

MARTIN MARIETTA ENERGY SYSTEMS LIBRARIES



3 4456 0360141 2

110318

CENTRAL RESEARCH LIBRARY

cy. 3

ORNL-4522

UC-10 - Chemical Separations Processes
for Plutonium and Uranium

COMPLETION REPORT - EVALUATION OF THE USE
OF PERMSELECTIVE MEMBRANES IN THE
NUCLEAR INDUSTRY FOR REMOVING
RADIOACTIVE XENON AND KRYPTON FROM
VARIOUS OFF-GAS STREAMS

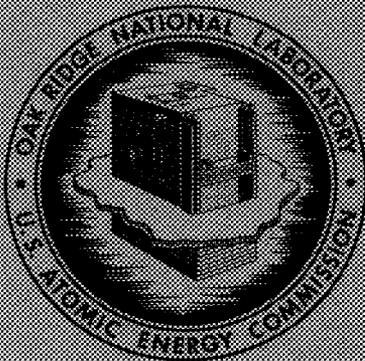
R. H. Rainey
W. L. Carter
S. Blumkin

OAK RIDGE NATIONAL LABORATORY
CENTRAL RESEARCH LIBRARY
DOCUMENT COLLECTION

LIBRARY LOAN COPY

DO NOT TRANSFER TO ANOTHER PERSON

If you wish someone else to see this
document, send in name with document
and the library will arrange a loan.



OAK RIDGE NATIONAL LABORATORY

operated by

UNION CARBIDE CORPORATION

for the

U. S. ATOMIC ENERGY COMMISSION

Printed in the United States of America. Available from
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road, Springfield, Virginia 22151
Price: Printed Copy \$3.00; Microfiche \$0.95

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.



3 4456 0360141 2

ORNL-4522

Contract No. W-7405-eng-26

CHEMICAL TECHNOLOGY DIVISION
Chemical Development Section B

COMPLETION REPORT – EVALUATION OF THE USE OF PERMSELECTIVE
MEMBRANES IN THE NUCLEAR INDUSTRY FOR REMOVING RADIOACTIVE
XENON AND KRYPTON FROM VARIOUS OFF-GAS STREAMS

R. H. Rainey, W. L. Carter, and S. Blumkin*

APRIL 1971

*Oak Ridge Gaseous Diffusion Plant.

OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee
operated by
UNION CARBIDE CORPORATION
for the
U. S. ATOMIC ENERGY COMMISSION

CONTENTS

	<u>Page</u>
Abstract	1
1. Introduction	1
2. Theory of Gas Separation by Permselective Membranes	7
3. Materials and Procedure	12
4. Laboratory Measurements of Permeability	16
4.1 Permeabilities of Pure Gases	16
4.2 Effective Permeabilities of Component Gases in a Mixture	19
4.2.1 Experiments with Membrane Supported on Both Sides	20
4.2.2 Experiments with Membrane Supported Only on the Low-Pressure Side	20
4.3 Parameters Affecting Stage Separation Factors	26
4.4 Effect of Temperature on Permeability Factors	31
4.5 Effect of Irradiation on Gas Permeation and Separation	35
5. Design of Engineering-Scale Membrane Unit	37
6. Calculations of the Costs of Membrane Plants for Nuclear Industry Applications	37
6.1 Cost of Removing Xenon and Krypton from an LMFBR Cover Gas	39
6.2 Cost of Removing Noble Gases from a Reactor Containment Building	45
6.3 Cost of a Permselective Membrane Plant for Processing Off-Gas from a Fuel Reprocessing Plant	48
7. References	51

COMPLETION REPORT – EVALUATION OF THE USE OF PERMSELECTIVE
MEMBRANES IN THE NUCLEAR INDUSTRY FOR REMOVING RADIOACTIVE
XENON AND KRYPTON FROM VARIOUS OFF-GAS STREAMS

R. H. Rainey, W. L. Carter, and S. Blumkin*

ABSTRACT

The effective permeabilities and separation factors of krypton, xenon, and several other gases were measured using sheets of thin silicone rubber membrane having areas as large as 2 ft²; the pressure drop across the membrane was varied from 25 to 150 psi. Processes using such membranes were evaluated for removing the radioactive noble gases from (1) the off-gas from a plant for recovering used nuclear fuels, (2) a reactor containment building following a nuclear accident, and (3) the cover gas of a liquid metal fast breeder reactor (LMFBR). Radiation exposure of the membrane would not be a limiting factor in the first two applications, but the LMFBR cover gas would have to be stored to allow the short-lived gaseous nuclides to decay before it could be processed in a membrane plant. The costs of removing the noble gases from these systems were estimated.

1. INTRODUCTION

We have conducted a study of some of the parameters involved in removing the radioactive noble gases from various off-gas streams by processes based on the use of thin silicone rubber membranes. This study consisted of (1) laboratory measurements of effective gas permeabilities and separation factors, (2) radiation stability measurements of assembled permeability units, and (3) engineering calculations for process optimization and estimated equipment costs. Methods were developed for supporting the membrane when the pressure drop across the membrane was high.

At the present time, only a few, comparatively small, nuclear power reactors are in operation. When long-cooled spent fuel elements from these reactors are dissolved for fuel recovery, the controlled venting of the off-gas up tall stacks constitutes

*Oak Ridge Gaseous Diffusion Plant.

only a minor problem. In some cases, the noble gases are adsorbed on charcoal beds and temporarily retained until the short-lived isotopes have decayed; the long-lived ^{85}Kr is subsequently discharged to the atmosphere. Studies have been made of the effects of meteorological conditions and siting on the concentration of noble gases that may be released from a reactor fuel processing plant.^{1,2} The presently operating, privately operated, fuel processing plant is authorized to release 3.3×10^6 Ci of radioactive noble gases per year under its certification. However, with the expected rapid increase in the production of power by nuclear energy, the amount of ^{85}Kr that is formed (Table 1) will soon exceed this amount.

Table 1. Predicted Generation of Radioactive Krypton to the Year 2000

	Calendar Year		
	1970	1980	2000
Installed nuclear capacity, 10^3 Mw (electrical)	6	150	940
Annual generation rate of ^{85}Kr , 10^6 Ci	0.6	120	1500

The "tolerance level" for whole-body exposure of persons in nonrestricted areas from all sources is 170 mrem per year. At present, individual exposures to released noble gases are maintained at less than the tolerable level by the wide dispersal of gases. Although these exposures are at present very low, it may be desirable to develop reasonably priced processes which can essentially eliminate this exposure. The AEC regulations are being modified to require that exposures be minimized as much as is practical. Provisions for the isolation and subsequent permanent storage of gaseous fission products may, therefore, need to be made just as they are presently made for nongaseous fission products.

At the end of a typical fuel cycle, a 1000-Mw (electrical) reactor would contain about 300 million Ci of radioactive krypton and about 400 million Ci of radioactive xenon. However, each gas contains several short-lived components so that, after a 24-hr decay period, only about one million Ci of krypton, chiefly ^{85}Kr ($t_{1/2} = 10.6$ years), and 100 million Ci of xenon, chiefly ^{133}Xe ($t_{1/2} = 5$ days), would

remain. After about a month, the principal remaining activity would be due to the ^{85}Kr .

The hazards associated with the release of noble gas fission products are recognized by the USAEC; consequently, several methods for decreasing the amounts that are released to the atmosphere have been investigated^{1,3} (Table 2). These methods include: (1) adsorption on charcoal or molecular sieves at ambient temperature, (2) adsorption on charcoal or molecular sieves at low temperature, (3) separation by cryogenic distillation, (4) extraction by hydrocarbons or chlorofluoromethanes, (5) precipitation as clathrates or as fluorides, and (6) separation by permselective membranes. Another alternative that has been considered is the injection of the gases into porous underground media.⁴

The adsorption of noble gases on charcoal or molecular sieves at ambient temperature is the process that has been studied most extensively.⁵ This is a simple method for delaying the release of the noble gases to the atmosphere in order to allow the short-lived isotopes (primarily xenon) to decay. However, it has certain disadvantages such as: (1) large beds of charcoal are required; (2) the charcoal burns readily, and molecular sieves are subject to explosion as the result of local heating of adsorbed gases by radioactive particles; and (3) the ^{85}Kr is released to the atmosphere instead of being concentrated for permanent storage. The fire and explosion hazards may be eliminated or minimized by suitable design or operational procedures.

Adsorption on charcoal or molecular sieves at low temperatures permits the use of a smaller adsorption bed; however, the fire hazard remains. Additional disadvantages are the costs incurred in cooling the bed and the explosion hazards associated with the adsorption of the ozone that is produced by the irradiation of oxygen. Materials that would freeze or condense must be completely removed from the gas prior to its injection into the bed in order to prevent plugging of the equipment. One gas, N_2O , which has been particularly troublesome in this system, may

Table 2. Processes for Removing ^{85}Kr from Off-Gas at a Fuel Reprocessing Plant^a

Process	% Kr Removed ^b	Development Status	Comments
Adsorption on ambient-temperature charcoal or molecular sieves	99	Pilot plant with reactors	Simple operation; charcoal can ignite. ^{85}Kr released to atmosphere.
Adsorption on low-temperature charcoal or silica gel	99	Pilot plant with reprocessing plant	Small bed volumes; charcoal can ignite.
Cryogenic distillation	99	Pilot-plant test with reprocessing plant	Small equipment; ozone is explosion hazard.
Extraction by hydrocarbons or chlorofluoromethanes	99	Nonradioactive pilot-plant tests	Small equipment; hydrocarbons can ignite.
Separation by permselective membranes	99	Laboratory studies	Small equipment; no fire hazard.
Precipitation as clathrates or as fluorides	Unknown	Laboratory studies	^{85}Kr collected as solid; degraded by radiation; slow precipitation, 150 atm.

^aVarying gas pretreatments required.

^bMinimum design values.

be removed with hydrogen and a palladium catalyst.⁶

In the cryogenic separation, the noble gases and part of the air, or other carrier gas, are first liquefied. Then the noble gases are separated from the bulk gases and are concentrated by fractional distillation. This process has been demonstrated at a gas flow rate equal to that of the off-gas from a 3-ton-per-day fuel processing plant, but at about one-fifth the radioactivity level.⁶ As in all of the low-temperature operations, water and other gases that would form solids must be essentially removed prior to the treatment of the noble gases. Solids in the system cause physical difficulties, and the presence of liquid ozone, which is formed from the radiolysis of oxygen, creates an explosion hazard.

The study of the separation of noble gases from air by absorption in (or extraction by) chlorofluoromethanes (Freon) has progressed to the nonradioactive pilot-plant stage.^{7,8} This is a very versatile system; since the operating temperature ($\sim 20^\circ\text{F}$) is higher than that used in low-temperature charcoal bed adsorption or the cryogenic distillation methods (-290°F), the concentration of condensable gases such as water need not be extremely low. Operation at, or near, ambient temperature appears to be possible and is, therefore, being investigated. Although degradation of the solvent due to radiation is not expected to be limiting, it has not been investigated. Possible carry-over of Freon or degradation products into reactor systems such as a sodium-cooled or a molten-salt reactor could cause difficulty.

Precipitation of the noble gases as clathrates⁹ or as fluoride compounds¹⁰ has been proposed. Although this type of process would yield a solid product, which would simplify permanent storage, it is not efficient because of the very low concentrations of noble gases in the off-gas streams and hence does not appear to be economically attractive. On the other hand, such a process may be quite useful for solidifying concentrated gases for storage.

