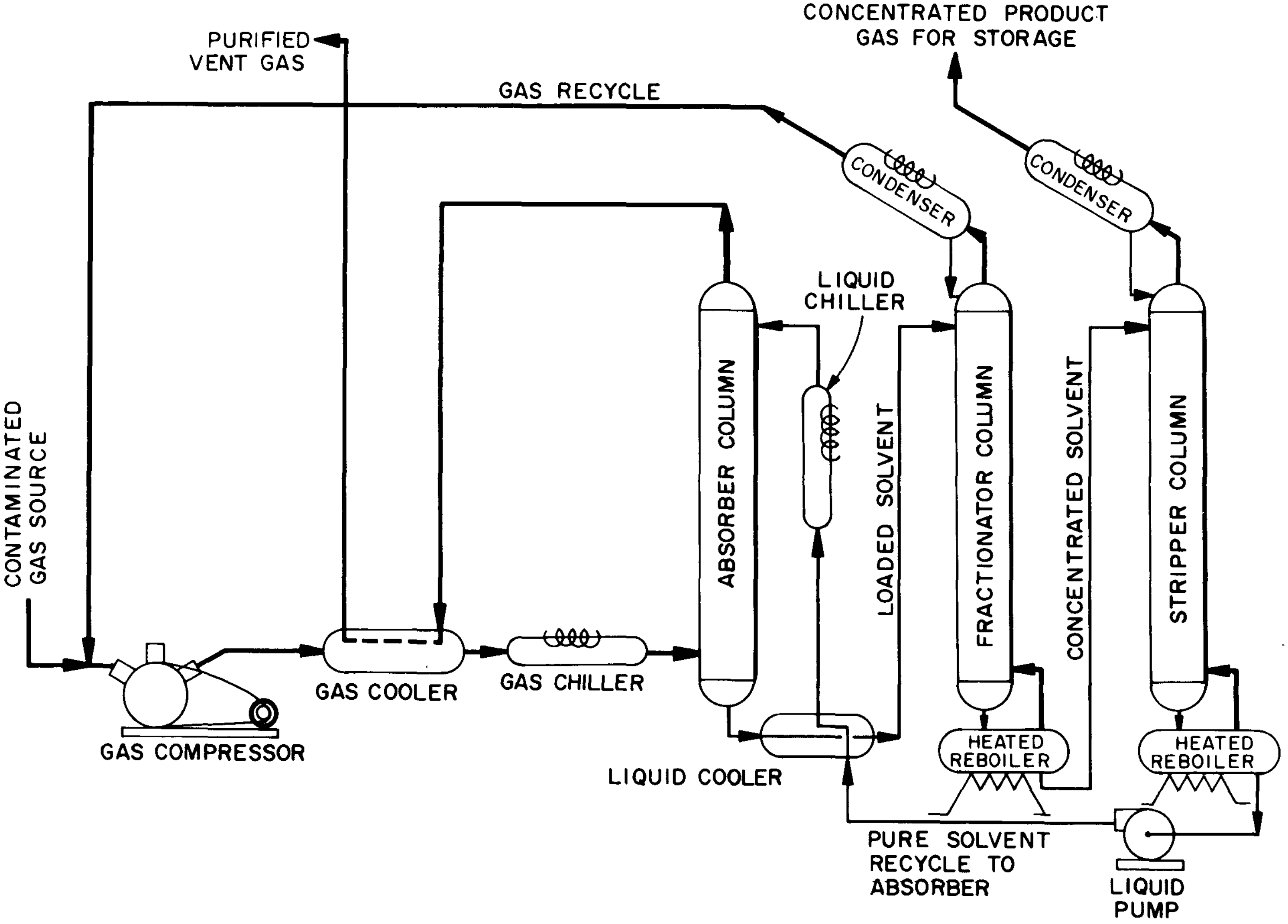

Figure 2

KRYPTON-XENON ABSORPTION PROCESS PILOT PLANT
SCHEMATIC FLOW DIAGRAM

liquid solvent by removing most of the oxygen, nitrogen, and argon. The fractionator column is also 3 inches in diameter, 10 feet tall, and contains 9 feet of Goodloe packing. Except for size, the stripper section is identical to the fractionator. The stripper functions to generate the gas product, highly concentrated in krypton and xenon, and to provide a pure solvent stream for recycle back to the absorber. The stripper column is 6 inches in diameter and contains 8 feet of Goodloe packing.

Process Flow

The contaminated process gas entering the plant is fed directly to the absorber after being compressed and cooled to the desired working pressure and temperature of the absorber column. Upon entering the bottom of the absorber column, the gas is intimately contacted with downflowing solvent and, under the proper operating conditions, essentially all of the krypton and xenon plus a significant quantity of oxygen, nitrogen, and argon is dissolved by the solvent. The cold process gas leaving the top of the absorber, depleted in contaminants, is used to help cool the incoming feed and is then vented or, for convenience in pilot plant operation, recycled for feed makeup. Liquid solvent passes from the bottom of the absorber by pressure difference, is warmed by the incoming solvent feed, and subsequently fed, after some additional heating, to the fractionator flash unit.

The fractionator is operated at a much lower pressure and higher temperature than the absorber. Consequently, part of the solvent is vaporized and a portion of the absorbed gases are liberated as the solvent enters the flash unit. The resulting solvent vapor-gas mixture passes into the fractionator overhead condensers while the remaining liquid is fed into the top of the fractionator packed column. Upflowing solvent vapor generated in the reboiler contacts the downflowing liquid. The solvent vapor-gas mixture leaving the top of the column passes directly into the condenser system where the condensed solvent drains back to the column.

As intended, the bulk of the diluent gases oxygen, nitrogen, and argon, is removed from the solvent during the fractionation step and, consequently, the remaining dissolved gas becomes further enriched in krypton and xenon. However, since a perfect cut cannot be achieved between krypton and xenon and these other gases, a measureable amount of krypton and xenon is also evolved during fractionation. The fractionator off-gas is, therefore, recycled back to the absorber and is mixed with the incoming feed.

