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UNION CARBIDE

OAK RIDGE GASEOUS DIFFUSION PLANT
OAK RIDGE, TENNESSEE

prepared for the U.S. ATOMIC ENERGY COMMISSION
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INTRODUCTION

This report relates specifically to the application of the selective absorption process for krypton-xenon removal to off-gas decontamination in a liquid metal fast breeder reactor fuels reprocessing system†. The fluorocarbon absorption system has been demonstrated to have an often remarkable tolerance for process impurities, such as iodine and nitrogen dioxide, which collect in the recirculating solvent§. With the addition of a solvent purification step, the process can actually become a recovery system for the impurities in question. The principles involved are neither complex nor peculiar to the one application and should be generally useful over the wide range of possible applications of the fluorocarbon absorption process. In fact, the system designed in this report will be used in testing a number of applications beyond the ones specifically considered here.

DESIGN BASIS

The assumed analysis of the gas stream fed to the fluorocarbon absorption system is shown in table I and represents that expected as the off-gas from the iodine removal system in the LMFBR-FRP. Because the disposition of iodine is of major importance, a second column of figures is given so that the case of iodine pretreatment failure can also be examined. Of the components shown, oxygen and nitrogen pass through the system in the

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* This document is based on work performed at the Oak Ridge Gaseous Diffusion Plant operated by Union Carbide Corporation, Contract W-7405 eng 26 with the United States Atomic Energy Commission.

† Yarbro, O. O., et al, *Effluent Control in Fuel Reprocessing Plants*, Union Carbide Corporation, Nuclear Division, Oak Ridge National Laboratory, To Be Issued (ORNL-TM-3899).

§ Merriman, J. R., et al, *Removal of ^{85}Kr from Reprocessing Plant Off-Gas by Selective Absorption*, Union Carbide Corporation, Nuclear Division, Oak Ridge Gaseous Diffusion Plant, September 15, 1972 (K-L-6201).

TABLE I

FLUOROCARBON ABSORPTION SYSTEM
FEED STREAM BASIS

	Iodine Pretreatment	No Iodine Pretreatment
Oxygen and Nitrogen, %	97.42	97.39
Nitrogen Dioxide, %	1.96	1.96
Iodine, ppm	0.03	300
Methyl Iodide, ppm	0.0003	3
Krypton, %	0.12	0.12
Xenon, %	0.50	0.50
Total Gas Flow, scfm*	12	12
Solvent Recycle, gpm*	1	1

* These are the design flows for the ORGDP fluorocarbon absorption process pilot plant demonstration facility, in which this solvent purification system will be installed.

Note: Percent and ppm are on a volume basis.

purified off-gas; krypton and xenon are collected as a product; and nitrogen dioxide, iodine, and methyl iodide are collected in the solvent, which is assumed to be refrigerant-12 (dichlorodifluoromethane) for the purpose of this design. Of the compounds relegated to the solvent, nitrogen dioxide has the lowest boiling point and thereby is the design key. A distillation process which removes nitrogen dioxide will do at least as well with higher boiling components, which include the small quantities of higher fluorocarbons formed by radiolytic decomposition of the refrigerant-12. Decontamination factors for all high boiling impurities should be very high, based upon scoping tests made with the nitrogen dioxide key*.

ABSORPTION PROCESS FEED METHODS

It is apparent that if the high boiling impurities reach the solvent in the fluorocarbon process, they can be removed in a straightforward manner using distillation. A schematic of the basic process with the solvent purification system is shown in figure 1.

The matter of getting the impurities into the solvent is an important consideration. High boiling components condense easily, and in the basic process, they must pass through both a gas cooler and a compressor with an interstage cooler. If a component is present in the gas stream at a partial pressure greater than its vapor pressure at the temperature of a cooling surface, it will condense. Table II shows the minimum temperatures allowable for the components and concentrations of the process feed, as determined from vapor pressure data. During normal operation, the 50°F requirement for nitrogen dioxide is the most strict, indicating that most of the nitrogen dioxide would condense (or desublime) in the gas cooler if the stream were to be cooled to minus 25°F before feeding it to the column. Although a special desublimer gas cooler could be designed

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* Stephenson, M. J., et al, "Experimental Demonstration of the Selective Absorption Process for Krypton-Xenon Removal", *Proceedings of the Twelfth AEC Air Cleaning Conference*, 1972 (CONF-720823, Volume 1).