The separation of noble gases by the use of permselective membranes has been proposed as an alternative to the processes described above, and was the subject of our investigation.¹¹ This process has a long history. More than 100 years ago,

Mitchell^{12,13} observed that various gases penetrated natural membranes at different rates. However, industrial separations of gases by this technique did not become practicable until methods were developed for preparing very thin, hole-free sheets of modern polymers. The range of the application of this technique to industrial separations may be deduced from the papers presented at the Symposium on Membrane Processes for Industry¹⁴ held in Birmingham, Alabama, in 1966.

Although any polymer may be used for the separation of gases,¹⁵⁻¹⁷ silicone rubbers have the highest permeabilities measured thus far; also, they yield high gas separation factors.¹⁸⁻²¹ Robb proposed the use of permselective membranes for separating xenon and krypton from air,²¹ while Holmes²² proposed the use of such membranes for removing noble gases in the atomic energy industry. Of course, the use of these membranes in an industrial process would be dependent on the availability of large, very thin sheets that are free of holes and adequately supported to withstand large pressure drops. Prior to our entry into this study, the General Electric Research and Development Center at Schenectady, New York, had developed methods for preparing 1- by 2-ft sheets, about 1.7 mils thick, which were supported so they could withstand a pressure of at least 150 psi.

The objective of our study was to investigate the effects of various parameters, such as pressure drop across the membrane, percentage of gas passing through the membrane, direction of flow of gas in a separations unit, and radiation and chemical degradation of the membrane, on the permeabilities and the separation factors of the gases. A mathematical model for the diffusion of gases in a separations unit based on gas flow and diffusion equations was developed for comparison with experimental observations. Several partially optimized cascade designs were developed for various process applications, and costs of selected processes were estimated.

Many people contributed to this study. A. Dounoucas, H. D. Briggs, and D. G. Willis of the General Electric Research and Development Center at Schenectady, New York, developed and built the membrane test units that we used; in addition, they very generously shared their techniques and experience. E. Von Halle of the

Oak Ridge Gaseous Diffusion Plant developed some of the mathematical relationships used in this study; he also helped design and optimize membrane cascades and evaluate data. D. E. Fain, also of the Oak Ridge Gaseous Diffusion Plant, measured the effect of temperature on permeability reported in Sect. 4.4. Students from the School of Chemical Engineering Practice, Massachusetts Institute of Technology, under the direction of S. M. Fleming and H. D. Cochran, helped to collect and evaluate experimental data. R. C. Lovelace, R. H. Shigley, C. L. Roggenkamp, T. E. Harmon, and A. H. Confer conducted many of the experiments. L. M. Ferris reviewed the draft of this report and made many helpful suggestions that have improved the clarity of our presentation.

2. THEORY OF GAS SEPARATION BY PERMSELECTIVE MEMBRANES

The transport of a gas through a permselective membrane requires the following steps: (1) contact of the gas with the high-pressure surface of the membrane, (2) dissolution of the gas in the membrane, (3) diffusion of the gas through the membrane, and (4) evaporation of the gas from the low-pressure surface of the membrane. This process is quite different from the transport of gases through a porous membrane (Fig. 1). With porous membranes, the separation of gases is proportional to the ratio of the square roots of their molecular weights. With a permselective membrane, the separation is proportional to the ratio of the products of the solubilities in, and the diffusivities through, the membrane.

Most gases in polymers have been found to obey Henry's law of solubility:

$$C_i = K p_i , \quad (1)$$

and Fick's Law for diffusion:

$$N_i = -AD_i \frac{dC_i}{dt^*} , \quad (2)$$

where

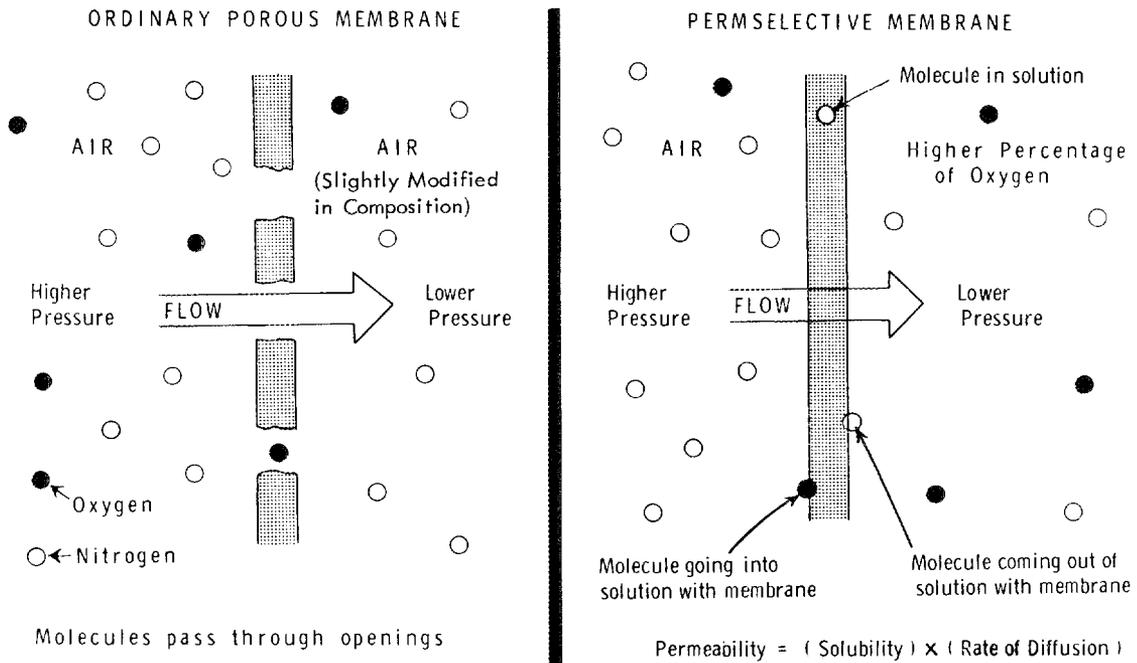


Fig. 1. Diagram Explaining Differences in the Actions of Gases Flowing Through (a) a Porous and (b) a Permselective Membrane.

C_i = concentration of gas i in the membrane,

K = Henry's law constant,

p_i = partial pressure of gas i,

N_i = flow rate of gas i through the membrane,

A = membrane area,

D_i = diffusivity of gas i in the membrane material,

t^* = distance into the membrane.

At a given temperature, if we assume that K is independent of the thickness of the membrane, substituting Eq. (1) into Eq. (2) and solving the differential equation yields

$$N_i = \frac{AK_i D_i \Delta p_i}{t} , \quad (3)$$

in which

Δp_i = the difference in the partial pressures of component i on the two sides of the membrane,

t = thickness of the membrane.

If we define the permeability factor of a particular gas, P_i , as

$$P_i = K_i D_i , \quad (4)$$

substituting Eq. (4) into Eq. (3) and rearranging yields:

$$P_i = \frac{N_i t}{A \Delta p_i} . \quad (5)$$

The units used in our study were:

N = ml (STP)/sec,

t = cm,

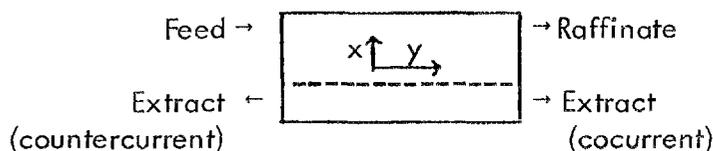
A = cm²,

Δp_i = cm Hg.

Flow through a permselective membrane is accompanied by a pressure drop across the membrane. If this pressure drop is not extremely high (e.g., not more than several hundred atmospheres), the permeability factor should be a constant for a given membrane and gas.

The permeation of gases through a permselective membrane has been shown to be related to the critical temperatures of the gases.²³ Thus it is possible to estimate the permeability factor of a gas that has not previously been measured if the permeability factor of a similar gas and the respective critical temperatures are known.

Our test equipment was arranged as follows:



The gases to be separated were fed to one side of the membrane at the upper left of the unit. Fractions of the gases passed through the membrane (extract); the remainder (raffinate) was removed from the upper right side of the unit. If both the extract and the raffinate were removed from the same end of the unit, the gas flow was designated as cocurrent. If the extract was removed from the same end of the unit as the feed entered, the flow was designated as countercurrent.

We assumed that there was no concentration gradient perpendicular to the membrane since this distance was only about 3 mm and the unit contained screens which mixed the gas. However, with gas mixtures, a concentration gradient did exist along the membrane (in the "y" direction) because of the different rates of transport of gases in the mixture through the membrane. This effect, along with the effect of the membrane backing (support), precluded the direct determination of permeability factors. At each set of experimental conditions an effective permeability could be determined, using Eq. (5), from measured values of N_i and Δp_i . In calculating Δp_i , we assumed that the changes in gas concentrations along the membrane were linear. For gas mixtures, in which one component was present at a concentration

of less than 0.5%, the partial pressure of the minor component on the high-pressure side of the membrane was taken as the average of its concentrations in the feed and in the raffinate. The concentration of this component in the extract stream was used as its partial pressure on the low-pressure side of the membrane.

We defined "cut" as the flow rate of the extract multiplied by 100, divided by the flow rate of the feed. At zero cut, there would be no flow through the membrane; therefore, no concentration gradient would exist in the "y" direction.

The stage separation factor for a two-gas mixture is defined as:

$$\alpha \equiv SF_{1,2} = \frac{E_1/E_2}{R_1/R_2} , \quad (6)$$

where

- E_1 = mole fraction of noble gas in gas that permeated the membrane,
- E_2 = mole fraction of carrier gas in gas that permeated the membrane,
- R_1 = mole fraction of noble gas in gas that did not permeate the membrane,
- R_2 = mole fraction of carrier gas in gas that did not permeate the membrane.

In our system, the mole fraction of the carrier gas was greater than 0.99 in both the extract and the raffinate (E_2 and R_2); therefore, the stage separation factor of the noble gas was approximately equal to the ratio of the concentration of noble gas in the extract to its concentration in the raffinate. With radioactive tracers, the stage separation factor was assumed to be the ratio of the radioactivities of the two exiting gas streams.

The stage separation factor of two gases at zero cut and zero pressure on the low-pressure side of the membrane, (i.e., α_o), may also be shown to be the ratio of the permeability factors of the two gases:

$$\alpha_o \equiv SF_{(zero)} = \frac{P_1}{P_2} . \quad (7)$$

Our system operated at approximately atmospheric pressure on the low-pressure side. The effect of this back pressure on the separation factor has been shown by Blumkin²⁴ to be:

$$\alpha^* = \frac{\alpha_o}{1 + R(\alpha_o - 1)} \quad (8)$$

where R is the low pressure divided by the high pressure and α^* is the separation factor at zero cut.

S. H. Jury²⁵ developed a model for the fractionation of gas mixtures using perm-selective membranes; this model takes into account (1) longitudinal diffusion in the bulk gas streams and plumbing connections, (2) normal diffusion through the membrane and its backings, (3) mixing effects due to turbulence-promoting screens inserted in the bulk gas streams, and (4) the two possible modes of operation, cocurrent and countercurrent flow. Analysis of the steady-state model leads to a set of ordinary differential equations that must, subject to appropriate limiting conditions, be solved simultaneously to evaluate experimental results or to design new equipment. A few tests of the model were made using experimental data. These tests showed that additional experimental data will be required before a detailed analysis of the engineering parameters can be made.