The enriched solvent is next routed, again by pressure difference, from the reboiler of the fractionator to the stripper for noble gas product generation and solvent purification. The basic action of the stripper is identical to that already described for the fractionator. The stripper column is operated at an even lower pressure and, consequently, lower temperature than used in the fractionator and, subsequently, the remainder of the absorbed gases is driven from the solvent. Nearly pure solvent flows from the reboiler of the stripper into a liquid storage tank prior to being pumped back to the absorber column. The product enriched in krypton and xenon is collected at the top of the stripper or, for convenience in pilot plant operation, recycled and mixed with the absorber off-gas to provide a simulated process feed. Dissolved gases that are not released in the fractionator are ultimately liberated in the stripper. The composition and flow rate of the product gas stream, therefore, depend in large part upon the relative operating conditions of the fractionator and stripper.

TEST RESULTS

In Phases I and II, the pilot plant was intentionally operated over a wide range of processing conditions to define, for each refrigerant solvent, the process capabilities and to establish parametric dependencies. In all, 34 pilot plant tests were conducted with refrigerant-12[14] and 40 tests were conducted with refrigerant-11[15]. Xenon was not used in the first two phases 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, because xenon is more soluble than krypton in the refrigerants. Tests are, however, tentatively planned with xenon during the Phase V work. A summary of the first and second phase test conditions and results is given in table I. In each and every 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. Consequently, some of the experimental runs were conducted with a relatively high absorber feed krypton concentration. While krypton removals to below detectable limits are impressive and, in fact, sometimes resulted in situations where the feed concentration was inadvertently allowed to drop too low, such removals do not provide quantitative information necessary for the exact analysis of column performance. As previously discussed, the lower concentration limits may be investigated later during Phase V of the scheduled program where tracer experiments are planned. No difficulties are anticipated in attaining good performance at these lower concentration levels.

Absorption pressures were varied from 164 to 512 psia, with temperatures from minus 77° to plus 25°F, absorber feed gas rates from 6.9 to 22.3 scfm, and solvent feed rates from 0.75 to 1.50 gpm. Krypton concentrations in the feed gas ranged from 42 to 8800 ppm. Absorber column krypton decontamination factors between 3 and 1000 were measured in the 9-foot column, with up to 99.9% of the krypton being removed. Stage heights were found to vary from 14 to 70 inches.

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* A gas chromatograph was employed for gas stream analysis. Particular details of the instrument are given in the Phase I report[14].

TABLE I

SUMMARY OF PILOT PLANT TESTS

	Phase I	Phase II
Reference	K-1780	K-1794
Solvent	R-12	R-11
Number of Runs	34	40
Absorber Column:		
Temperature, °F	- 77 to - 21	- 27 to + 25
Pressure, psia	164 to 437	314 to 512
Gas Feed Rate, scfm	9.5 to 22.3	6.9 to 16.4
Solvent Feed Rate, gpm	0.75 to 1.25	0.75 to 1.50
Feed L/G Ratio (mole basis)	1.4 to 4.2	1.4 to 8.0
Krypton Concentration in Feed, ppm	42 to 8800	145 to 1180
Krypton Removal, %	71.0 to 99.9	62.9 to 99.7
Krypton Decontamination Factor	3.4 to 1000	2.7 to 333
H_{OG}, inches	14 to 70	17 to 68
HETP, inches	18 to 46	18 to 38
Fractionator Column:		
Temperature, °F	32 to 35	140 to 185
Pressure, psia	44.0	55.7 to 93.7
Stripper Column:		
Temperature, °F	1 to 5	90 to 118
Pressure, psia	24.0	19.7 to 31.7

The experimental data indicate that the performance of the absorber column and hence, the process, is strongly related to the absorber feed L/G ratio, pressure, and temperature. Efficient absorber operation favors higher L/G ratios and pressures and lower temperatures. Economic studies, however, indicate that higher operating pressures and generally higher temperatures are preferable for optimum plant design because of the significant reduction in refrigeration costs. A plant designed for refrigerant-12, with an absorber temperature of minus 30°F and pressure of 425 psia should give a good balance between economics and performance. With a feed L/G ratio of 3 to 3.5 (mole basis), pilot plant tests indicate that an absorber decontamination factor of 300 to 400 can be expected. In order to achieve similar operation with refrigerant-11 as the process solvent, the absorber would have to be maintained at a pressure of 510 psia or greater, with a feed L/G ratio of 5 to 5.5. Tests show that for the refrigerant-11 system absorber temperatures as high as plus 25°F can be used.

Tests performed during the Phase II program where the pressure and temperature of the fractionator were varied demonstrated that the concentration of krypton in the stripper could be controlled by specifying the operation of the fractionator. A more concentrated stripper product resulted as the pressure of the fractionator was made to approach that of the stripper. At the same time, the overall stripper product flow decreased as a larger portion of the diluent gases were driven from the solvent during fractionation. Other tests where the operating conditions of the stripper were varied demonstrated that good stripper operation is essential to the overall efficiency of the plant. If the operating conditions of the stripper are not carefully selected and maintained, some gas will remain in the solvent. Subsequently, the removal efficiency of the absorber will be more or less restricted by the associated mass transfer equilibrium relationship that exists between the various gas constituents composing the process gas stream leaving the absorber and those gases contained in the recycled solvent entering the absorber. Tests show that the stripper pressure should be maintained at a relatively low value, particularly with the refrigerant-11 system.

MASS TRANSFER PARAMETERS

The major specific goal of this project, aside from establishing general feasibility, was to analyze the pilot plant data and develop the mass transfer correlations necessary for plant design work. The absorber column design is simplified by the nature of the solubility differences that exist between the nonradioactive gases, argon, oxygen, and nitrogen, and the two gases which will have active isotopes, krypton and xenon. Krypton and xenon are considerably more soluble in the refrigerant solvents 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. Accordingly, stage heights for krypton separation were determined for each of the runs.

There are several approaches that can be taken in analyzing and correlating mass transfer data. In this respect, three related factors must be dealt with: (1) the gas-liquid equilibrium values, (2) the stage model, and (3) the stage height correlation form. In assembling the Phase I and II data, these three items were looked at as comprising an overall design package rather than viewed independently. The objective of our data analysis, then, was to arrive at a total package which would best meet two criteria:

1. The procedures should not be overly complex and should be equally adaptable to either the refrigerant-11 or the refrigerant-12 data.
2. Of the various methods considered, the ones selected should be those which afford the best overall match of the actual pilot plant separation data.

This guideline--the desire to provide a column analysis package amenable to conventional engineering design calculations and most consistent with the experimental performance observations--is woven into the discussions which follow.

Because each has some advantages, two basic models were used in the determination of stage heights. In both cases, the 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.

