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SINGLE-COLUMN-BASED ABSORPTION PROCESS FOR TREATING DISSOLVER OFF-GAS

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CONTENTS

	<u>Page</u>
SUMMARY	7
INTRODUCTION	7
PROCESS BASIS	8
PROCESS DESCRIPTION	10
EXPERIMENTAL TESTING AND RESULTS	13
PRODUCT PURIFICATION EQUIPMENT	25
CONCLUSIONS	28

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SUMMARY

The fluorocarbon absorption process for krypton and xenon removal from dissolver off-gas is based on exploitation of solubility differences which exist among noble gases and other gas-phase constituents in the fluorocarbon solvent dichlorofluoromethane (refrigerant-12). Process performance and reliability have been demonstrated on an engineering scale with over 10 years of pilot plant operation, including testing with ^{85}Kr , ^{133}Xe , and ^{131}I . The culmination of this work is a single-column design which results in a simplified process with improved reliability and lower cost. Data are presented summarizing recent single-column development activities. These include data plots depicting decontamination factor (DF)* vs. feed gas flow rate, DF vs. process absorption factor (kg/L), and location of the concentration peak via the solvent flow rate. In general, 99% removal is easily obtainable for Kr, Xe, and CO_2 while attaining concentration factors (CF)** on the order of 10^3 to 10^4 . Further concentration of the Kr product is investigated using solid sorbent and cold trapping technologies. Effective removal of entrained fluorocarbon solvent and CO_2 from the single-column product stream is demonstrated using 13X and 5A molecular sieves, respectively. Additional separation of Xe is studied using a silver mordenite bed and compared to existing methods using cryogenic charcoal beds or selective cold trap sublimation. Regardless of the method for Xe removal, Kr is ultimately concentrated via a simple cold trap to > 90% purity from a feed gas containing 10 ppm.

INTRODUCTION

Since the late 1960s the fluorocarbon selective absorption process has been under development at the Oak Ridge Gaseous Diffusion Plant (ORGDP) in conjunction with the Oak Ridge National Laboratory (ORNL). Development efforts have been predicated on a 1975 Environmental Protection Agency (EPA) ruling that accumulation of ^{85}Kr in the atmosphere from nuclear power operations could not be allowed on a long term basis. Since the necessary control technology was either available or nearly so, the EPA mandated ^{85}Kr removal by 1983. The standard, as finally adopted by the EPA, calls for approximately 87% of fission product Kr to be removed from the LWR uranium fuel cycle.¹ Primarily, this burden falls to the fuel reprocessor.

*DF is defined as (amount of Kr in feed gas)/(amount of Kr in vent gas)

**CF is defined as (concentration of Kr in product gas)/(concentration of Kr in feed gas)

The ORGDP fluorocarbon development program has been structured to demonstrate the removal of radioactive noble gases for a number of potential applications. Based initially on reactor safety issues, the fluorocarbon program was verified and proven with three generations of pilot plants. In recent years support for the program has been maintained through the Liquid Metal Fast Breeder Reactor (LMFBR) program and currently is continued in conjunction with the Consolidated Fuel Reprocessing Program (CFRP) at ORNL. The result of this extended experimental program has been demonstrated pilot plant performance, operability, and tolerance for various feed gas impurities. In addition, it became obvious that the fluorocarbon process being developed for ^{85}Kr removal could also be used for effective simultaneous removal of ^{14}C as CO_2 and as a backup for elemental and organic iodine recovery.

The objective of the ORGDP fluorocarbon work is to complete all process development activities necessary to allow the design of a demonstration off-gas decontamination facility. This goal has nearly been realized through the completion of solvent chemistry studies, a reliability analysis, and near completion of fluorocarbon process and associated peripheral equipment testing.

PROCESS BASIS

The basis for selective absorption is the solubility differences which exist among the various feed gas components and the particular solvent chosen for the process. The solvent used in most of the Oak Ridge work and selected as the baseline design solvent is dichlorodifluoromethane, CCl_2F_2 , commonly referred to as refrigerant-12 or simply R-12. This particular solvent was first suggested by Steinberg,² primarily because of its noble gas capacity, noble gas/bulk gas separation factors, and relatively good thermal and radiation stability, as well as overall process safety and economic considerations. R-12 is one of the major evaporative coolants used in commercial and home refrigeration units, and, consequently, a substantial amount of detailed thermodynamic and physical property data are available for the process solvent.

Of course, in the absorption application the most important information needed is the vapor-liquid distribution of the various gaseous components in the solvent liquid. The key components for design are Kr and Xe. Consideration also has to be given to the relative solubility differences between the key components and the bulk gas being processed. In conjunction with program goals, a considerable amount of equilibrium vapor-liquid data now exists for solutions of noble gases in R-12.^{2,3,4,5} A critical review discussing most of the published data has been made by Merriman.⁶ Since nitrogen is the primary carrier gas, its solubility in R-12 is also of particular importance. Figure 1 provides solubility data and predictions for N_2 in R-12 as measured by many different researchers. The newest data submitted by Van Brunt of the University of South Carolina show values measured near those presented

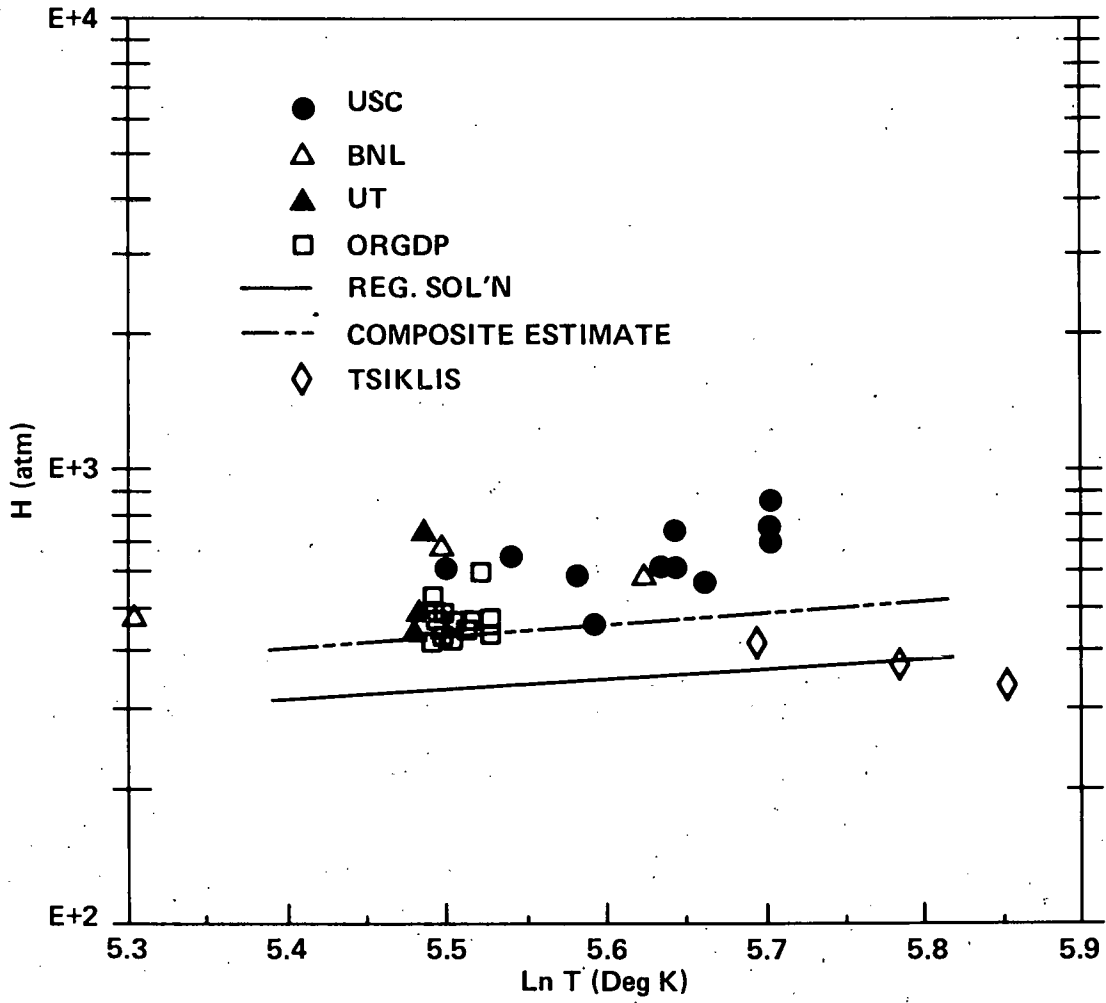


Figure 1
NITROGEN SOLUBILITY IN R-12

by Brookhaven National Laboratory and the University of Tokyo but having the same slope predicted by Merriman's model based on Hildebrand's regular solution theory. The Russian data (TSIKLIS) is most closely grouped with values measured at ORGDP and predicted by Merriman, although the data show a negative slope over the temperature range measured. Furthermore, through the solubility studies it was confirmed that the presence of feed gas impurities such as I_2 and NO_x present no adverse chemistry effects that might jeopardize the fluorocarbon process safety or efficiency. This tolerance to impurities is one of the major process advantages as compared to other Kr removal methods, i.e., cryogenic systems.