Recently, Stern and Walawender²⁶ published an "Analysis of Membrane Separation Parameters," which will be very valuable to future investigators in this field.

3. MATERIALS AND PROCEDURE

The membrane used in our study was prepared by the General Electric Company. It had the following composition:

- 100 parts (by weight) methylphenyl polymer containing 5.3 mole %** phenyl groups and 0.1 mole %** vinyl groups; specific gravity = 0.98.
- 44 parts (by weight) fumed silica.

** Calculated as the percentage of total substituent groups on the silica.

Volume fraction of filler (calculated) = 0.164.

It had been partially cured with 0.5% bis-2,4-dichlorobenzoyl peroxide and then heated at 150°C for 1 hr in an oven. It was supplied in the form of 30- by 60-cm sheets that were about 4.6×10^{-3} cm thick and free of holes. In most of our work, the membrane was bonded between two 0.01-cm-thick sheets of Dacron fibers. However, some data were obtained with membrane supported by Dacron on only one side (the low-pressure side). The membrane described above, with its backing, was supported on polyester screens, which acted as gas turbulence promoters. The test packages (i.e., the membrane, mats, and screens) were sealed around the edges with a silicone rubber bonding material (RTV-11), which served to secure the package between stainless steel plates. Gas inlets and/or outlets were fitted onto the plates.

The equipment for regulating the pressure and the flow of gas, determining and recording the radioactivities of the gas streams, and recycling the used gas to the feed vessel is shown in Figs. 2 and 3. The gases normally used in the experiments were oxygen, nitrogen, or argon, either pure or mixed with less than 0.5 vol % krypton or xenon containing ^{85}Kr or ^{133}Xe , respectively, as a radioactive tracer. Carbon dioxide was used in a few experiments.

Each gas under study was fed to the test unit at a regulated pressure. The downstream side of the membrane was maintained at atmospheric pressure. The cut (i.e., the percentage of gas passing through the membrane) was varied by changing the rate at which gas was removed from the high-pressure side of the membrane.

Both the extract and the raffinate streams were continuously routed through small duplicate vessels mounted over scintillation crystals in shielded containers. The radioactivities of the two streams were thus monitored during alternate 10-sec intervals by using a modified 400-channel Victoreen analyzer, which was adjusted to count only the energy of the principal gamma ray emitted by the tracer gas. The accumulated counts were automatically printed out for evaluation. This type of experiment was continued until the radioactivity levels of the gas streams were constant to within about 1%.

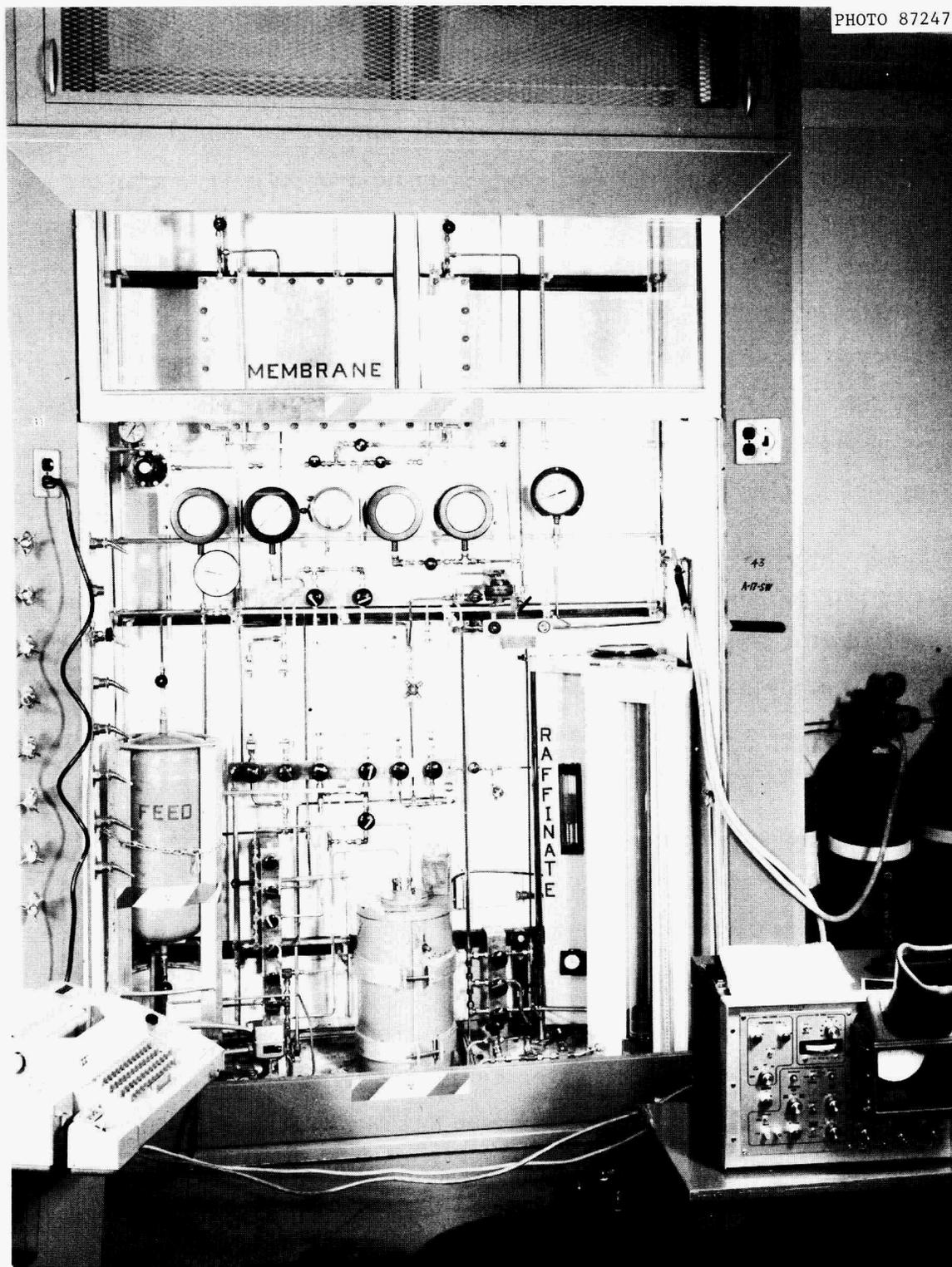


Fig. 2. Photograph of Laboratory Equipment for Determining the Effective Permeabilities and Separation Factors of Gases by Using a Permselective Membrane.

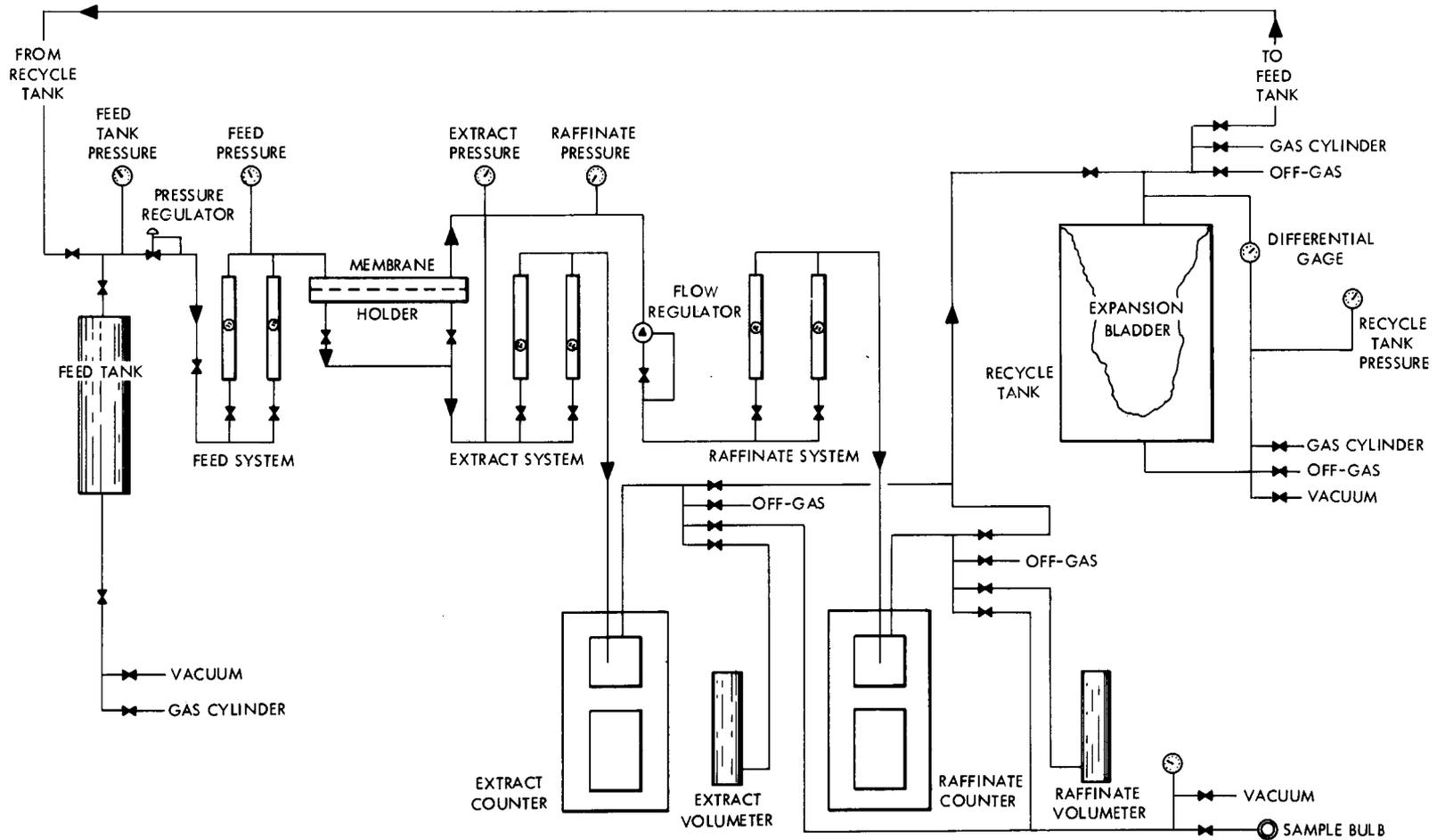


Fig. 3. Diagram of Laboratory Equipment for Determining the Effective Permeabilities and Separation Factors of Gases by Using a Permselective Membrane.

On exiting from the counting chambers, the gases were accumulated in separate Vol-U-Meters (Brooks Instrument Company, Inc.). An accurate flow rate for each was determined by measuring the time required to collect a volume of the gas in the appropriate calibrated collection cylinder. When the Vol-U-Meters were full, the gases were transferred into a recycle tank containing a flexible plastic liner. Each test gas could be repressurized by introducing nitrogen outside of the liner and could then be returned to the feed tank. In this way, the feed gas could be maintained at a constant composition for a series of experiments.

4. LABORATORY MEASUREMENTS OF PERMEABILITY

4.1 Permeabilities of Pure Gases

The effective permeabilities of nitrogen, oxygen, and argon were determined at room temperature, and at about 30% cut, using membrane that was supported between two sheets of Dacron mat. The data obtained are shown in Fig. 4; the values for nitrogen and oxygen are about a factor of 2 lower than the permeability factors obtained by Robb,²¹ who used a similar membrane; however, Robb's membrane was not bonded to a support material. Robb obtained permeability factors of 28×10^{-9} , 60×10^{-9} , 98×10^{-9} , and 203×10^{-9} for nitrogen, oxygen, krypton, and xenon, respectively. The results of the present study are in agreement with those of H. P. Briggs,²⁷ of the General Electric Company, in showing that the effect of the support material generally is to make the effective permeability lower than the permeability factor. Also, with a support material present, the effective permeability decreases regularly with increasing pressure drop across the membrane (Fig. 4).