Differential Stage Approach

An equation of the form

$$Z = (N_{OG})(H_{OG})$$

where Z = required column height, inches;

N_{OG} = number of transfer units required to perform the stated separation; and

H_{OG} = height of the transfer unit, inches, is commonly employed for the design of packed columns.

For calculation of the number of transfer units, Colburn[1] gives

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

where k = gas-liquid equilibrium coefficient;

G = gas flow rate, moles/min-sq ft;

L = liquid flow rate, moles/min-sq ft;

y = gas phase mole fraction of absorbing component;

x = liquid phase mole fraction of absorbing component; and

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

Naturally, the system to which the Colburn equation is being applied must reasonably satisfy certain basic assumptions or restrictions inherent in the derivation of the Colburn model. The restrictions may or may not be too severe to permit application to a particular problem. Considering only the key assumptions of this particular Colburn equation, the gas-liquid equilibrium coefficient, k, and the column liquid-to-gas flow rate ratio, L/G, must be taken as constant throughout the column. The assumption of a constant equilibrium coefficient is not difficult to make for the noble gas absorption column, especially if isothermal conditions are maintained. The assumption of a constant L/G ratio, however, is clearly not good for gas absorption where as much as half of the total feed gas might be dissolved in the solvent in some cases.

With respect to the k values, the Phase I data were analyzed initially assuming that the various equilibrium constants could be taken as the measured Henry's Law constants[13]. Component material balances in the column indicated that the true or effective values were actually smaller than the respective Henry's Law constants. Equilibrium coefficients were therefore re-established on a semiempirical basis, obtaining values partly on the basis of empirical observation and relative consistency with the Henry's Law data. Values of k for each constituent gas in refrigerant-11 and -12 were then fitted to the following equation:

$$k = \exp[A + BT]/P_{\text{Total}}$$

where k = gas-liquid equilibrium constant;

T = absorption temperature, °F; and

P_{Total} = total pressure, atmosphere.

This form was used in preparing the design package, and the specific A and B values used are listed in table II.

An arithmetic average L/G ratio was also employed with the Colburn equation to describe this absorption problem more acceptably. The use

TABLE II

PARAMETERS FOR GAS-LIQUID EQUILIBRIUM COEFFICIENTS

Gas	Solvent	A	B
Xenon	Refrigerant-11	3.1827	0.013491
	Refrigerant-12	2.6486	0.013491
Krypton	Refrigerant-11	4.3508	0.010197
	Refrigerant-12	3.8167	0.010197
Argon	Refrigerant-11	5.6348	0.004185
	Refrigerant-12	5.1007	0.004185
Oxygen	Refrigerant-11	5.8836	0.004341
	Refrigerant-12	5.3495	0.004341
Nitrogen	Refrigerant-11	6.3902	0.001944
	Refrigerant-12	5.8561	0.001944

of an average L/G ratio, however, while making the model more attractive for this system, does present another problem in the 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 what the average will be. For this reason, correlations were developed using the experimental data for each refrigerant to predict the average L/G ratio based upon the known feed L/G ratio:

For refrigerant-11

$$(L/G)_{avg} = 0.548\ (L/G)_{feed}^{1.118}\ P^{0.195}$$

and for refrigerant-12

$$(L/G)_{avg} = 0.443\ (L/G)_{feed}^{1.116}\ P^{0.318}$$

where the liquid and gas flows are both on a mole basis and the pressure, P, is expressed in atmospheres. The agreement between the actual average L/G ratios observed in the pilot plant tests and those computed using the above correlations is good, as can be seen in figures 3 and 4.

Using the k values and the average L/G ratios just presented, the Colburn equation was applied to the krypton absorption data to establish the number of overall gas-phase transfer units for the 9-foot absorber column. The resultant H_{OG} values were then correlated according to the following equations:

For refrigerant-11

$$H_{OG} = \frac{2200\ G^{1.32}}{\alpha^{0.886}\ P^{1.24}\ L^{0.341}}$$

and for refrigerant-12

$$H_{OG} = \frac{1.36 \times 10^{6}\ G^{1.46}}{\alpha^{0.525}\ P^{1.74}\ L^{1.61}}$$

where H_{OG} = stage height, inches;

G = column feed gas flow rate, lb/hr-sq ft;

α = ratio of the gas-liquid equilibrium coefficient for nitrogen, the bulk component to that of krypton, the key component;

P = absorption pressure, atmosphere; and

L = solvent flow rate, lb/hr-sq ft.