The vapor-liquid equilibrium data for various R-12 binary solutions are summarized in Figure 2.

PROCESS DESCRIPTION

Figure 3 is a schematic of the selective absorption process as it was originally conceived. The process serves to remove volatile radioactive contaminants from nuclear facility off-gas streams and subsequently concentrates the contaminants for long-term radioactive waste storage. Absorption, intermediate stripping, and final stripping steps are performed in order to accomplish these two process objectives. The main separation of radioactive components from the bulk gas is effected in the absorber. The intermediate or fractional stripper serves to remove the coabsorbed carrier gas from the solvent, thereby enriching the remaining dissolved gas in the more soluble components. The final stripper removes remaining dissolved gases from the process solvent for collection and regenerates the solvent for recycle to the absorber. The absorption section consists of a packed column for gas-liquid contacting. The intermediate and final strippers are each composed of a packed column, a reboiler, and an overhead condenser. Support equipment items for the basic process include a process gas compressor, feed gas heat exchanger, solvent pump, solvent cooler, storage tanks, and several refrigeration compressors. If the feed gas contains significant quantities of high boiling components, i.e., I_2 or CH_3I , a solvent purification still can be added as an in-line option to prevent these materials from accumulating in the recirculating solvent. If required, the still would not be operated continuously but in a batch mode as needed. Solid sorbents could also be used to purify the solvent.

In the course of the pilot plant operation optimization studies, a soluble gas concentration peak was observed in the intermediate column. The concentration peak was due to the gross internal condensation of the upflowing stripping vapor as it met the cold downflowing liquid. Further definition of the internal peaking phenomenon showed that when the internal condensation zone was raised in the column, the magnitude

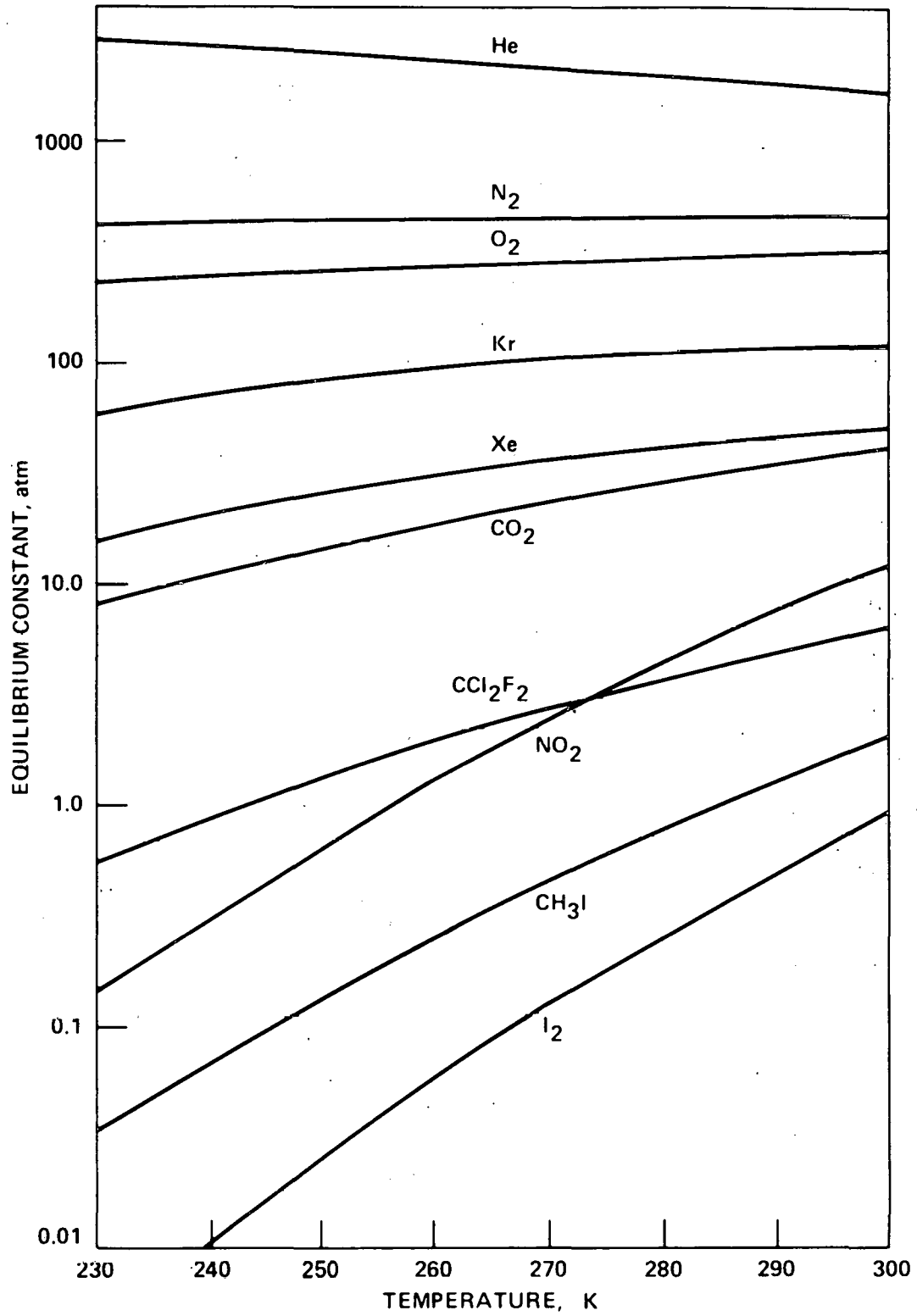


Figure 2

EQUILIBRIUM DISTRIBUTION COEFFICIENTS OF VARIOUS
FEED GAS COMPONENTS IN REFRIGERANT-12 (CCl₂F₂)