Briggs²⁷ and his co-workers have shown that about 40% of the loss in effective permeability at a pressure drop of 150 psi may be recovered by bonding the membrane to a properly selected mat on only the low-pressure side and by proper selection of support and turbulence promoting screens. They tested numerous backing materials and supporting screens in order to select a combination of materials that would give the lowest flow resistance in the directions normal and parallel to the membrane.

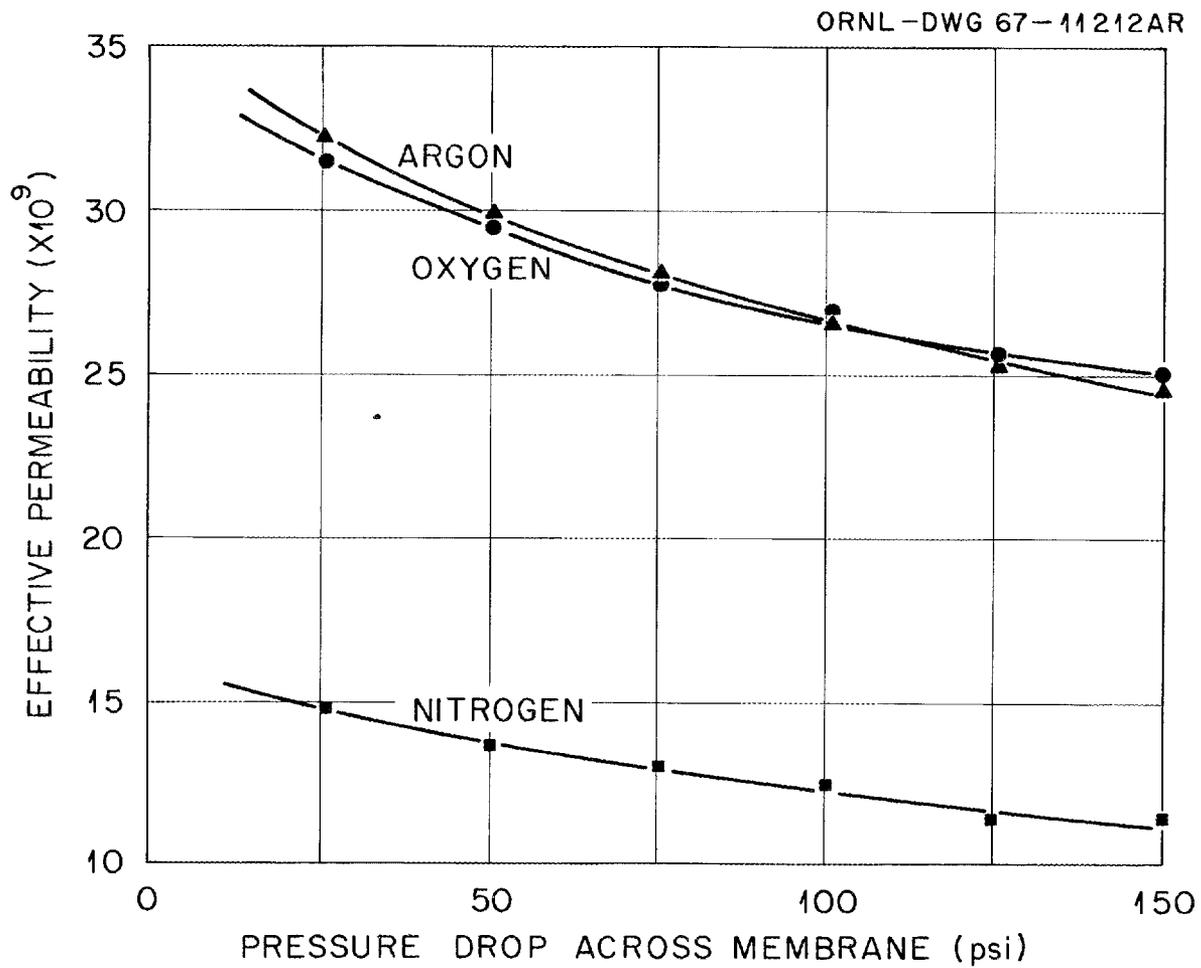


Fig. 4. Effect of Pressure Drop Across the Membrane on the Effective Permeabilities of Argon, Nitrogen, and Oxygen. Membrane supported on both sides. About 30% cut.

The tests consisted in measuring the permeation of oxygen under pressure drops ranging from 15 to 150 psi for each support combination. Using similar membrane samples, some backing materials exhibited low permeation rates, whereas other samples of the same materials, but having different thicknesses and weights, exhibited higher permeation rates. Also, some of the samples were found to have a satisfactory porosity normal to their surfaces under low pressure drops but were relatively non-porous (i.e., showed a decrease in the permeation rate) as the pressure drop across the membrane increased to 150 psi. In many of the tests, the membrane showed evidence of being depressed, or deformed, by the openings in the supporting screen. The effective permeabilities obtained when these supporting materials were used were generally lower than those obtained with the other materials, and they decreased as the pressure increased. Deformation of the support mat into the openings in the screen tends to reduce the cross-sectional volume of the screen that is available for gas flow; it also creates many points of high stress. Therefore, the fibers of the support mat must have sufficient strength to span the openings in the screen, as well as exhibit high resistance to compression. However, the fibers must not puncture the membrane.

The most favorable permeability data reported by Briggs²⁷ were obtained with a 0.018-cm-thick mat, weighing 30 g/m^2 , that was composed of polyester fibers and a polyvinyl binder. The effective permeability of oxygen with this material was 56.5×10^{-9} , as compared with the permeability factor of 60×10^{-9} obtained with an unbonded membrane. No decrease in permeability occurred as the pressure drop across the membrane was increased to 150 psi.

Briggs²⁷ and his co-workers conducted a similar study to choose the most effective screen support. They investigated screens made of polyester monofilament or stainless wire having various diameters and sizes of mesh openings. They found that two screens on the low-pressure side of the membrane provided the most satisfactory arrangement. A polyester screen (0.028-cm threads, 60 threads/cm, 0.081-cm mesh opening, 55% open area) was positioned adjacent to the support mat, and a stainless steel screen (0.019-cm wire, 61 wires/cm, 0.087-cm mesh openings, 67.2% open area)

was placed behind the plastic screen. These two screens had similar fiber spacings, but the stainless steel wire was smaller than the plastic filament, thereby resulting in a larger open area. The stainless steel screen could not be used immediately adjacent to the mat because it contained sharp wire points that would puncture the membrane. Also, it had a tendency to buckle under high stress conditions to form sharp ridges, which would also puncture the membrane.

A polyester screen (0.114-cm threads, 44.5 threads/cm, 0.114-cm mesh opening, 58% open area) was included on the high-pressure side of the membrane to induce turbulent flow. The large, smooth fibers of this screen exhibited a negligible tendency to puncture the unprotected rubber membrane.

4.2 Effective Permeabilities of Component Gases in a Mixture

The effective permeability of each gas in mixtures composed of low concentrations of krypton and xenon in air or other gases such as helium or argon was of particular interest in this work. Consequently, laboratory studies were carried out in which we measured the effective permeability of each gas in mixtures containing less than 0.5% xenon or krypton in nitrogen or oxygen. Data were obtained using a membrane supported on both sides by Dacron mats and also with a membrane supported by Dacron only on the low-pressure side. Since only the feed stream and the exit streams from the membrane unit could be analyzed, the composition of the gas on the high-pressure side of the membrane was assumed to be the average of the feed and raffinate streams, and the composition of the gas on the low-pressure side was assumed to be that of the extract stream. Since there was such a small change in the concentration of carrier gas flowing through the unit, we could not measure changes in its effective permeability due to the presence of xenon or krypton. In contrast, the calculated effective permeabilities for xenon and krypton varied with pressure drop across the membrane, the percentage of the gas permeating the membrane (cut), and the identity of the carrier gas.

4.2.1 Experiments with Membrane Supported on Both Sides

In these experiments, the low-pressure side of the membrane was at atmospheric pressure, the pressure on the high-pressure side was varied from about 25 to 150 psi, and approximately 40% of the gas was allowed to pass through the membrane. The effective permeabilities of xenon in oxygen were much greater than those obtained using nitrogen as the carrier gas (Fig. 5). Moreover, over a wide range of pressure drops, the effective permeability of xenon at about 40% cut was proportional to the effective permeability of the carrier gas (Fig. 6).

Extrapolation of plots of the effective permeability of a component of a gas mixture vs cut to zero cut (i.e., to zero flow of gas through the membrane) eliminates the effect of the carrier gas. Data obtained with krypton-oxygen and krypton-nitrogen mixtures are shown in Figs. 7 and 8. At zero cut, the effective permeabilities of krypton in oxygen were about 54×10^{-9} at 25 psi and 48×10^{-9} at 100 psi (Fig. 7); in nitrogen, the corresponding values were approximately 56×10^{-9} and 48×10^{-9} (Fig. 8). The decrease in effective permeability with increase in pressure drop across the membrane is due to the presence of the support material. As seen in Figs. 7 and 8, no significant differences in the effective permeabilities were produced by changing from cocurrent to countercurrent flow conditions.

4.2.2 Experiments with Membrane Supported Only on the Low-Pressure Side

The effective permeabilities of krypton, using nitrogen as the carrier gas (Fig. 9), were higher when the membrane was supported only on the low-pressure side than when the membrane was supported on both sides (Fig. 8); the effective permeabilities also were less sensitive to pressure drop across the membrane. Use of countercurrent, rather than cocurrent, flow resulted in significant differences in the effective permeabilities, especially when the pressure drop across the membrane was only 25 psi (Fig. 9).