TABLE II

MINIMUM SURFACE TEMPERATURE ALLOWABLE
AT 25 ATMOSPHERES PRESSURE

Component	Minimum Temperature, °F
NO_2 at 1.96%	50
I_2 at 0.03 ppm	-25
I_2 at 300 ppm	150
CH_3I at 0.3 ppm	Very Low

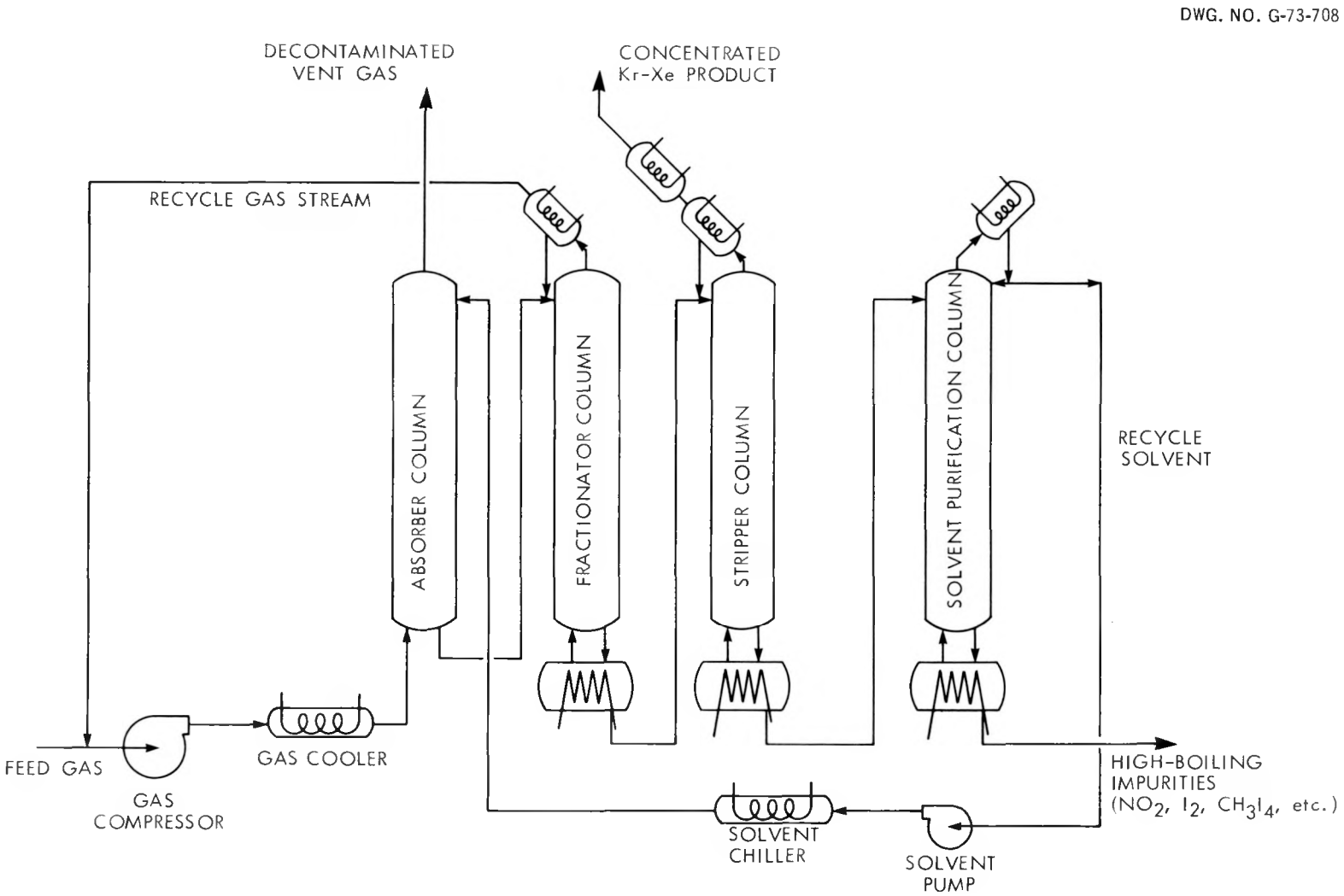

FIGURE 1

SCHEMATIC DIAGRAM OF THE
FLUOROCARBON ABSORPTION PROCESS WITH SOLVENT PURIFICATION

for this application, the alternative approach of feeding hot gas directly to the absorber column shows much more promise as an operational procedure. This will result in a liquid temperature gradient of about 15°F near the base of the absorber but should have no serious effect on its operation. Flanges and fittings leading to the contacting area must be heated, of course, to prevent deposition of solid nitrogen dioxide, and operating conditions will have to be altered to compensate for the 15°F liquid temperature rise. The compressor interstage cooler must also be checked to ensure that the coolant temperature cannot cause nitrogen dioxide to freeze out. Since the pressure in the cooler is lower than the final 25 atmospheres, however, a temperature lower than 50°F can be tolerated, the exact temperature depending upon the working interstage pressure level.

In the event of an iodine pretreatment failure, iodine becomes the key factor and the conditions become much more restrictive. Such failures are expected to be rare, if they occur at all, and the restrictions imposed by this case should not be used to dictate the design for normal operation. It is quite feasible to deal with high iodine levels by altering process conditions when a failure situation occurs. The interstage coolant temperature can be raised (or interstage cooling eliminated), and the temperatures of flanges and fittings leading to the absorber can be raised to satisfy the 150°F criterion.