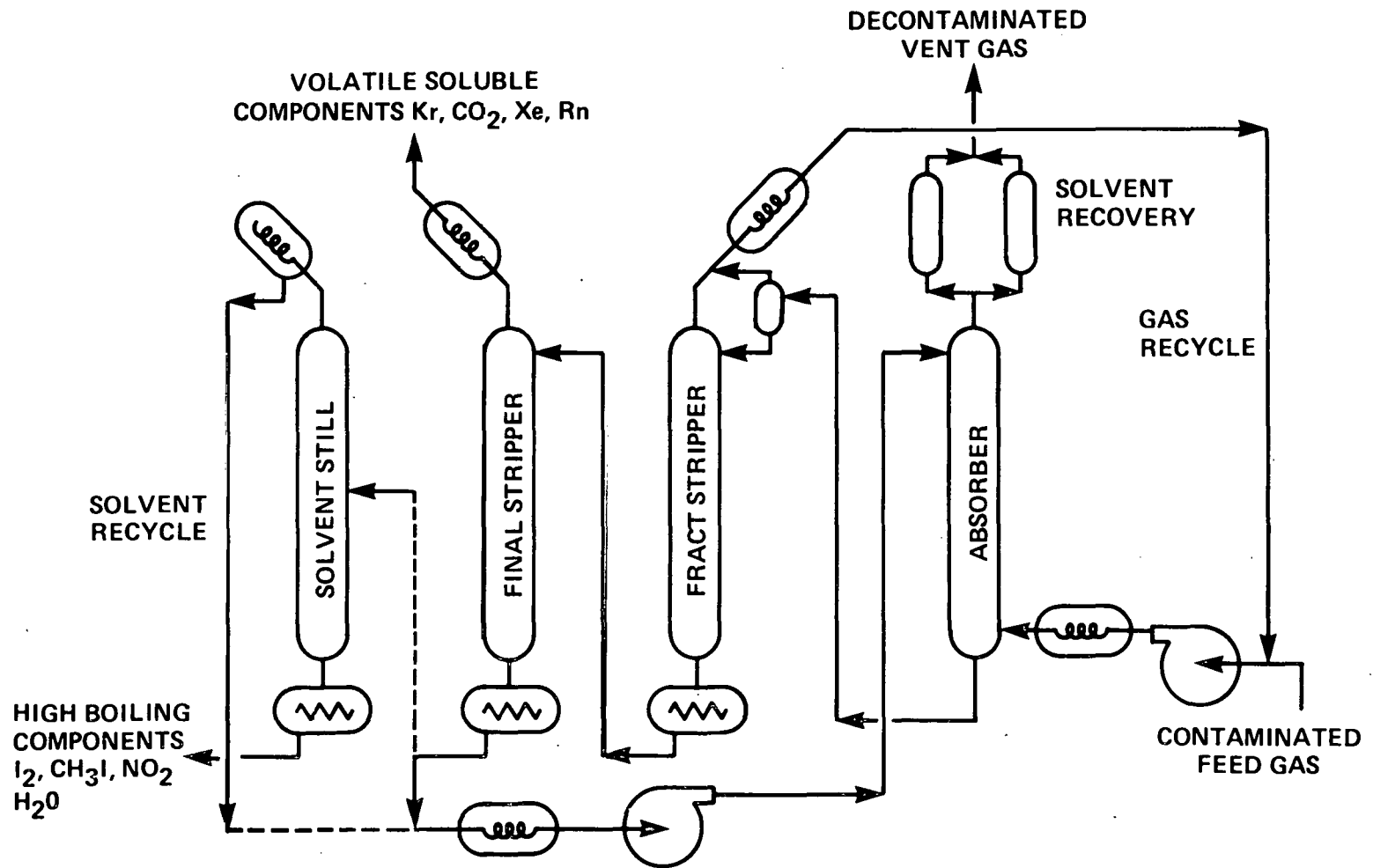


Figure 3

SCHEMATIC OF THE CONVENTIONAL FLUOROCARBON PROCESS

of the soluble gas concentration peak increased dramatically. It became apparent that if sufficient stripping stages were provided below the condensation zone, the final stripping column of the 3-column process could be eliminated with the product being collected as a side stream. Furthermore, it also seemed feasible to place the intermediate section directly below the absorber and operate the entire assembly at a common pressure. Subsequently, a single column was designed that combines the 3 functional steps of absorption, intermediate stripping, and final stripping into a continuous contactor.⁷ Figure 4 gives a schematic of this piece of equipment. Decontaminated off-gas flows from the top of the combination column and regenerated solvent from the bottom, while the fission product gases are collected as a side stream. The combination column requires substantially less equipment and control instrumentation than the conventional flow sheet, and, because of its greater simplicity, it offers numerous operational and economic advantages. Figure 5 is a photograph of the column. The column is approximately 7.3 m tall and has the same flow capacity and performance capability as the previous 3-column development facility. The absorber section is 7.6 cm in diameter, while the fractional stripper is 10.1 cm, and the final stripper is 15.2 cm.

The combination column has been undergoing performance evaluations over the past several years. These tests not only established the overall feasibility of the concept, but showed conclusively that the combination column could perform as well as the three separate columns. The obvious primary advantages include simplified construction, increased reliability, easier operation, lower noble gas and R-12 inventories, lower costs, less hot cell space requirements, and a better demonstrated performance combination of DF and CF. The less significant drawbacks include less freedom in design which requires all column operations to take place at the same pressure; thus, the solvent reboiler temperature is fixed and greater stripper vapor upflow is required. On the basis of a comparison of the two options, the combination column was selected as the preferred version of the process for the reprocessing plant application.

EXPERIMENTAL TESTING AND RESULTS

Fluorocarbon process performance and general versatility have been well demonstrated on an engineering scale with over 10 years of pilot plant operation using 3 different experimental facilities. Virtually all aspects of the process and many different process options and variations have been examined. Extended pilot plant tests have been conducted with ^{85}Kr , ^{133}Xe , and ^{131}I , with and without various feed gas impurities such as CO_2 , NO_2 , N_2O , NO , CH_4 , and H_2O . These tests show that better than 99% of the noble gas can be efficiently removed from such carrier gases as air, N_2 , Ar, He, and H_2 .¹⁵ Feed gas impurities had little discernible effect on either the process operability or noble gas removal performance. Figure 6 is a summary of the experimental range of values used over the 10 years of testing.