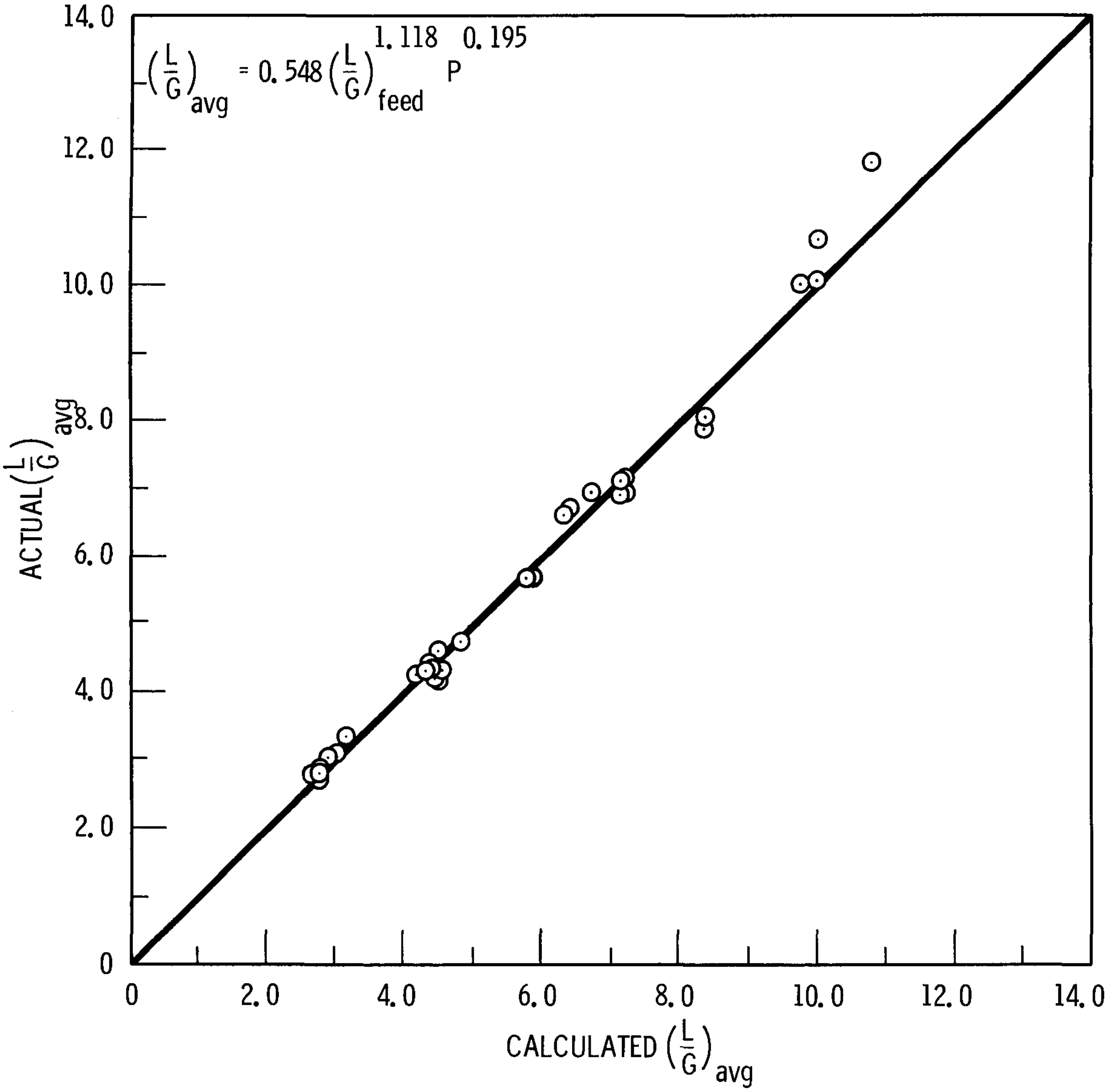


Figure 3

COMPARISON OF ACTUAL AND CALCULATED $(L/G)_{avg}$ VALUES FOR REFRIGERANT-11 PROCESS

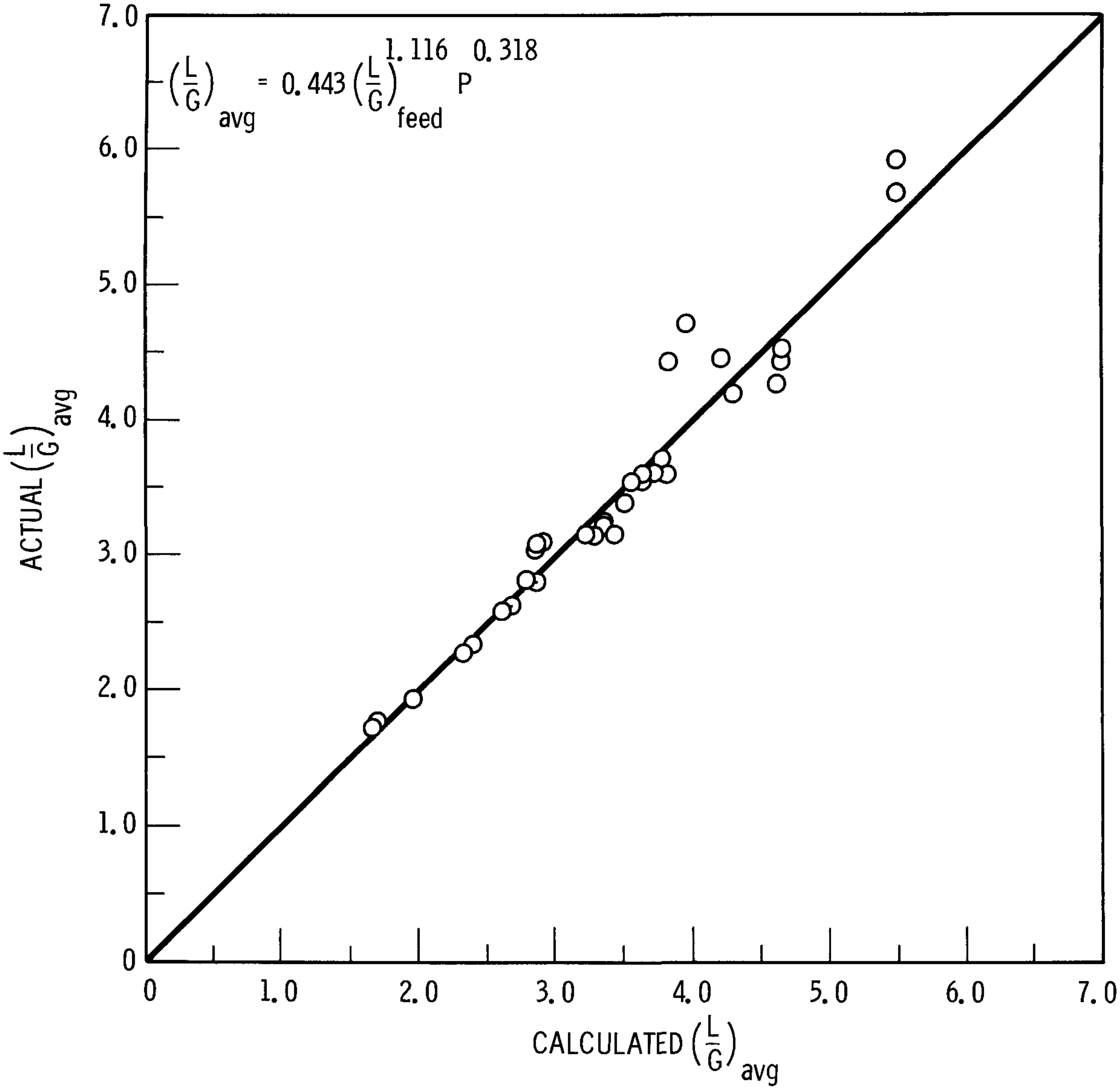


Figure 4

COMPARISON OF ACTUAL AND CALCULATED $(L/G)_{avg}$ VALUES FOR REFRIGERANT-12 PROCESS

From the data listed in table II, the parameter α can be seen to decrease with increasing temperature:

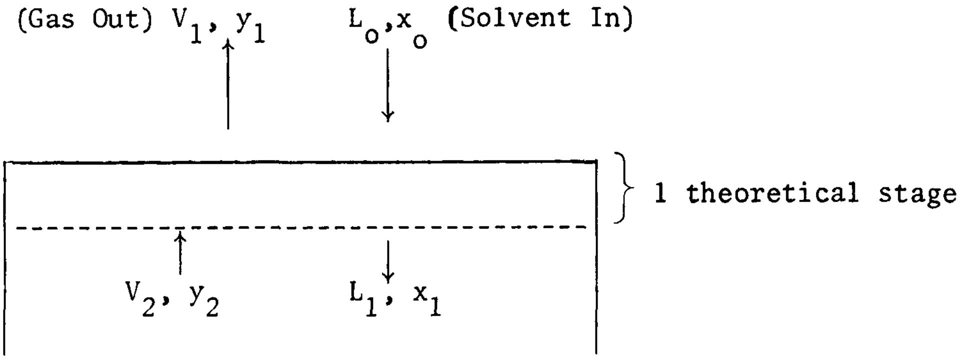
$$\alpha = \exp\,(2.0394 - 0.008253\ T)$$

where T is in °F.

The correlating equations for H_{OG} were arrived at by starting with the Murch equation[10] and adding pressure and solvent flow rate dependencies to account for the variable gas flow rate. The final results are illustrated in figures 5 and 6, where stage heights predicted from the correlations are compared with those determined experimentally.

Plate-to-Plate Approach

The problems 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 sizable 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:



where V_1, L_o, all y_1 and all x_o are known from pilot plant data.

The non-solvent components in liquid stream 1 (L_1) may be obtained from equilibrium:

$$x_{1i} = y_{1i}/k_i\ ,$$

and the solvent in stream 1 is:

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

where subscript f refers to solvent.