In either of the cases, solubility of nitrogen dioxide, iodine, or methyl iodide in refrigerant-12 is not a limitation as long as the solvent purification system is designed to remove the bulk of these impurities from the stream that passes through it. In each case, the amount of impurity in the feed stream is well below the amount which could be dissolved in the recirculating solvent stream.

SOLVENT PURIFICATION SYSTEM DESIGN

The key components in the solvent purification system are refrigerant-12, which recirculates at 1 gpm or 0.10 lb-mol/min, and nitrogen dioxide, which is fed as 1.96% of the 12-scfm* inlet gas stream, or $6.1 \cdot 10^{-4}$ lb-mols/min. It can be considered that these quantities mix exactly to form the feed for the solvent purification system; but the recirculating solvent, it must be noted, will also contain any nitrogen dioxide left in it after cycling through the solvent purification treatment, and this must be added to the incoming material.

Since the system operates on a recirculating stream, it is more precisely a removal system rather than a purification system. As long as the bulk of the high boiling impurities is removed, there is no particular merit in producing an ultrapure solvent stream to be returned to the absorber column. With nitrogen dioxide held below the 1% level in the solvent recycled to the absorber, it can be expected that the purified vent stream from the absorber will contain no more than about 1 ppm of nitrogen dioxide†. For this design, a removal efficiency of 90% has been selected, and the composition of the feed to the removal system is thus:

0.67 mol percent NO_2
99.33 mol percent refrigerant-12

Figure 2 shows the vapor-liquid composition diagram estimated for refrigerant-12 and nitrogen dioxide at atmospheric pressure, assuming that Raoult's law holds. For high nitrogen dioxide concentrations, Raoult's law gives a K-value of 5.8, and at high refrigerant-12 concentrations, the corresponding value is 17. Molecular model techniques estimate the latter at 37, so that Raoult's law appears to be conservative, at least in the high refrigerant-12 region.