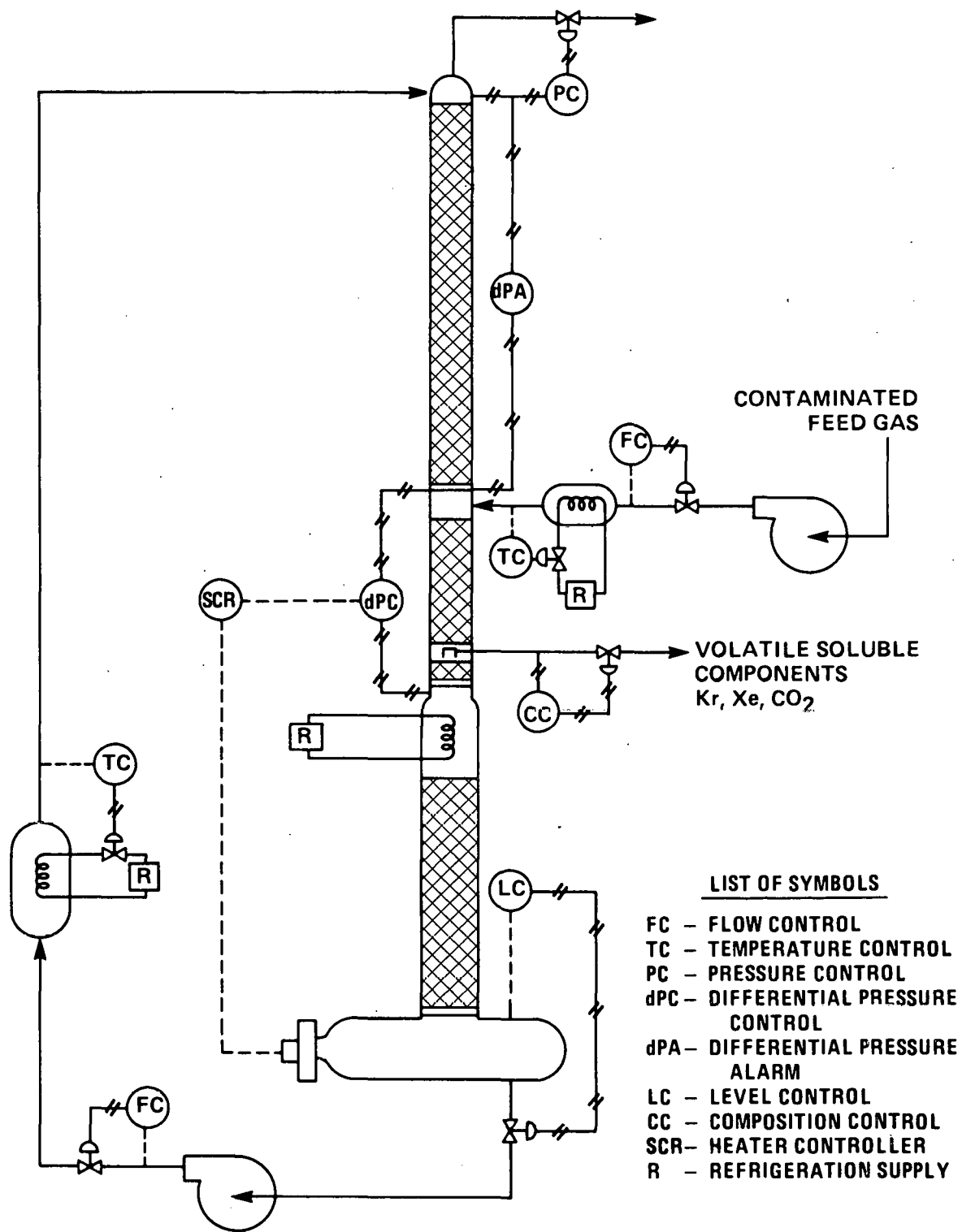


Figure 4
SCHEMATIC OF THE SIMPLIFIED SELECTIVE ABSORPTION PROCESS

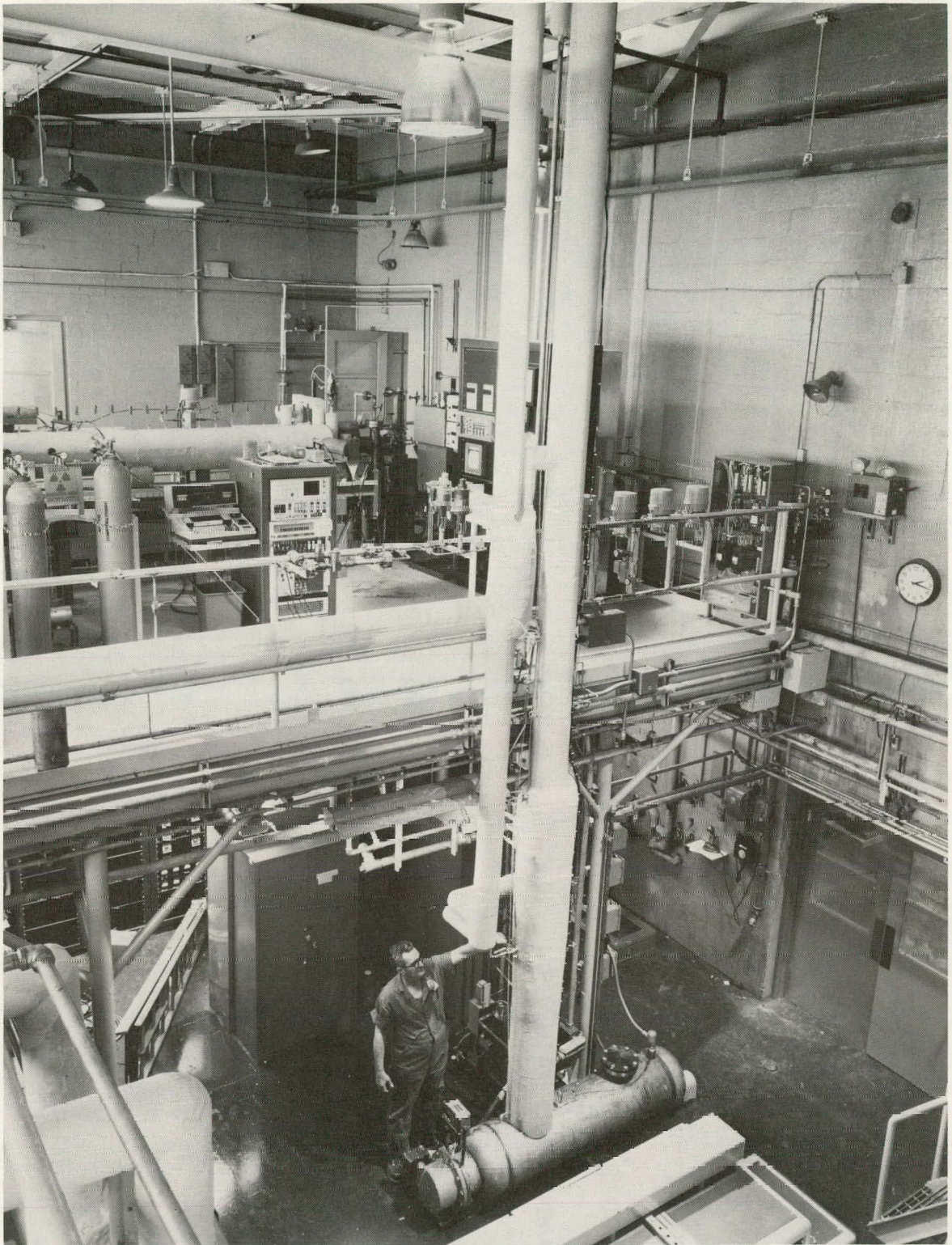


Figure 5

VIEW OF THE COMPACT COMBINATION COLUMN

SOLVENTS	CCl ₂ F ₂ (REFRIGERANT-12), CCl ₃ F (REFRIGERANT-11), CO ₂
CARRIER GASES	AIR, N ₂ , Ar, H ₂ , He, CO ₂
NOBLE GASES	Kr, WITH ⁸⁵ Kr; Xe, WITH ¹³³ Xe
IMPURITIES	CO ₂ , NO, NO ₂ , N ₂ O, CH ₃ I, I ₂ , CH ₄
TEMPERATURE, °F	-75 TO +25 (-59 TO -3.9°C)
PRESSURE, ATM	6.10 TO 34.8
SOLVENT FEED RATE, GPM	0.75 TO 2.0 (2.8 TO 7.6 lpm)
GAS FEED RATE, SCFM	1.13 TO 22.2 (.03 TO 0.63 scmm)
FEED CONCENTRATIONS - Kr, PPM	0.014 TO 8800
- Xe, PPM	0.002 TO 100
- IMPURITIES, PPM	50 TO 6700 (FOR INDIVIDUAL COMPONENTS)
REMOVAL PERCENTAGES - Kr	62.9 TO 99.95
- Xe	99.96 TO 99.99

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Figure 6
SUMMARY OF SELECTIVE ABSORPTION EXPERIMENTS

It is important to note that the basic experimental testing and technology, i.e., the solubilities, impurity tolerance, and peripheral equipment, are applicable to both the 3-column and combination column systems. However, while the overall performance can be obtained by either system, they still have significant differences. Most notable, of course, is the fact that the combination column design must accommodate a highly coupled flow and pressure system with an internal condensation zone, whereas the 3-column process accomplishes these steps in separate columns. In consideration of this difference, a great deal of experimental data has been taken with the combination column to verify control and performance. These data have confirmed much of the previous 3-column work and more importantly provide the designer with a roadmap of suitable operating conditions that will allow high DFs and CFs simultaneously with the control to maintain them.

Figure 7 depicts typical Kr concentration and temperature profiles of a test run showing that acceptable DFs and CFs are readily achievable simultaneously in the single column. The plot shows all concentrations normalized to the feed position which was assigned an arbitrary value of 1. Note the emphatic correlation of the internal condensation zone (as indicated by the temperature profile) with the Kr concentration peak location. Repeated tests have consistently shown that during normal steady-state operation this correlation holds. External temperature monitoring can be used to locate the concentration peak. The stability of the condensation zone, and hence the Kr product withdrawal point, depends upon good column pressure and reboiler controls. These two variables cannot be controlled independently. Excellent column control was achieved through the use of conventional control devices as indicated in Figure 4. The concentration profile presented in Figure 8 shows that by increasing pressure and decreasing temperature, the DF can be increased. Furthermore, decreasing the gas flow rate results in even higher DFs (Figure 9). For each of these plots, note again the sharp condensation zone set up when the hot vapor upflow meets the cold downflowing liquid and the correlation of the concentration peak with the condensation zone. Figure 10 shows that the inclusion of xenon and large amounts of carbon dioxide does not detrimentally affect the Kr DF or CF. Figure 11 presents the DF as a function of the commonly used design parameter absorption factor, kg/L . Finally, Figure 12 shows more clearly the effect of gas flow rate variation in the decontamination factor.