One type of nuclear power reactor fuel is made by dispersing fissionable and fertile materials in graphite. A proposed process for recovering this used fuel involves burning of the graphite. Since the noble gases would be expected to be

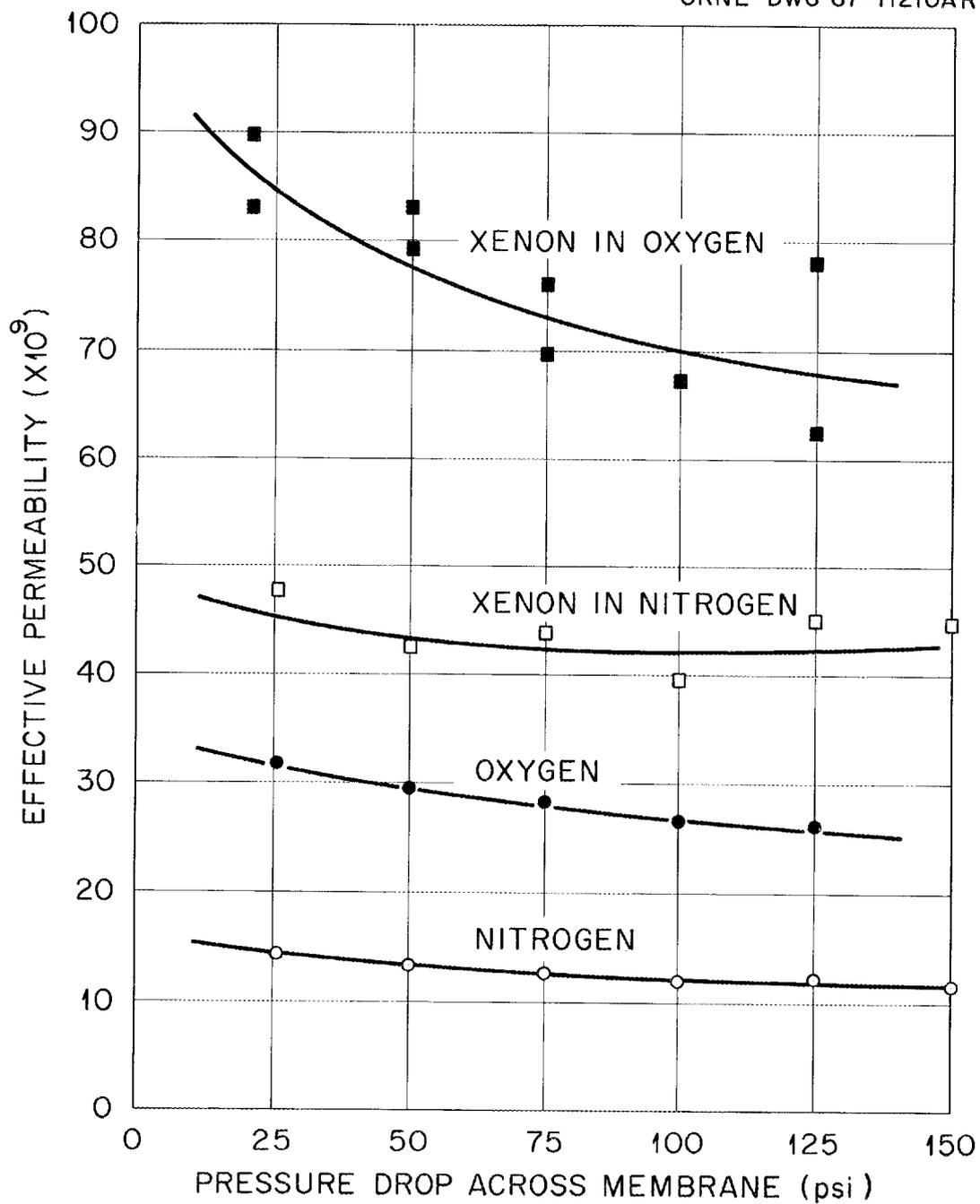


Fig. 5. Effect of the Carrier Gas on the Effective Permeability of Xenon in a Mixture Containing Less than 0.5% Xenon in Nitrogen or Oxygen. Membrane supported on both sides. About 40% cut.

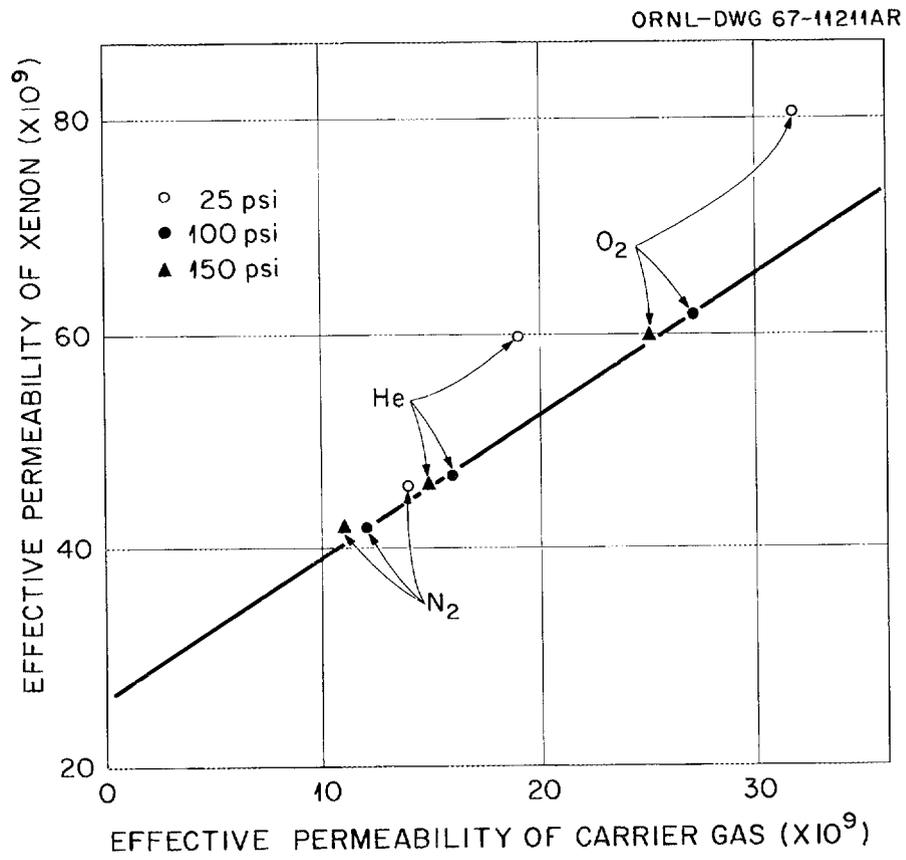


Fig. 6. Effect of the Permeability of the Carrier Gas on the Effective Permeability of Xenon in Mixtures Containing Less than 0.5% Xenon in Nitrogen, Oxygen, or Helium. Membrane supported on both sides. About 40% cut.

ORNL-DWG 68-11333 R

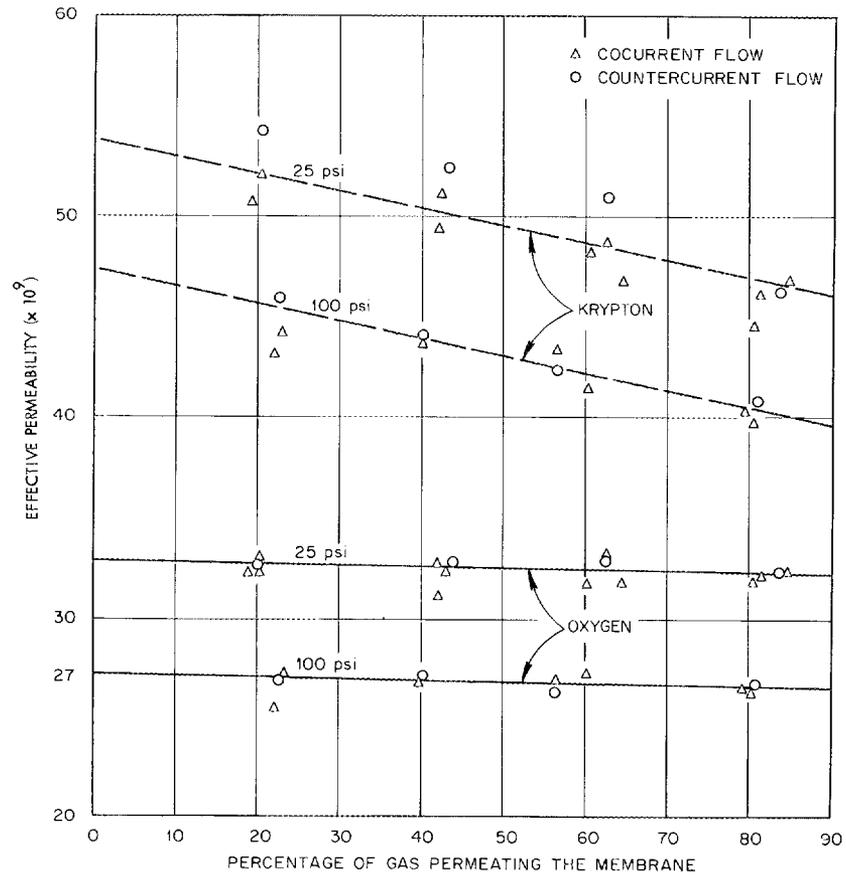


Fig. 7. Effective Permeabilities of Krypton and Oxygen as a Function of Cut (< 0.5% Krypton in Oxygen). Membrane supported on both sides.

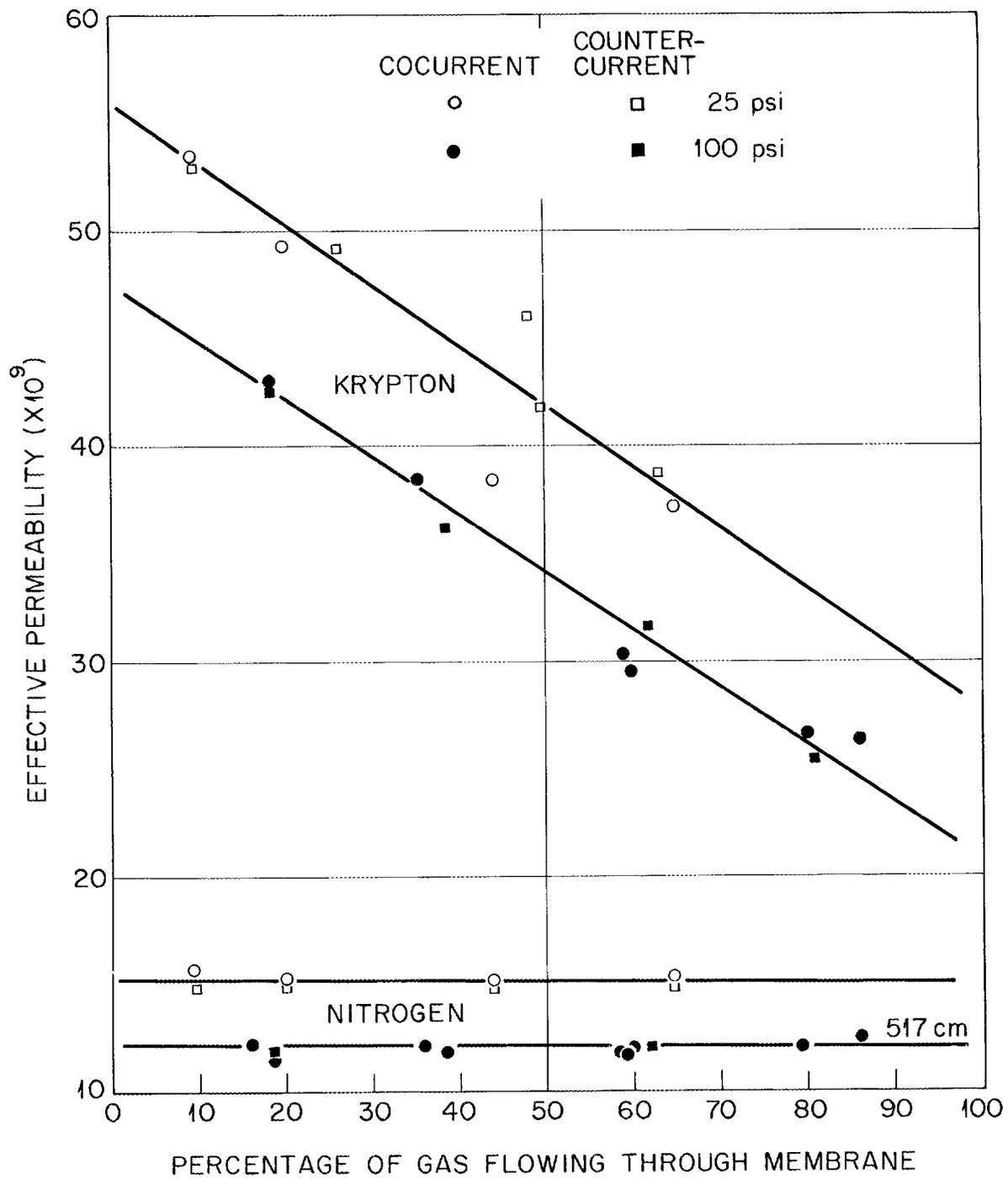


Fig. 8. Effective Permeabilities of Krypton and Nitrogen as a Function of Cut and Pressure Drop Across the Membrane. Membrane supported on both sides.