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* Standard conditions taken as 70°F and 1 atmosphere.
† CONF-720823, Volume 1, loc. cit.

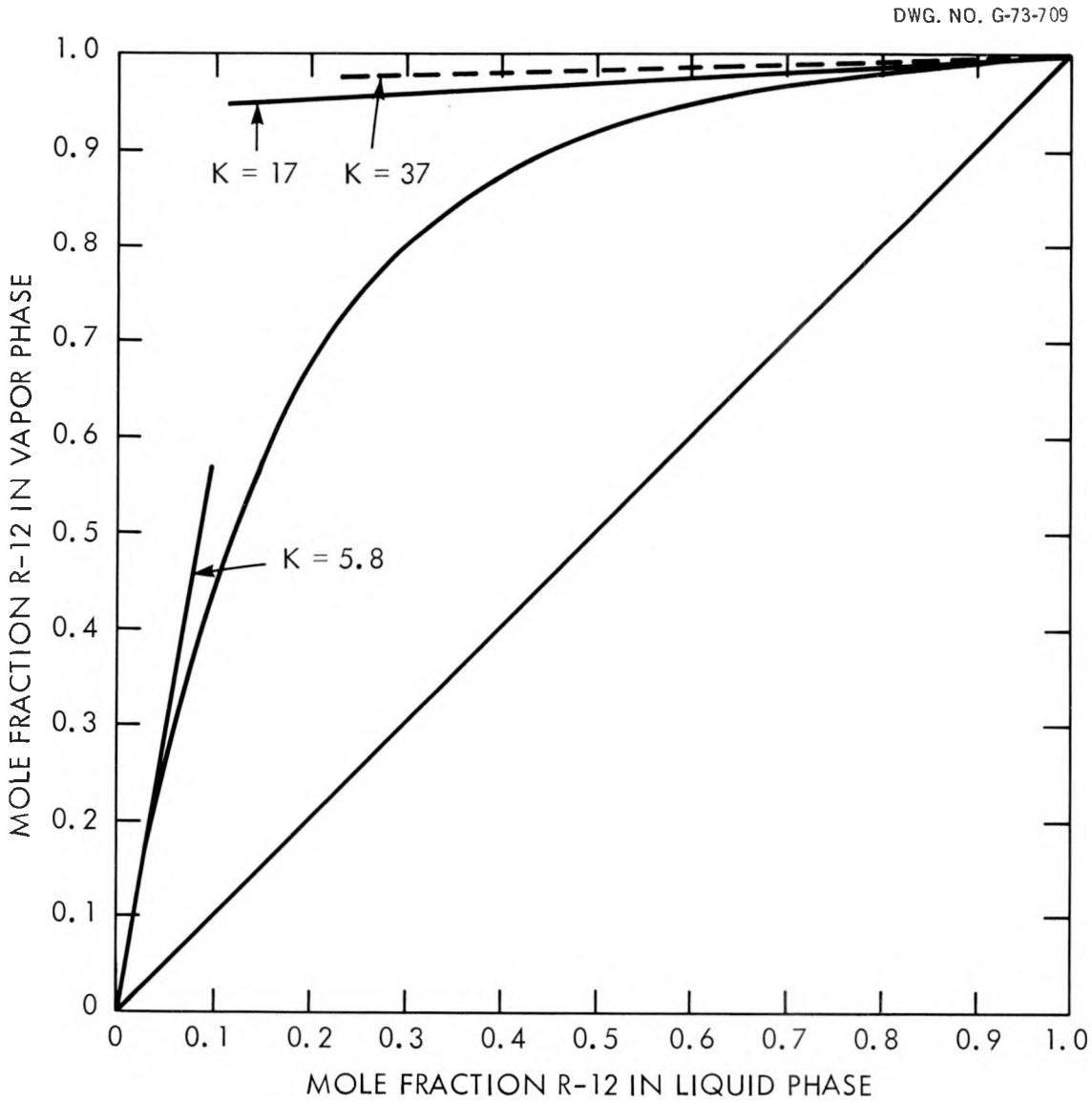

FIGURE 2

VAPOR-LIQUID COMPOSITION DIAGRAM FOR
REFRIGERANT-12—NITROGEN DIOXIDE
(RAOULT'S LAW)