In addition, in any given system the location of the condensation zone and, hence the concentration peak of Kr, can be easily controlled and maintained for product withdrawal using the solvent flow rate. Figure 13 shows how a modest doubling in solvent flow rate will allow operating flexibility over a region 120 cm wide. In this manner differences in the design and location of the product withdrawal can be accounted for. Fortunately, location of the peak at a given flow rate does not appear to be a problem as it depends simply on relatively easy control of the solvent flow itself. Normal operations show fluctuations of the peak

RUN: 048001

DF	9.85Kr
CF	2744
PRESSURE	7.8 ATM
SOLVENT FEED	7.9 L/MIN
SOLVENT TEMP	-23.5 DEG C
FEED GAS RATE	.17 SCMM
FDP	2 In H2O
HEAT INPUT	9.88 KW
IMPURITY FEED	12.9 ppm Kr

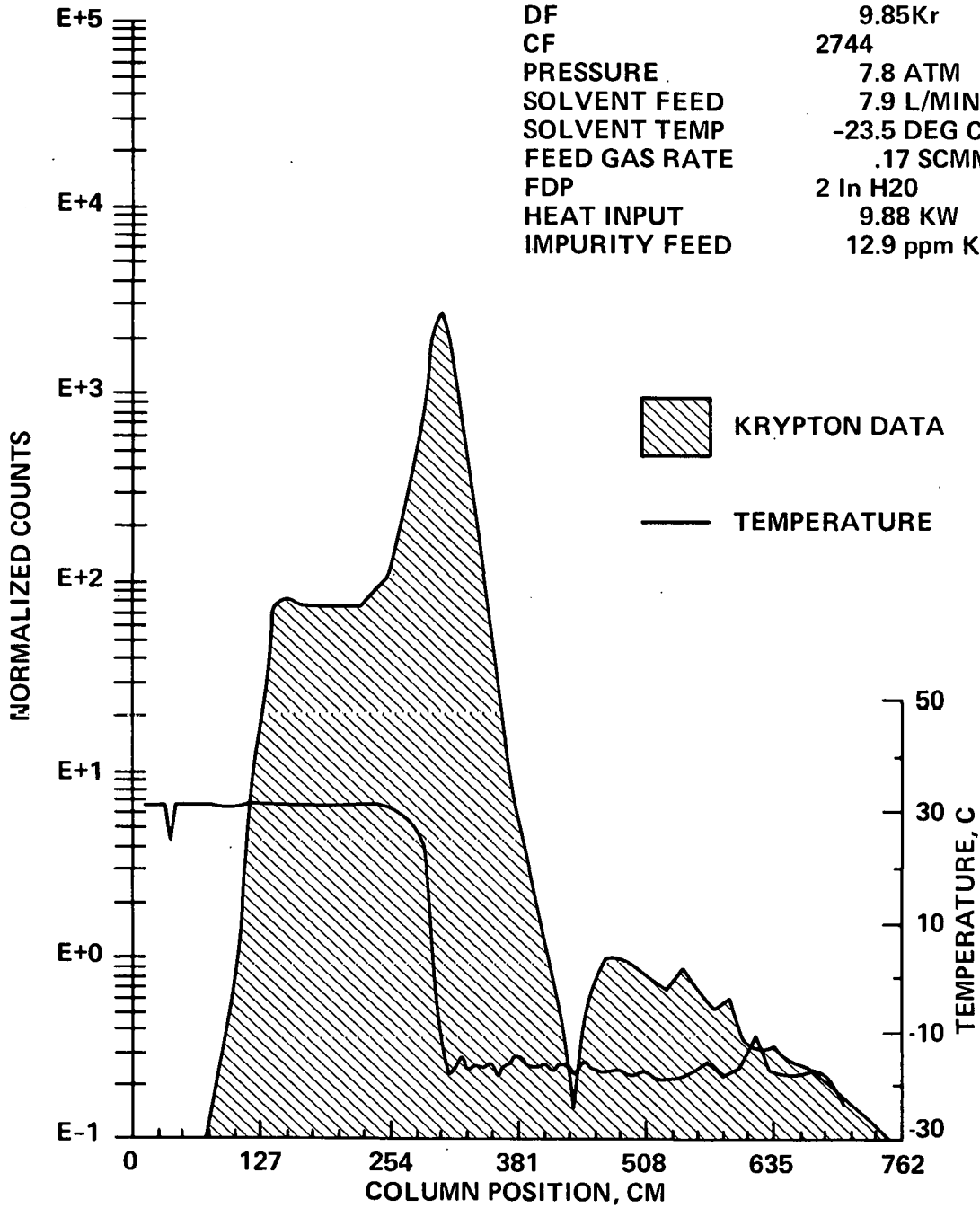


Figure 7

TYPICAL Kr CONCENTRATION PROFILE AT
HIGH TEMPERATURE AND LOW PRESSURE

RUN: 028105

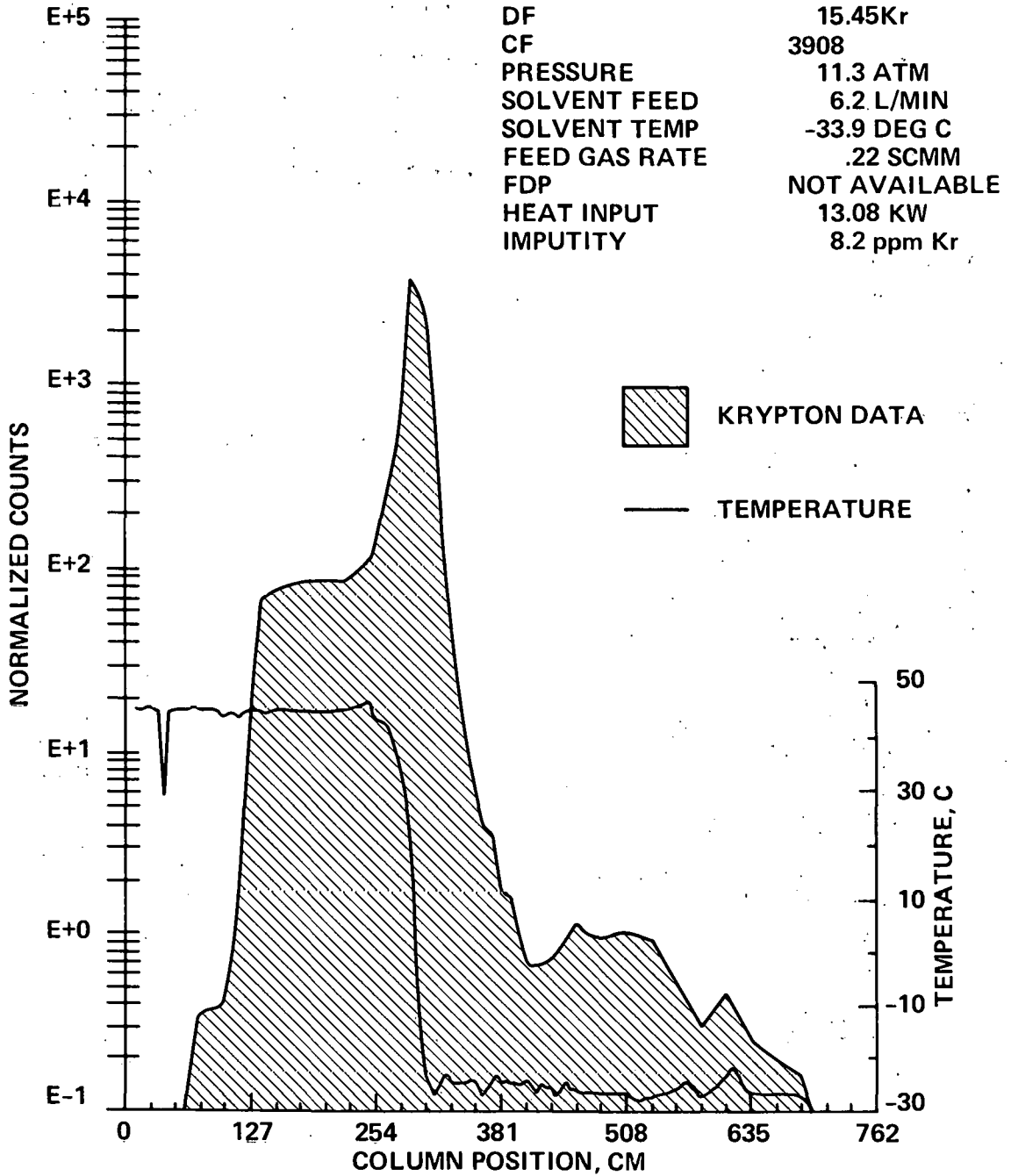


Figure 8
TYPICAL Kr CONCENTRATION PROFILE AT
LOW TEMPERATURE AND HIGH PRESSURE

RUN: 028104

DF	500.00 Kr
CF	9389
PRESSURE	11.3 ATM
SOLVENT FEED	6.2 L/MIN
SOLVENT TEMP	-32.8 DEG C
FEED GAS RATE	.08 SCMM
FDP	NOT AVAILABLE
HEAT INPUT	13.37 KW
IMPURITY FEED	11.2 ppm Kr