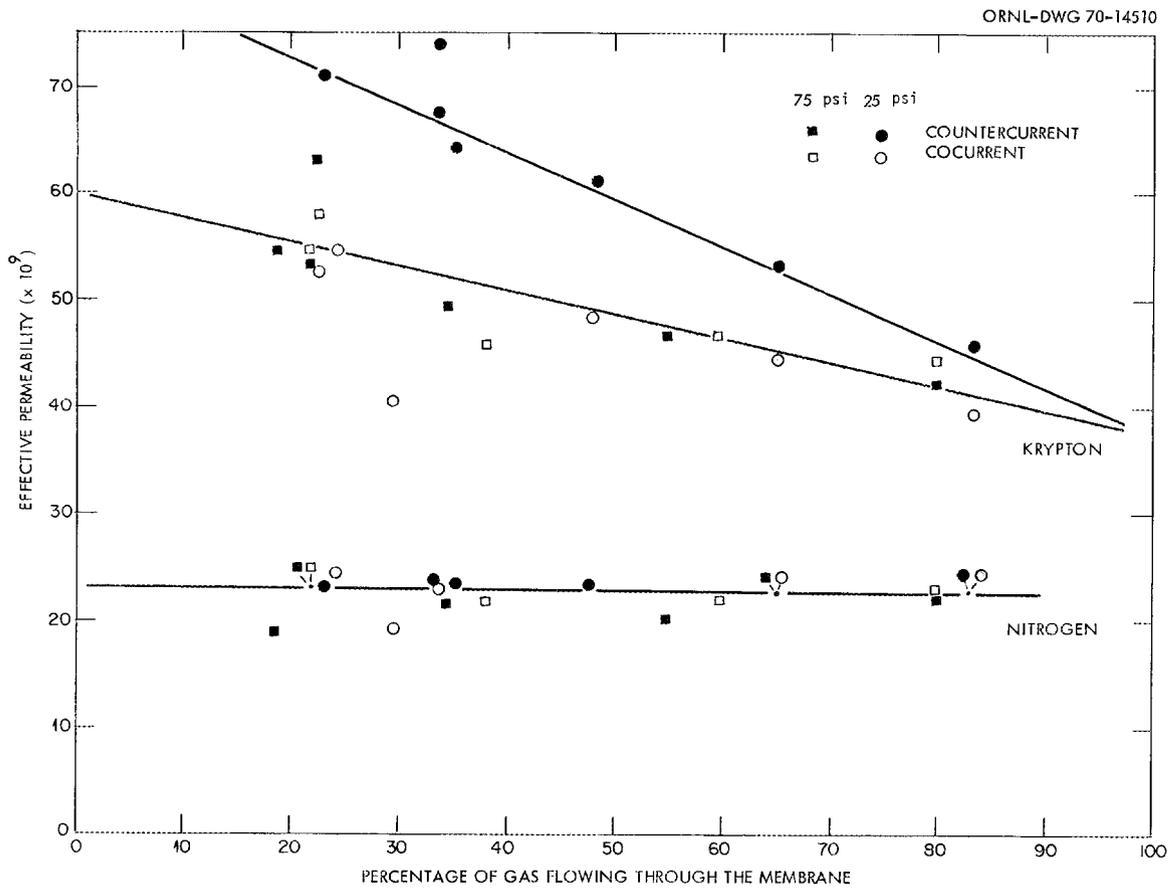


Fig. 9. Effective Permeabilities of Krypton and Nitrogen as a Function of C_{ut} , Pressure Drop, and Flow. Membrane supported only on low-pressure side.

released during burning, a few experiments were conducted to determine the effect of CO_2 on the permeability of krypton. Results obtained by using a mixture of nitrogen, krypton, and 1.5% CO_2 showed that the permeability of the krypton was within the limit of error of the data at pressure drops across the membrane of 50 and 100 psi (Figs. 10 and 11). However, when the CO_2 concentration was increased to 15%, the effective permeability of the krypton increased. The CO_2 was more permeable than either nitrogen or krypton and concentrated with the krypton.

4.3 Parameters Affecting Stage Separation Factors

In addition to the effective permeability, the stage separation factor is an important parameter in the design of a membrane cascade for noble gas removal. The permeability of the membrane determines the membrane area required to obtain a given flow through a single stage, and the separation factor determines the number of stages required to obtain a given separation and concentration of the noble gas. In the case of gas mixtures containing only a few tenths of a percent of xenon or krypton together with their respective radioactive tracer (^{133}Xe or ^{85}Kr), the stage separation factor (α) is essentially equal to the ratio of the radioactivity in the gas passing through the membrane to the radioactivity in the gas which leaves the stage without passing through the membrane (see Sect. 2).

Stage separation factors were measured using krypton-nitrogen and krypton-oxygen mixtures. The effects of varying the cut, the type of flow (countercurrent vs cocurrent), the manner in which the membrane was supported, and the pressure drop across the membrane were determined. The pressure on the low-pressure side of the membrane was always 1 atm. Data obtained for the krypton-nitrogen system at 25°C, using a membrane that was supported on both sides, are shown in Fig. 12. Similar data for the krypton-oxygen system are shown in Fig. 13. The values of α^* , the separation factor at zero cut for a given pressure on the high-pressure side and a 1-atm back pressure, were computed from the permeability factors reported by Robb,²¹ using Eq. (8):

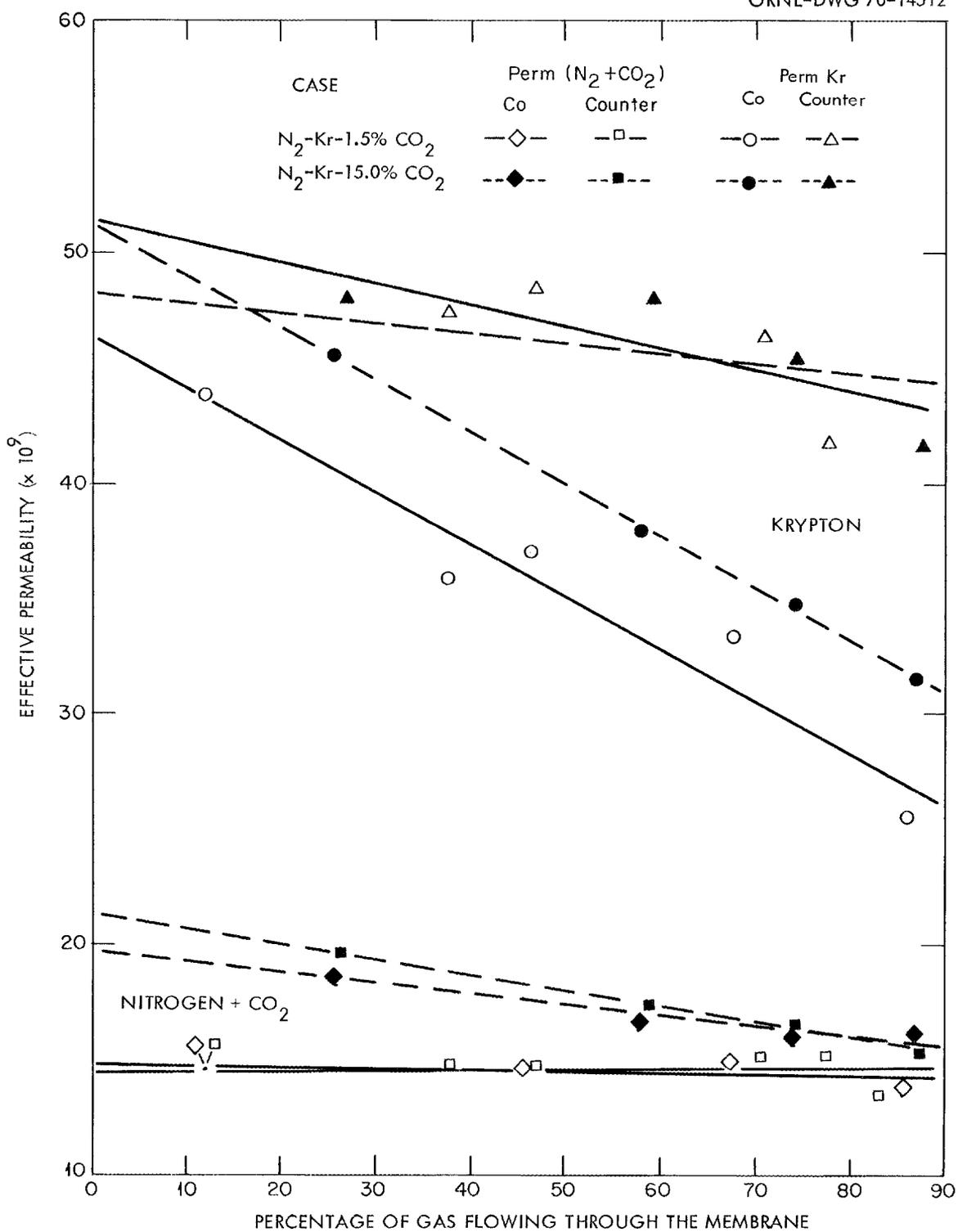


Fig. 10. Effect of Carbon Dioxide on the Effective Permeabilities of Krypton and Nitrogen. Pressure drop across membrane, 50 psi.