MINIMUM REFLUX

The minimum reflux ratio may be calculated from*

$$R_{D_{min}} = \frac{O_R}{D} = \frac{X_D - Y_C}{Y_C - X_C}$$

where

$R_{D_{min}}$ = minimum reflux ratio

O_R = liquid molal overflow rate at minimum reflux

D = tops product rate at minimum reflux

X_C, Y_C = coordinates of the point at which the equilibrium line and upper operating line intersect on a McCabe-Thiele diagram. X and Y are mol fractions of refrigerant-12.

In the area of high refrigerant-12 concentrations, the equilibrium line is straight with a slope of about K = 17, as previously indicated:

$$Y_C = 1 - (1 - X_C)/K$$

A nitrogen dioxide recovery factor may be defined as:

$$RF = \frac{(1 - X_C)}{(1 - X_D)}$$

assuming that the feed is a saturated liquid. The value of RF has already been chosen as 10 (90% recovery) for this design. Continuing,

$$X_D = 1 - (1 - X_C)/RF$$

$$R_{D_{min}} = \frac{1 - (1 - X_C)/RF - 1 + (1 - X_C)/K}{1 - (1 - X_C)/K - X_C} = \frac{(1 - X_C)}{(1 - X_C)} \frac{(\frac{1}{K} - \frac{1}{RF})}{(1 - \frac{1}{K})}$$

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* Robinson, C. S., and Gilliland, E. R., *Elements of Fractional Distillation*, 4th Edition, McGraw-Hill Publishing Company, New York, p 129 (1950).

or

$$R_{D_{min}} = \frac{RF - K}{RF\ (K - 1)}$$

From this, it is seen that since RF is less than K, $R_{D_{min}}$ is negative, and there is no minimum reflux rate required. The column can be operated by feeding at the top stage, the vapor from this stage being the purified solvent product. It should be pointed out that although reflux need not be used, there is no harm in using it to control the recovery if desired.

NUMBER OF STAGES

The number of equilibrium stages required for the column separation will be determined both on a theoretical plate and a transfer unit basis for comparison purposes. Returning to the McCabe-Thiele construction*, the lower operating line passes through the points $(X_F,\ 1 - (1 - X_F)/RF)$, and $(X_W,\ X_W)$ so that:

$$Y = \frac{(1 - X_W) - (1 - X_F)/RF}{(X_F - X_W)} \cdot X - \frac{X_W(1 - X_F)(1 - 1/RF)}{(X_F - X_W)}$$

where

X_F = mol fraction of refrigerant-12 in the saturated liquid feed

X_W = mol fraction of refrigerant-12 in the bottoms product

The precise value of X_W has little effect on the construction for refrigerant-12 mol fractions above 0.02, and between X = 0.9933 and X = 0.02, five theoretical plates can be stepped off between the equilibrium line and the operating line using the McCabe-Thiele method.

Below X = 0.02, it can be assumed that the equilibrium line is straight again and that

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* McCabe, W. L., and Smith, J. C., *Unit Operations of Chemical Engineering*, McGraw-Hill Publishing Company, New York, p 689 (1956).

$$Y = 5.8X$$

The number of theoretical plates below X = 0.02 can be computed from*:

$$N_W = \frac{\ell n\left[\frac{\left(\frac{VK}{0} - 1\right)\left(\frac{X_M}{X_W} - 1\right)}{(V/0)(K - 1)} + 1\right]}{\ell n[VK/0]}$$

where

V = molal vapor flow rate

0 = molal liquid flow rate

V/0 = slope of operating line

X_M = 0.02

X_W = bottoms mol fraction of refrigerant-12

N_W = number of theoretical plates required

For this application, it is desirable to keep the refrigerant-12 below one part per million in the nitrogen dioxide bottoms product. The above equation gives N_W = 5.65 under these conditions, and thus a total of 10.65 theoretical plates is required for the entire column.