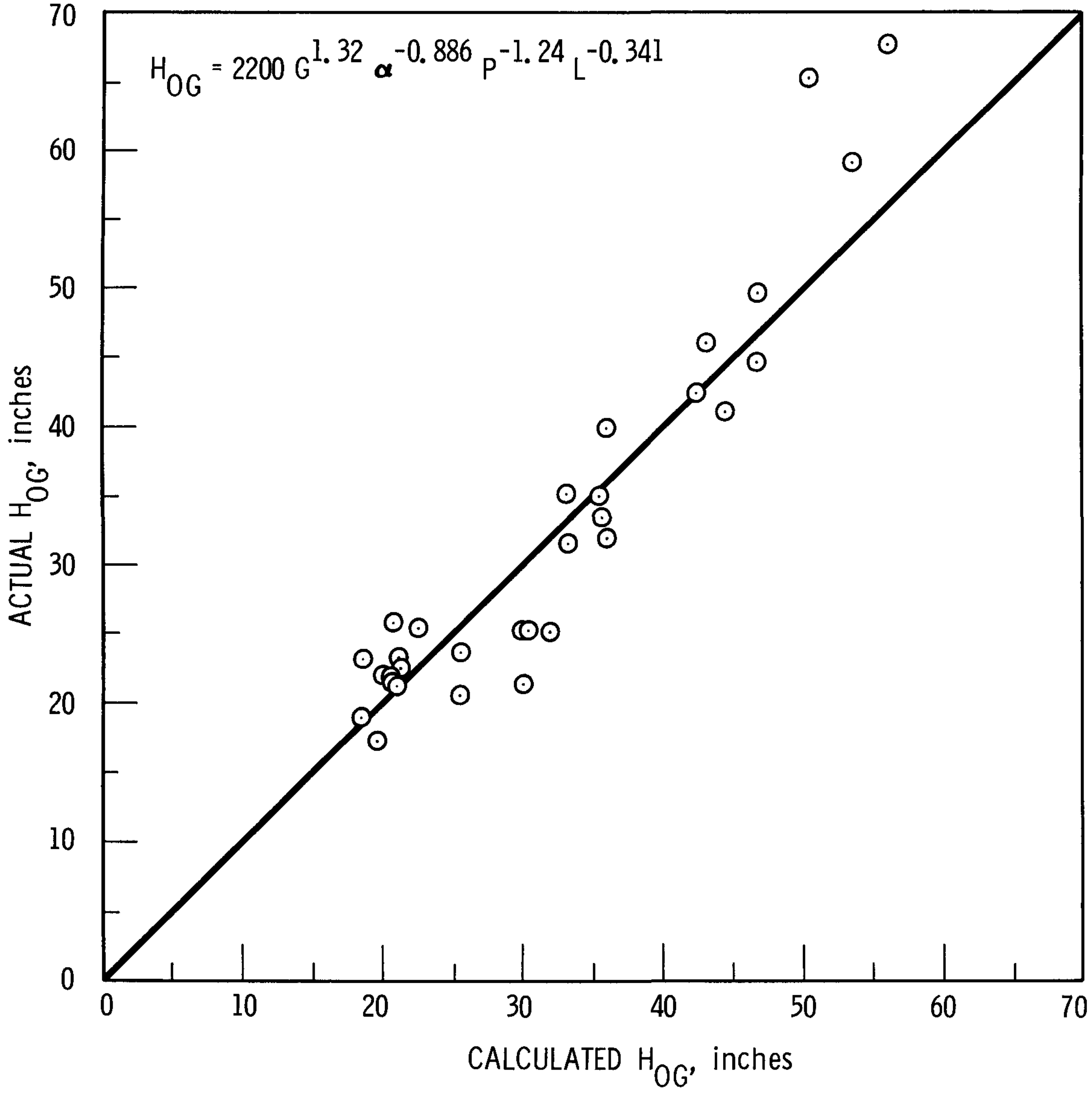


Figure 5

COMPARISON OF ACTUAL AND CALCULATED H_{OG}
VALUES FOR REFRIGERANT-11 PROCESS

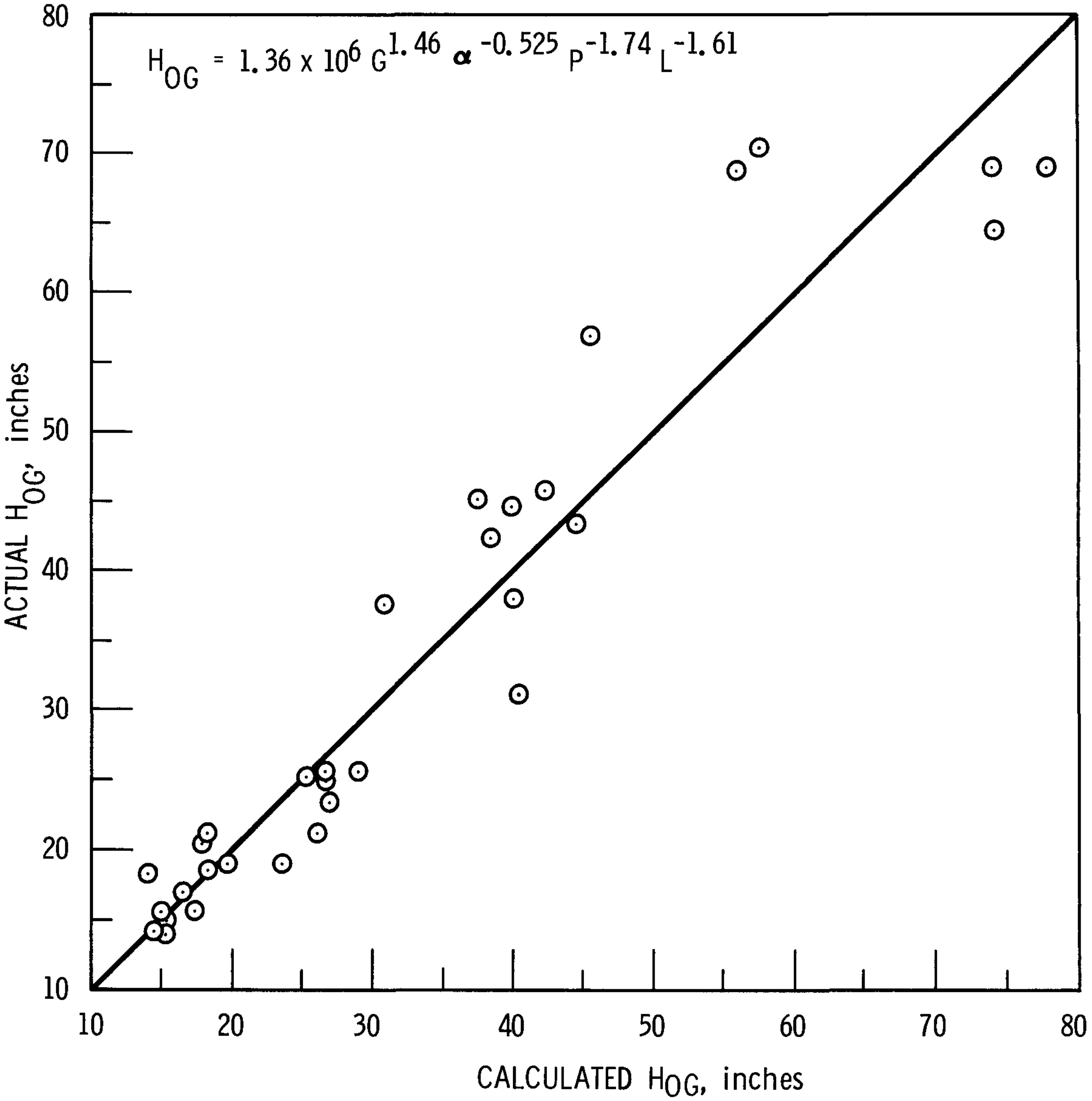


Figure 6

COMPARISON OF ACTUAL AND CALCULATED H_{OG} VALUES FOR REFRIGERANT-12 PROCESS

A solvent balance about the stage is:

$$V_1 y_{1f} + L_1 x_{1f} = V_2 y_{2f} + L_o x_{of} ,$$

and an overall balance shows that

$$L_1 = V_2 - V_1 + L_o .$$

Thus:

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

or

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

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,

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

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

$$y_{j+1,i} < y_{bi} < y_{j,i} ,$$

or

$$y_{j+1,i} > y_{bi} > y_{j,i} ,$$

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 provides an estimate of the number of theoretical plates (NTP), was used to examine the pilot plant data. HETP values were obtained by dividing the respective NTP values into the 9-foot column height. The HETP's were then correlated according to the following equations:

For refrigerant-11

$$\mathrm{HETP} = \frac{24.9\ G^{0.564}}{P^{0.457}}$$

and for refrigerant-12

$$\mathrm{HETP} = \frac{2210\ G^{0.774}}{P^{0.806}\ L^{0.798}}$$

where all units are the same as those in the H_{OG} equations.

In figures 7 and 8, the HETP's obtained from the experimental results are compared with those predicted using the above equations.

Comparison of Approaches

For quick absorber column calculations, the Colburn model is probably the easier to use of the two described. Once the feed conditions for the particular case are specified, an average L/G ratio and equilibrium constant k can be estimated using the appropriate correlations, and subsequently, the number of transfer units N_{OG} calculated from the Colburn equation. The height of the transfer unit can then be determined from one of the H_{OG} correlations. The required absorber column height follows immediately. On the other hand, the plate-to-plate model is attractive because the constant L/G assumption is not required and also because it shows promise of consistent application to the other system gases.

PLANS FOR FUTURE WORK

Phase III

As noted previously, the third phase of our program is aimed at seeing what happens to the absorption process if an upstream air cleaning system fails, releasing such impurities as iodine, methyl iodide, or nitrous oxide to the absorption plant. This problem is more or less common to all noble gas removal processes, and the work is being carried out in four steps:

1. Theoretical prediction of the fates of different impurities in the absorption process.

2. Experimental confirmation of these predictions.

3. Based on 1 and 2, assessment of the need for including impurity removal systems as auxiliaries to the absorption process equipment. Also, determination of the best location of such systems if they