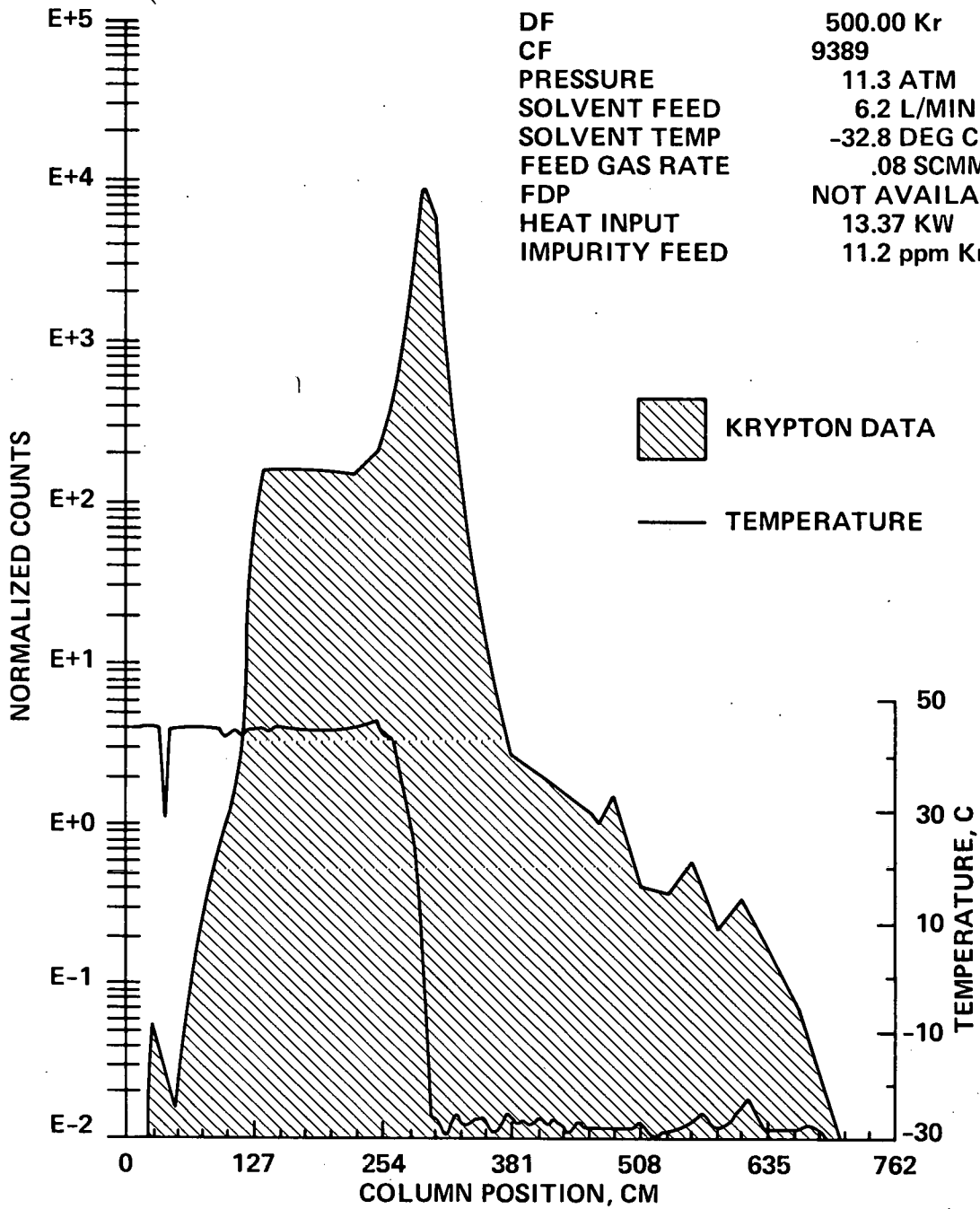


Figure 9
TYPICAL Kr CONCENTRATION PROFILE AT
A LOW GAS FLOW RATE

RUN: 078002

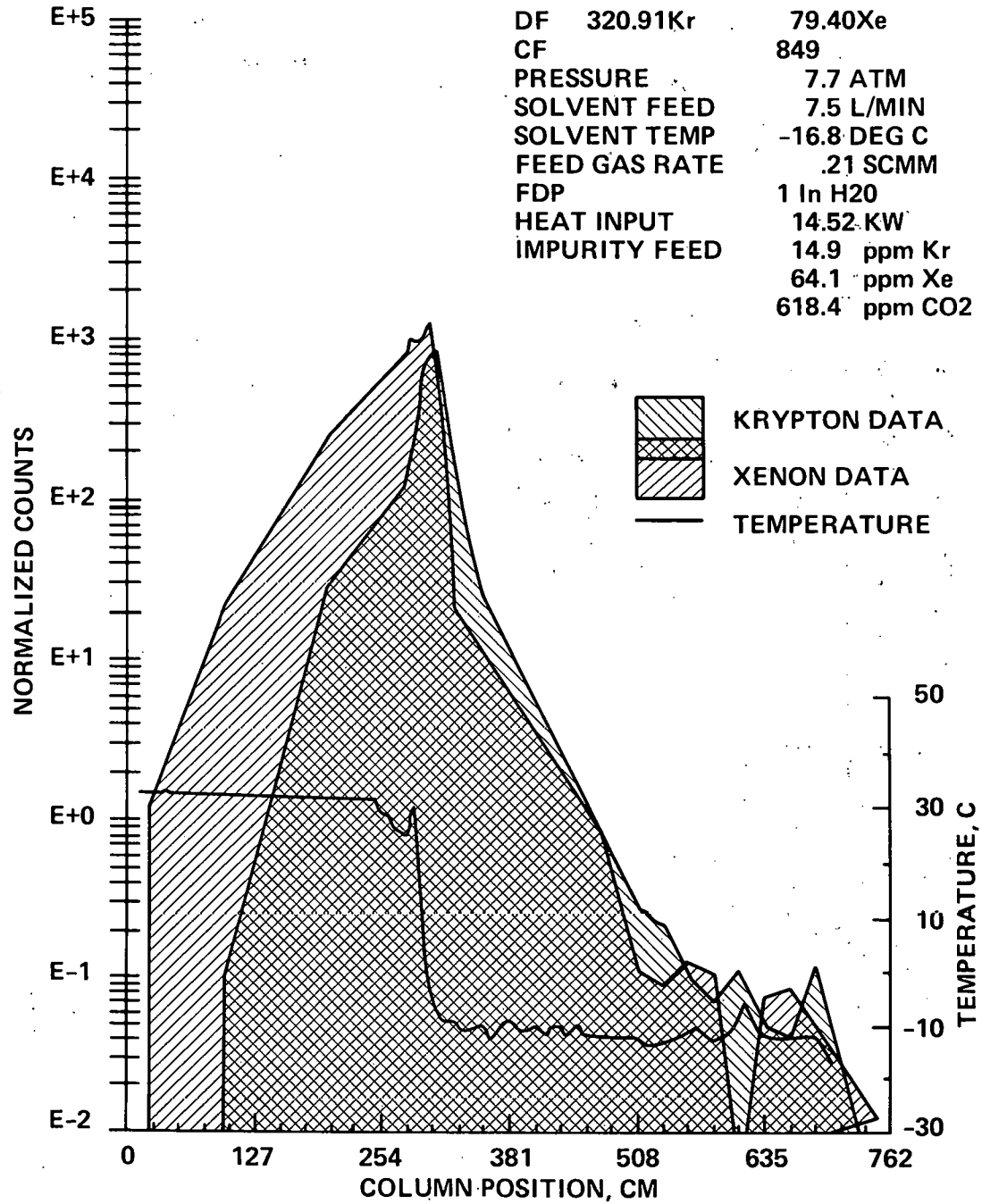


Figure 10
Kr CONCENTRATION PROFILE WITH Xe AND CO₂ IMPURITIES

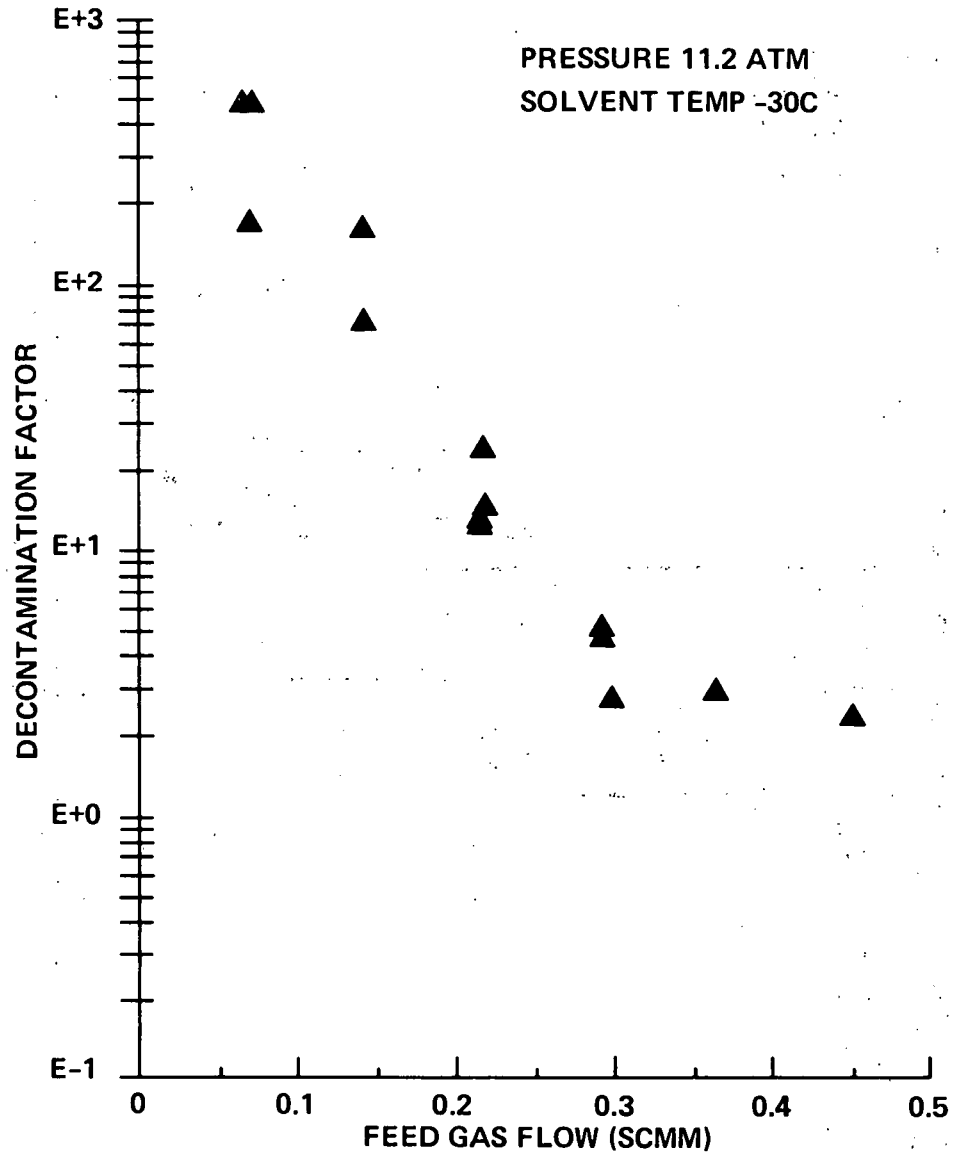
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Figure 12
EFFECT OF GAS FLOW ON DF

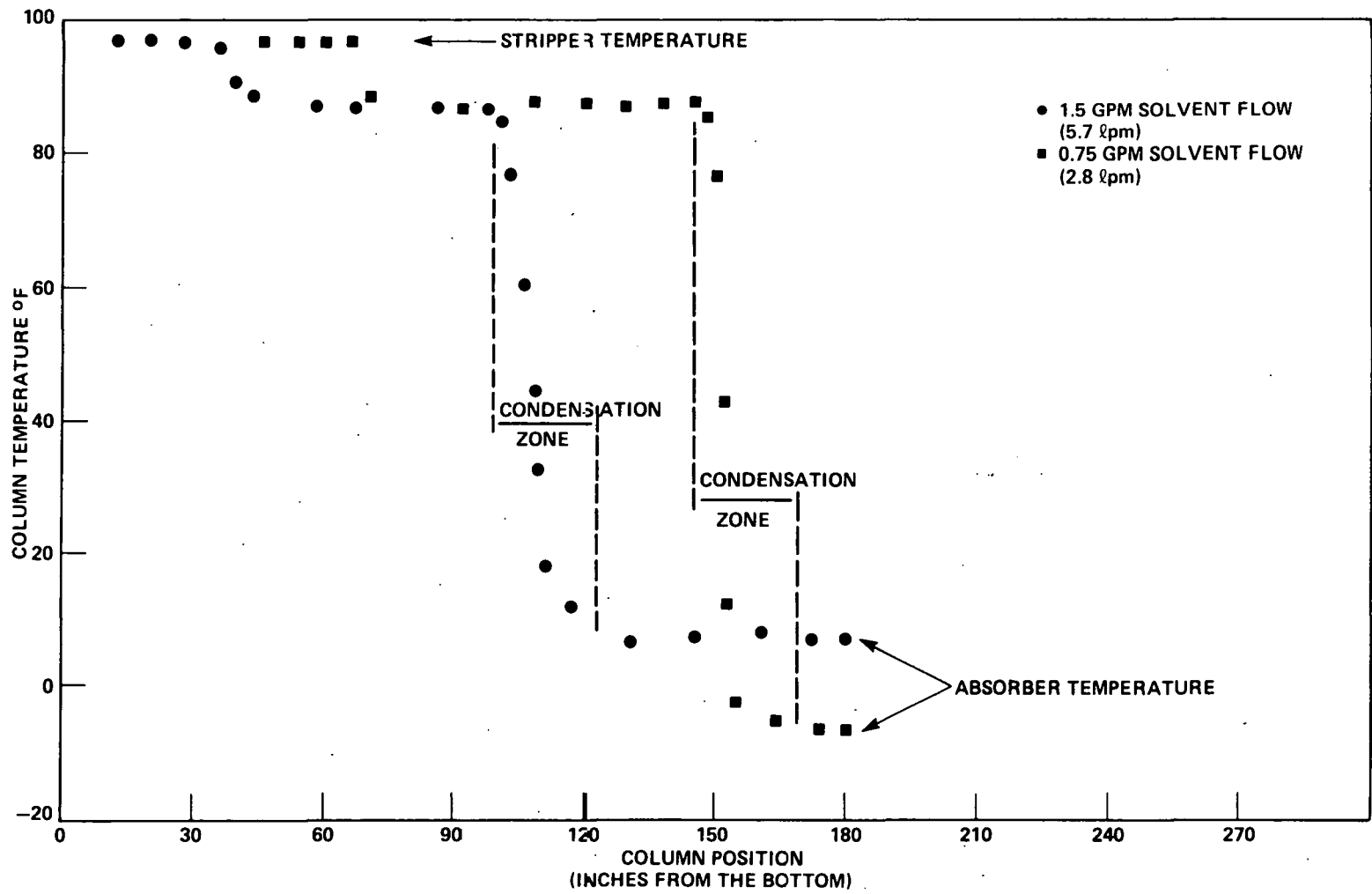


Figure 13
CONDENSATION POSITION CONTROL VIA SOLVENT FLOW RATE

location within a fairly narrow region of less than 10 cm, which does not affect product removal capabilities. Regarding the performance roadmap, one would intuitively expect that operation of the system to provide high CFs would similarly restrict the DFs obtainable. Lowered overall removal performance can result when Kr is allowed to build up excessively within the column, thus creating a large internal Kr recycle and hence greater overall Kr flow to the absorber section. As shown in Figures 7 through 10, however, the combination of high CFs and DFs are easily achievable at expected column operating ranges.