Similarly, the number of transfer units required for the entire separation was evaluated using a computer program to integrate:

$$N_{OG} = \int_{Y_W}^{Y_T} \frac{dY}{(Y^* - Y)}$$

where

N_{OG} = number of transfer units (gas-phase controlled)

Y_W = mol fraction of refrigerant-12 in vapor at bottom of column

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* Robinson, C. S., and Gilliland, E. R., *Elements of Fractional Distillation*, 4th Edition, McGraw-Hill Publishing Company, New York p 183 (1950).

Y_T = mol fraction of refrigerant-12 in vapor at top of column

Y^* = mol fraction of vapor in equilibrium with liquid composition on the operating line

For $Y_T = 0.9933$ and $Y_W = 10^{-6}$, the number of transfer units, N_{OG}, is calculated to be 8.18 as compared with the 10.65 theoretical plates required.

STAGE HEIGHT

To maintain consistency with the rest of the absorption process design, the column will be packed with Goodloe packing*. The manufacturer's literature gives stage heights (HETP) for distillation ranging as high as 4 inches, but the absorption work done at ORGDP has, in general, yielded much larger stage heights, typically on the order of one foot. Since the manufacturer's data are on distillation, they are likely to be more nearly correct for this application, but it would be expedient to be quite conservative with the large uncertainties involved. For the approximately eleven theoretical plates required, a column height of 6 to 8 feet should be sufficient.

COLUMN DIAMETER

The maximum gas velocity in the packed column is given by†:

$$U_{max} = \frac{0.0942}{\mu^{0.33}} \left[\frac{\ell - V}{V}\right]^{0.57}$$

where

U_{max} = maximum vapor velocity, ft/sec

μ = liquid viscosity, cp

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* Product of Packed Column Company, Division of Metex Corporation, Edison, New Jersey, U.S.A. This is a knitted wire-mesh type of packing rolled into cartridges.

† *How to Design a Goodloe Column*, Manufacturer's Literature, Packed Column Company.

ℓ = liquid density, lb/cu ft

V = vapor density, lb/cu ft

At the top of the column, the flows will be essentially pure refrigerant-12 at about minus 21°F and thus:

$$U_{max} = \frac{0.0942}{(0.38)^{0.33}} \left[\frac{93 - 0.41}{0.41}\right]^{0.57} = 2.9 \text{ ft/sec}$$

and at the bottom of the column, the flows will be essentially pure nitrogen dioxide at about 70°F.

$$U_{max} = \frac{0.0942}{(0.42)^{0.33}} \left[\frac{90 - 0.21}{0.21}\right]^{0.57} = 4.0 \text{ ft/sec}$$

The vapor loading, assuming equimolal overflow, can be determined from the refrigerant-12 recycle rate. The nominal solvent rate of 1 gpm has been mentioned previously, but here it is important to use the maximum design rate of 1.5 gpm which is 1.0 scf/sec. Combining this with the calculated maximum vapor velocities and temperatures, a minimum column area requirement of 0.29 sq ft is established as set by conditions at the top of the column. Thus, an 8-inch column would be adequate, giving 83% of flooding (55% at the nominal 1-gpm solvent rate) and a 10-inch column would be quite operable at 49% of flooding (33% at the nominal 1-gpm solvent rate).

HEAT LOAD

With no reflux, the column upflow will equal the feed rate of 1.5 gpm. The latent heat of vaporization of nitrogen dioxide at its boiling point is about 8,300 Btu/lb-mol and that of refrigerant-12 is about 8,600 Btu/lb-mol (indicating that the assumption of equimolal overflow should be quite accurate). The larger of these two figures corresponds to 80,000 Btu/hr which means that about 25 kw of heat will be required in the reboiler and 6.7 tons of refrigeration will be required at the condenser.