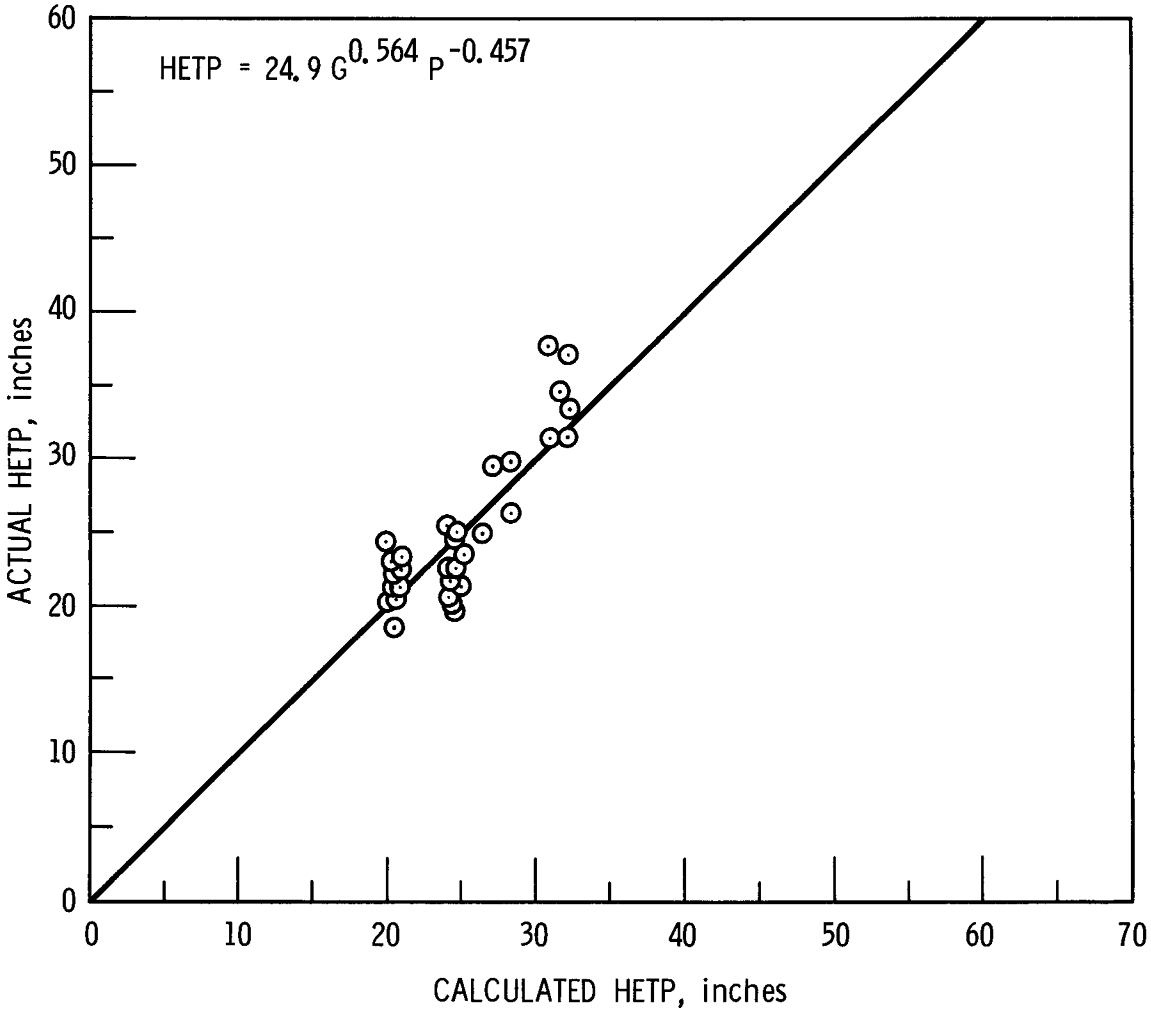


Figure 7

COMPARISON OF ACTUAL AND CALCULATED HETP VALUES FOR REFRIGERANT-11 PROCESS

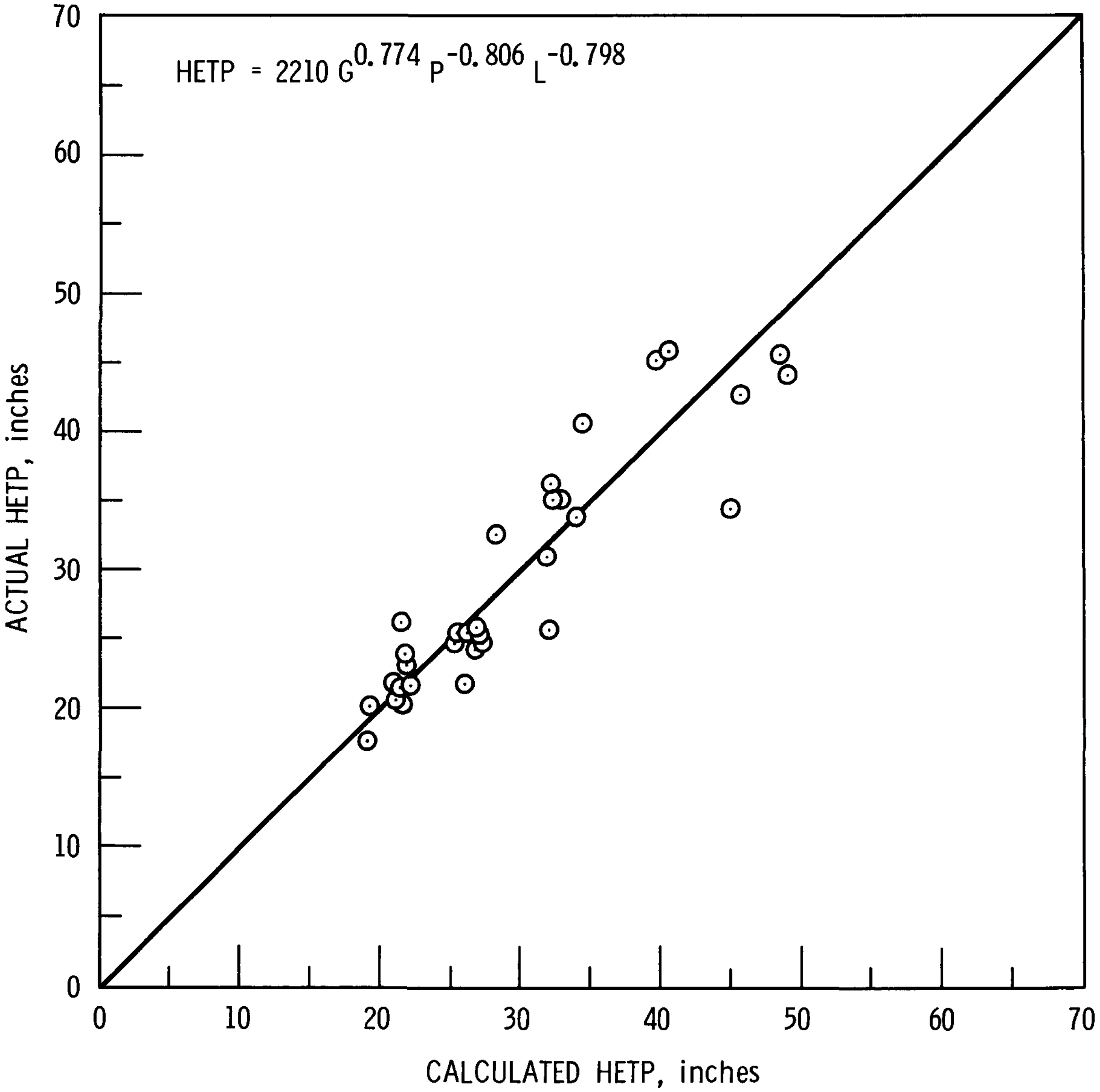


Figure 8

COMPARISON OF ACTUAL AND CALCULATED HETP VALUES FOR REFRIGERANT-12 PROCESS are required, e.g., in the feed line or in the concentrated product line.