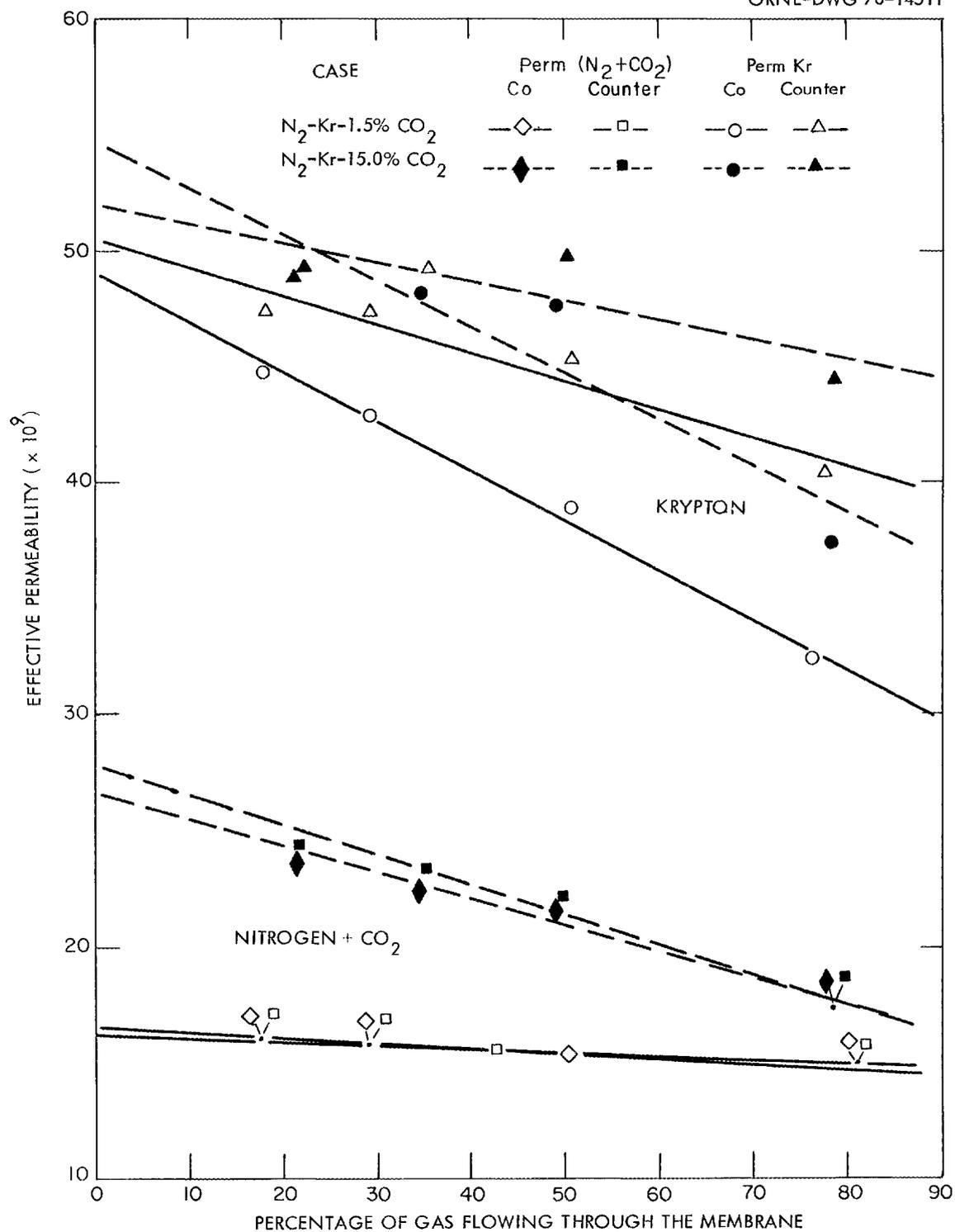


Fig. 11. Effect of Carbon Dioxide on the Effective Permeabilities of Krypton and Nitrogen. Pressure drop across membrane, 100 psi.

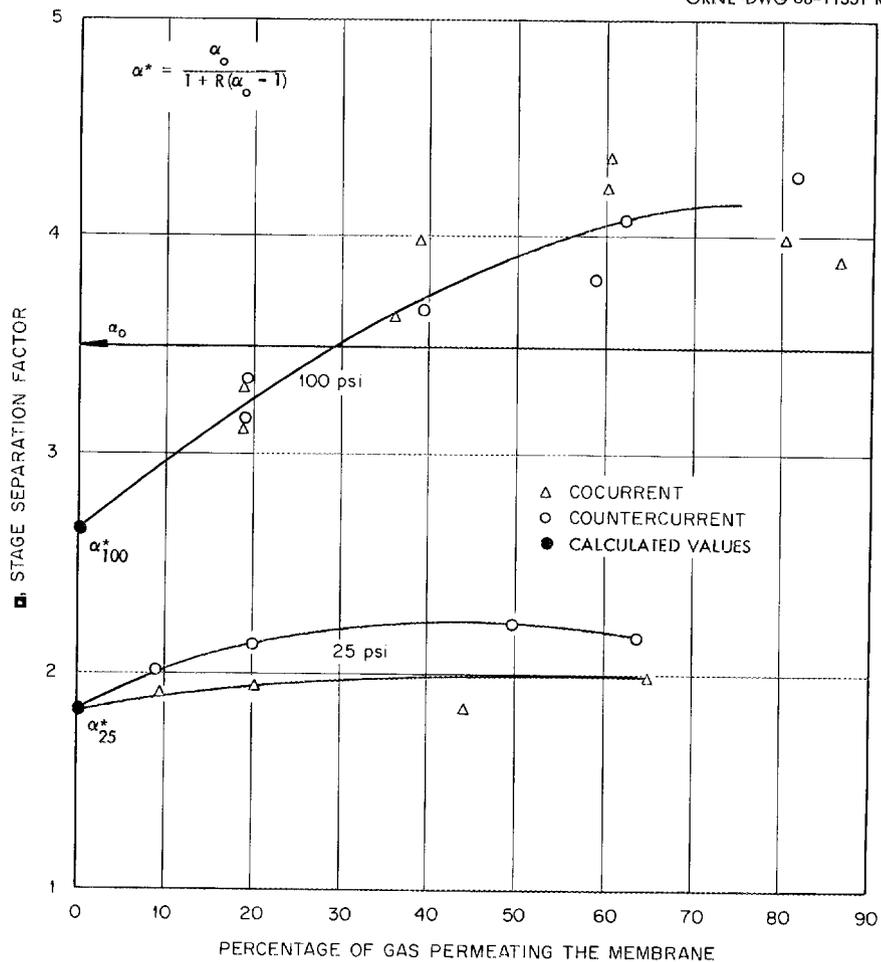


Fig. 12. Increase in Stage Separation Factor for Krypton from Nitrogen with Increasing Percentage of Gas Flowing Through the Membrane. Membrane supported on both sides.

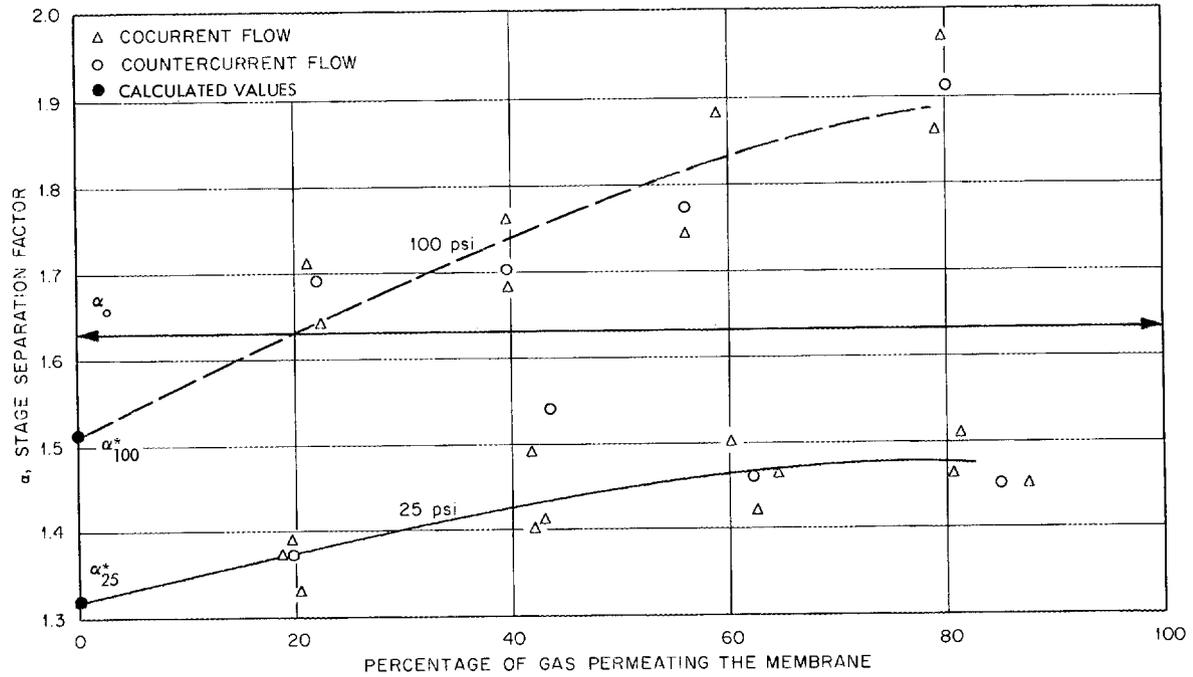


Fig. 13. Stage Separation Factors for Krypton from Oxygen as a Function of Cut. Membrane supported on both sides.

$$\alpha^* = \frac{\alpha_o}{1 + R(\alpha_o - 1)} \cdot$$

The values of α_o for krypton in nitrogen (3.50) and in oxygen (1.63) are about a factor of 2 lower than those for xenon in nitrogen (7.25) and in oxygen (3.38). In each system, the stage separation factors increased both with cut and with the pressure (25 or 100 psi) on the high-pressure side of the membrane. However, the separation factors increased more rapidly with cut when the pressure on the high-pressure side of the membrane was at 100 psi (Figs. 12 and 13). When the pressure on the high-pressure side of the membrane was 100 psi and the cut was greater than 30% with nitrogen carrier gas, or 20% with oxygen carrier gas, the stage separation factors were greater than α_o . The stage separation factors were always less than α_o when the high-pressure side was at 25 psi. Cocurrent and countercurrent flow gave similar results (Figs. 12 and 13). This is contrary to theory, which indicates that countercurrent flow should result in increased separation factors.

Figure 14 gives krypton-nitrogen separation factors measured at 25°C using membrane that was supported only on the low-pressure side. As shown, the factors obtained with countercurrent flow increased more rapidly with increasing cut than those obtained with cocurrent flow. At cuts greater than about 40%, the separation factors were higher than those obtained with membrane supported on both sides.

A few experiments were conducted to determine the effect of the presence of CO₂ on the krypton-nitrogen separation factor at 25°C. Membrane that was supported only on the low-pressure side was used in these studies; the pressure on the high-pressure side was either 50 psi or 100 psi. Under each set of experimental conditions, the separation factor decreased regularly as the CO₂ concentration in the gas mixture was increased from 0 to 15% (Figs. 15 and 16).