CAPACITY AND EQUILIBRIUM TIME

Since most of the column must be filled with a liquid comprised primarily of nitrogen dioxide while the feed material is mostly refrigerant-12, it will require time before enough nitrogen dioxide has been fed to the column to put it in its working equilibrium state. The 12 scfm of gases fed to the absorption process contain 1.96% nitrogen dioxide, or about 1.7 lb/hr. The capacity of a 10-inch column of 6-foot height, however, would be about 45 pounds if it is assumed that the liquid loading is about 15% of the column volume. This calculation does not account for reboiler holdup, which is likely to be even larger. Thus, it would take on the order of days for enough nitrogen dioxide to be fed to the column for it to approach its steady state operation point. In a production operation, this is largely immaterial; but for an experimental setup, it would be expedient to charge the column with nitrogen dioxide in advance, especially if the experimental run is to be of short duration.

CONCLUSIONS

The solvent purification system can consist of a distillation column with reboiler and condenser auxiliaries. Experimental results have shown that recycling of a solvent stream with subpercentage levels of nitrogen dioxide results in a very low loss to the purified air vent stream, and thus the column can be top fed without reflux under conditions which allow the removal of 90% of the nitrogen dioxide from the recirculating solvent stream. Although use of a column rectifying section with refluxing is not necessary, it would not be detrimental to the process if it were used to lower the level of nitrogen dioxide in the solvent sent to the absorber column.

Equilibrium time for the column is on the order of days, and it is recommended that nitrogen dioxide be charged to the column to initialize the system for short duration runs. Final design conditions for the column are shown in table III.

TABLE III

FINAL DESIGN FOR THE SOLVENT PURIFICATION COLUMN
FOR THE ORGDP FLUOROCARBON ABSORPTION PROCESS PILOT PLANT

Column Packing:	Goodloe
Column Diameter:	8-inch minimum, 10-inch acceptable
Column Height:	Stripping Section - 6-foot minimum
	Rectifying Section - Not Required
Reflux Rate:	Not required
Reboiler Heat Load:	25 kw at 1.5 gpm, 17 kw at 1.0 gpm
Condenser Heat Load:	6.7 tons at 1.5 gpm, 4.5 tons at 1.0 gpm
Pressure:	Nominal 1 atmosphere
Reboiler Temperature:	70°F
Condenser Temperature:	Minus 21°F
Feed Condition:	Saturated liquid at 1 atm and minus 21°F

APPENDIX

PHYSICAL PROPERTIES

Nitrogen Dioxide

Melting Point = 11.8°F

Boiling Point = 70.1°F

Molecular Weight = 46.01

Viscosity at 70°F = 0.42 cp

Liquid Density at 70°F = 90 lb/cu ft

Vapor Density at 70°F = 0.21 lb/cu ft

Latent Heat of Vaporization at 70°F = 8,300 Btu/lb-mol

Liquid Vapor Pressure, atm = $\exp\left(15.7730 - \frac{9466}{t°F + 530.1}\right)$

Refrigerant-12

Boiling Point = minus 21.6°F

Molecular Weight = 120.9

Viscosity at minus 21°F = 0.38 cp

Specific Heat of Liquid = 28 Btu/lb-mol-°F

Liquid Density at minus 21°F = 93 lb/cu ft

Vapor Density at minus 21°F = 0.41 lb/cu ft

Latent Heat of Vaporization at minus 21°F = 8,600 Btu/lb-mol

Liquid Vapor Pressure, atm = $\exp\left(9.5789 - \frac{3908.6}{t°F + 429.6}\right)$

Iodine

Molecular Weight = 253.8

Solid Vapor Pressure, atm = $\exp\left(14.4191 - \frac{10393}{t°F + 390.7}\right)$

Methyl Iodide

Melting Point = minus 84°F

Molecular Weight = 141.9

Liquid Vapor Pressure, atm = $\exp\left(9.6006 - \frac{4900}{t°F + 401.9}\right)$