4. Engineering-scale demonstration of those impurity removal systems which might be needed and for which adequate design data are not available at the present time.

Currently, we are in the process of planning experiments to confirm predictions of impurity disposition in the absorption system.

Phase IV

The fourth phase of the ORGDP program involves study of different methods of permanently storing the concentrated noble gas product produced by the absorption (or even some other) process. This portion of the program is divided into two parts--paper studies and experimental work. In the study area, we plan to consider the economic and safety features of various schemes for further processing noble gas products to make them more suitable for safe, low-cost retention. Also, we hope to identify technology roadblocks which are associated with otherwise promising schemes. The experimental portion of our work in this program area will then be directed toward solution of these specific problems. According to the present schedule, we do not plan on initiating experimental work on this phase of the program for several more months.

Phase V

The fifth phase of our noble gas program is a collection of special experiments. These experiments are mainly oriented toward selected process applications, where the results of Phase I and Phase II tests might have to be extrapolated. Included here, for example, are argon-krypton separation tests (vented fuel LMFBR), hydrogen-krypton separations (possibly for PWR), and low noble gas concentration, tracer level tests (LWR and "hot" demonstration). It is planned that these tests will be sandwiched between experimental work on the other program phases, so that they can be expedited and so that full use can be made of the pilot plant system.

OUTLOOK FOR APPLICATION OF THE ABSORPTION PROCESS

Based on the experimental results obtained to date and our economic evaluations, we are optimistic about application of the absorption process to a variety of nuclear gas cleaning jobs. Although each application would, of course, need to be considered in detail, some general comments can be made about possible plant-scale uses of this process.

BWR Systems

In dealing with the condenser off-gas from an operating BWR, the process feed rate will probably be in the neighborhood of 50 scfm, and the noble gas concentration will be at very low levels (1 to 2 ppm or below). Scale-up of pilot plant results to this flow rate should be straightforward, and handling of low concentrations of krypton and xenon does not appear to present unusual difficulties. In this respect, theoretical material balance and process design calculations made for this situation have not revealed any problems in equipment design or process operation. Also, correlation of the Phase I and Phase II data with krypton concentrations ranging over three orders of magnitude did not indicate any significant dependence of performance on concentration. Furthermore, some of the British studies of the absorption process[17] conducted using carbon tetrachloride as the solvent, were made at low feed concentrations, and the krypton removal was apparently satisfactory under these conditions. In any event, the tracer experiments which we are currently planning to make in the near future should answer any questions which linger about the effect of concentration. It might be noted that noble gas releases from operating reactors are already normally well below the current release limits, but the absorption process is being looked at as a promising candidate for inclusion in the "near-zero" release packages currently receiving attention.

PWR Systems

Removal of krypton and xenon from operating PWR off-gas streams might involve separation from hydrogen or from nitrogen. The process feed rates for this application are expected to be low, 10 scfm or below, and the noble gas concentrations in the feed should again be at low levels. We are currently considering hydrogen-krypton tests as part of our Phase V work, and the other general comments just made about system designs for the BWR case also apply here.

Fuel Reprocessing Plant

In terms of compliance with current discharge regulations, large fuel reprocessing plants might present the most immediate need for some noble gas removal process. In this application, the process feed rates might be in excess of 100 scfm, with noble gas concentrations in the range of 50 to 1000 ppm. Design of an absorption plant for this flow rate will involve some scale-up of the pilot plant results, but this should be a conventional procedure. The concentration range anticipated is well within the range already used in the ORGDP experimental work. One additional factor is the likely presence of nitrogen oxides in the feed gas, and the consequences of this possibility are presently being considered in our Phase III work. It may be that the absorption process will not require any feed pretreatment in this case, but this important aspect is being looked at carefully.

Vented Fuel LMFBR

In this application, a portion of the LMFBR core cover gas (e.g., argon) might be continuously withdrawn and routed to an absorption system for removal of krypton and xenon. The feed rate to the absorption plant is expected to be in the neighborhood of 10 scfm, and the noble gas concentration may be in the lower part of the Phase I and II test range. Some of the miscellaneous tests planned for the fifth phase of the ORGDP program should add definition to this application.

LWR Accident Case

In the case of an LWR core meltdown, an absorption system might be employed to reduce the activity of the containment vessel gas. Depending on the degree of cleanup required and the schedule for effecting this reduction in activity, the absorption process feed rate might be above 1000 scfm. The noble gas concentration would be high initially, decreasing, of course, as processing continued[4]. Sizing of absorption equipment to handle this large feed flow would involve considerable extrapolation of the pilot plant mass transfer data, so that inclusion of some contingencies in the column designs would be appropriate. The other characteristics of the process are well enough defined--and conventional enough--to permit reasonably confident selection of the other process hardware.

CONCLUSION

Two years of testing have shown that the continuous selective absorption process can be used confidently to remove krypton and xenon from contaminated gas sources. Mass transfer parameters have been defined over broad ranges of operating conditions for two promising solvents, refrigerant-11 and -12. Operation of the pilot plant was not difficult, even though some of the instrumentation is not particularly sophisticated.

The design, construction, and operation of the plant can be accomplished in a relatively straightforward manner, and based on these development studies, the process lends itself well to nuclear applications where a high degree of reliability is essential.

On the basis of preliminary economic and process design considerations, the outlook for application of this process to a variety of gas cleaning jobs certainly appears to us to be very promising. Of course, each application must eventually be considered in terms of the specific requirements which might evolve, but the ORGDP program is being conducted in a manner felt to be responsive to changes in the various plant requirements. The experimental and study work now being planned is expected to supplement the basic reliability and performance data already collected and to provide further definition of overall solutions to noble gas cleanup problems.

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