PRODUCT PURIFICATION EQUIPMENT

Although relatively high concentrations (> 10%) of Kr have been obtained from the combination column product stream directly, final Kr disposal requirements may dictate further purification. It is not clear at this point what final product purity will be necessitated however, because the method of final disposition has not yet been decided. The goal of the product purification system in the interim is to further concentrate the Kr product taken from the fluorocarbon absorption process to a level near 90%. This concentration level will satisfy any of the disposal processes currently being considered. Once the decision is made, the product purification train will be tailored to meet the needs of the specified process. If high pressure cylinders are to be used, it might be best from a licensing aspect to keep the product Kr purity in the level of 1 to 10% to effectively limit the curies and associated heat generation per cylinder. Ion implantation methods, on the other hand, would favor the highly concentrated Kr product. In any manner, the additional purification system is preferred where ultimate disposal methods are expensive or would require prohibitively large storage areas.

Depending on the actual operating conditions, the product from the combination column fluorocarbon process will contain 1 to 10% Kr with a balance of R-12 vapor, CO₂, Xe, N₂, O₂, and Ar. Once the R-12 is removed, the Xe and CO₂ will be the main constituents in the combination column product. Generally, the ratio of Xe and CO₂ to Kr in the feed gas is maintained in the product, thus limiting the purity of the Kr obtainable from the fluorocarbon system alone. Xenon, if not removed from the product, increases storage requirements by more than a factor of 5.⁸

With these considerations in mind, considerable effort has been directed towards improving and revising the product purification system. In 1976, trapping studies were initiated to evaluate solid adsorbents for removing R-12 vapor from the Kr product.⁹ Experiments proved the 13X molecular sieve to be an excellent trapping material for the process solvent. Later a cold trapping capability was developed by Eby and others which identified selective sublimation as a technique for purification of the fluorocarbon product.¹⁰

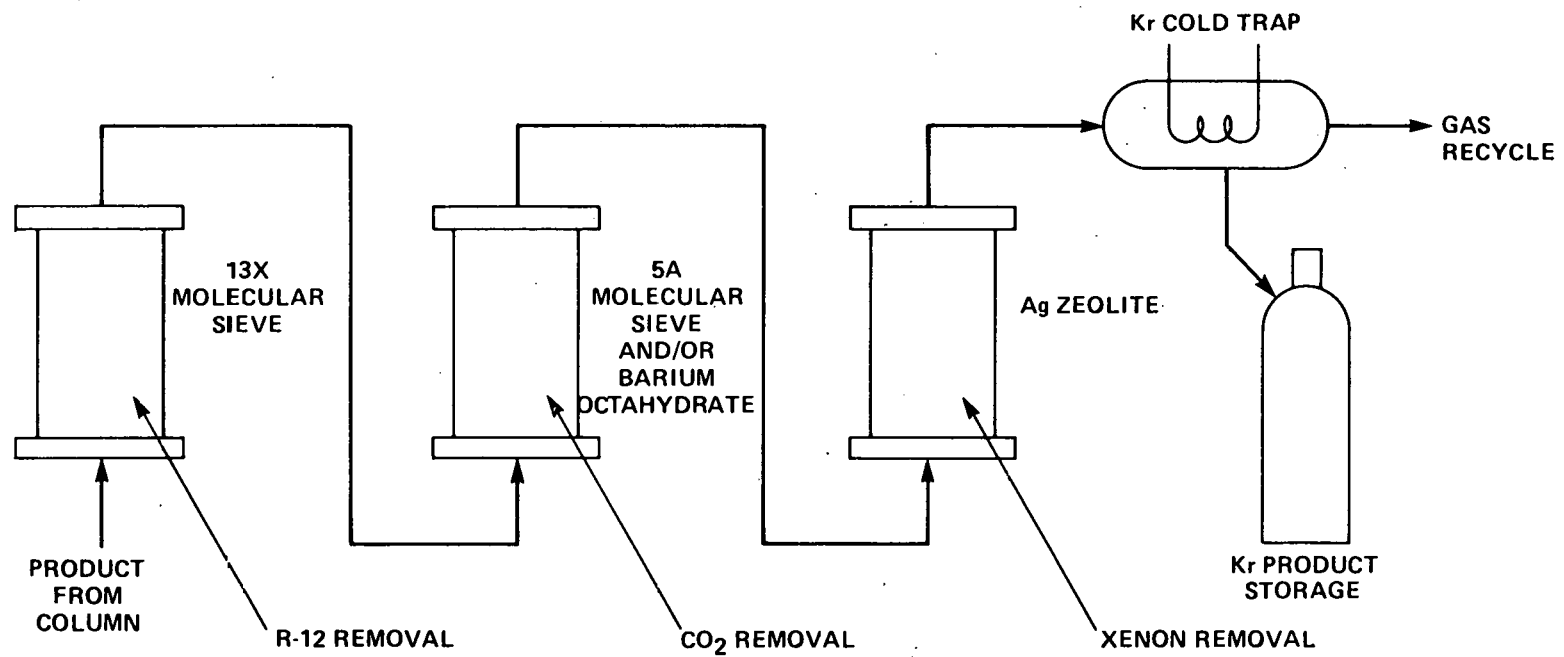
Based on this initial effort, the ground work was established for an integrated product purification train. Following a 13X sieve to first remove R-12 vapor, two batch operated cold traps were proposed - the first to separate the Xe and CO₂ and the second to remove the Kr from the remaining gases. By controlling the operating temperature of the traps via backpressure on the liquid N₂ coolant, the traps could be operated at different temperatures allowing selective desublimation (freeze-out) of the product gases. This system appeared to provide satisfactory separation performance, but, due to its very nature (cryogenic temperatures), cost and operability became a concern.

A review of solid sorbent capabilities identified several possible methods which could perform the separations desired. Forsberg and others have demonstrated Kr separations from CO₂ and O₂ using a 5A molecular sieve.¹¹ In addition, Pence and Kirstein recommend a silver zeolite to separate Xe from the Kr.¹² Certainly the most proven of all Kr purification methods is cryogenic charcoal absorption which is capable of providing research grade purity. It has been used in the Isotope Sales Department at ORNL for more than 20 years to purify Kr recovered at the ICP facility in Idaho Falls.

Recently, the ORGDP experimental program was expanded to include testing of silver zeolite for Xe removal as well as 13X and 5A molecular sieves for R-12 and CO₂, respectively. Ultimate Kr removal is provided by a simple cold trap. Figure 14 is a schematic of the system. Testing of this system was performed based on a typical fluorocarbon system product. The average flow rate during these tests was selected at 2000 sccm which corresponds roughly to a fluorocarbon system feed gas of 70 scfm. It is important to emphasize this difference between the relative flow rates of the fluorocarbon system and its product purification subsystem. Since the bulk gas separation takes place in the fluorocarbon process, the product from that system is reduced to less than 2% of the total feed gas flow. As a result, the purification equipment sizes are quite small. No scaleup from existing technologies is required. In fact, using solid sorbent technology at these low flows appears to present cost and operational advantages over other systems.

In verification tests, analyses showed R-12, CO₂, and Xe removals from the product were greater than 90% when their respective sorbents of 13X, 5A, and silver zeolite were used. Furthermore, loadings on the beds averaged 13.7% for R-12 on 13X, 17% for CO₂ on 5A, and 8.8% for Xe on silver zeolite. While certainly not conducted under optimum conditions, these tests did verify previous work which identified separational capabilities of the various adsorbents and provided the feasibility for Kr purification to any level desirable for the fluorocarbon process. Studies are being performed to optimize the product purification train on the basis of performance, cost, and required control standards.

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Figure 14
SCHEMATIC OF PRODUCT PURIFICATION SYSTEM

CONCLUSIONS

In general, the performance data of the combination column, combined with previous 3-column testing, provides more than sufficient information to allow confident design of an effective, safe, efficient, and reliable Kr removal system.

With regard to the product purification studies, the feasibility of several methods to separate major components from the fluorocarbon product stream has been demonstrated. Verification tests at ORGDP and preliminary work done by others have shown that 13X and 5A sieves can be used effectively to separate R-12 and CO₂, respectively. In addition, should Xe removal be required for Kr product purity, several methods have been tested and have demonstrated operational feasibility. Tests are currently being conducted to optimize the final purification steps.

In summary, by combining fluorocarbon absorption with selective desublimation and solid adsorption, the technology exists to provide efficient removal and concentration of Kr, Xe, and CO₂ from radioactive off-gas streams which will meet and/or exceed current proposed standards.

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