4.4 Effect of Temperature on Permeability Factors**

Permeability factors for several gases were measured over the temperature range of 25 to 80°C, using a single membrane sample for each experiment. As has been

**Data obtained by D. E. Fain and co-workers at the Oak Ridge Gaseous Diffusion Plant.

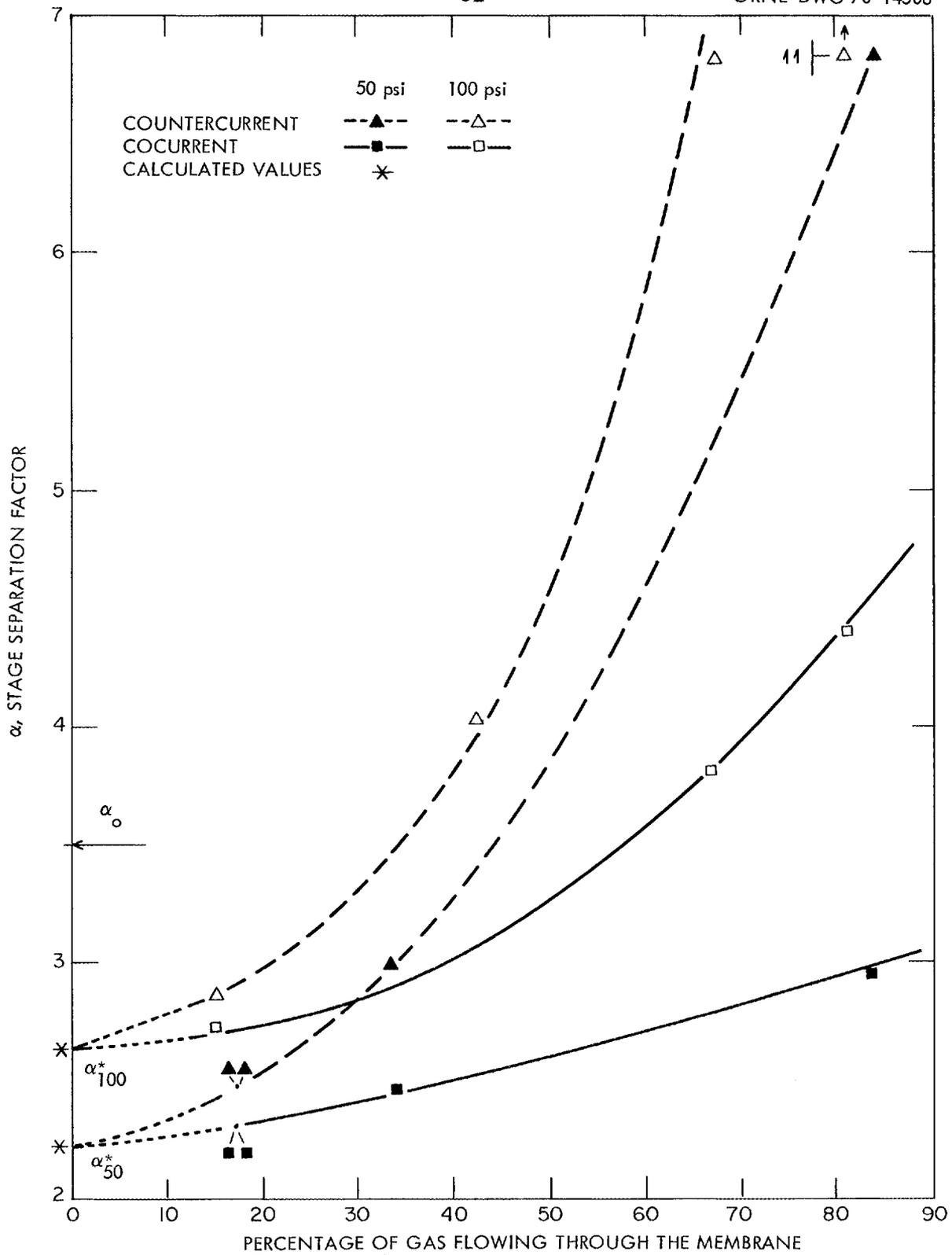


Fig. 14. Separation Factor for Krypton from Nitrogen at Various Pressures, Cuts, and Flow Conditions. Membrane supported on low-pressure side only.

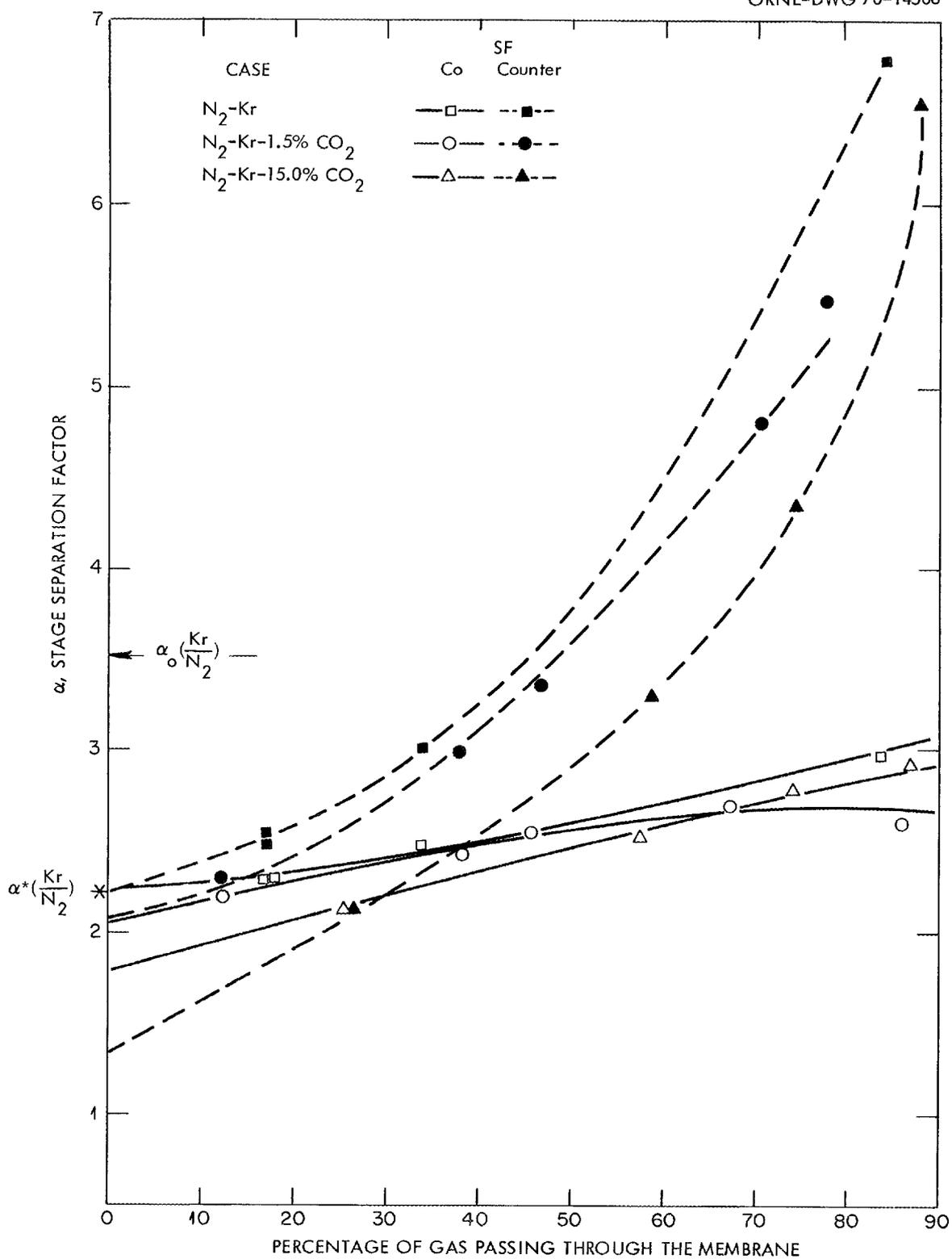


Fig. 15. Separation of Krypton from Nitrogen or from Nitrogen Containing 1.5 or 15% CO_2 . Operating pressure, 50 psi. Membrane supported only on low-pressure side.

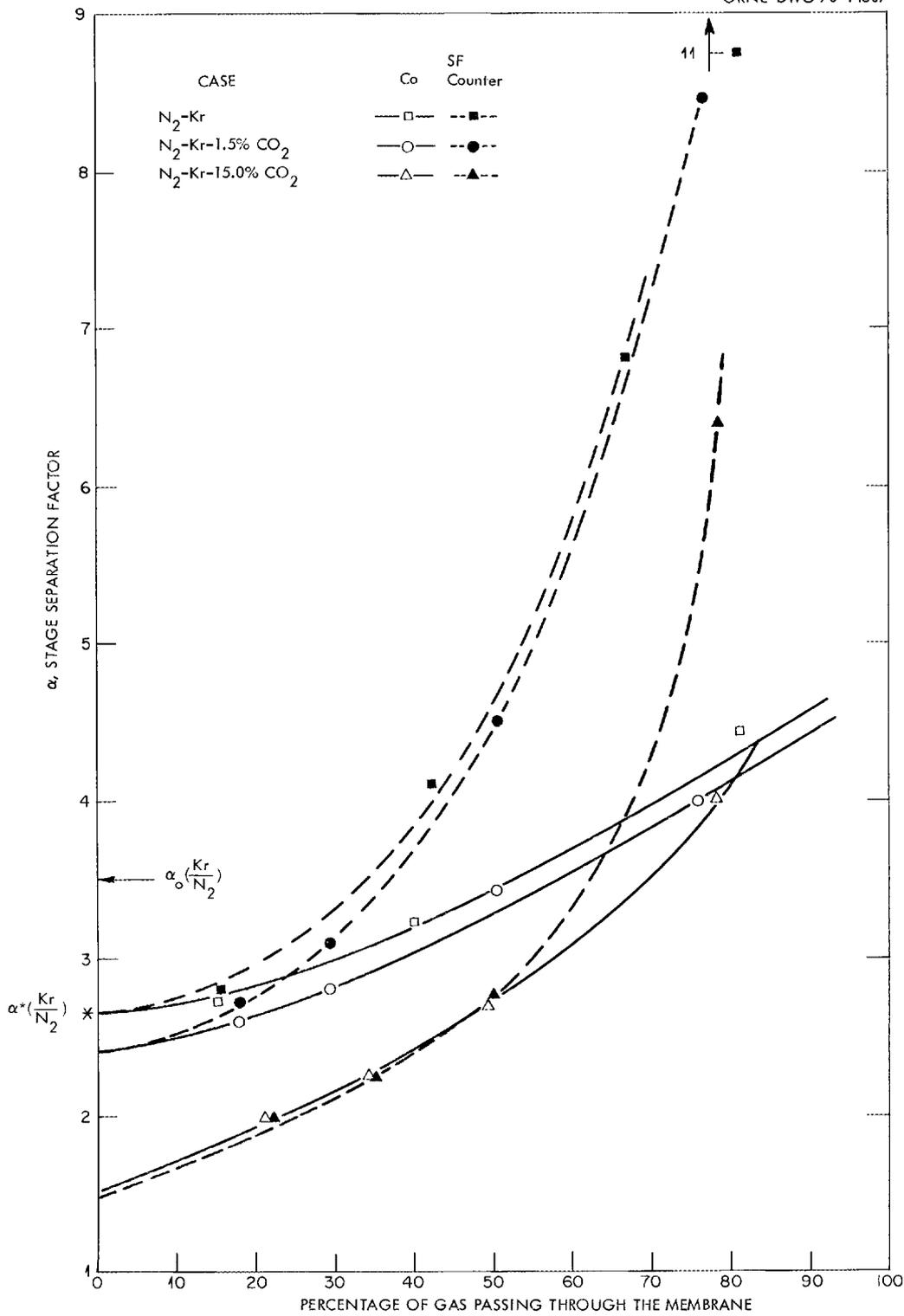


Fig. 16. Separation of Krypton from Nitrogen or from Nitrogen Containing 1.5 or 15% CO_2 . Operating pressure, 100 psi. Membrane supported only on low-pressure side.

shown in other studies,^{19,28} plots of the logarithm of the permeability factor vs $1/T(^{\circ}\text{K})$ are linear (Fig. 17). Due to the uncertainty in the thickness of the membrane, the values of the permeability factors plotted in Fig. 17 are probably accurate to only $\pm 20\%$.

4.5 Effect of Irradiation on Gas Permeation and Separation

A membrane unit being used to remove radioactive noble gases from off-gas streams would be subjected to constant irradiation. To test for irradiation effects, we conducted five experiments with membrane units (membrane, backing material, screens, and sealant) having 25 in.² of exposed membrane area; the units were mounted in steel holders. Each unit was exposed in a ⁶⁰Co source calculated to give a dose of 8.6×10^6 rads per day at the membrane surface. Separation factors among oxygen, nitrogen, and CO₂ were determined periodically during each experiment. Each unit failed after irradiation to between 1.4×10^8 and 1.7×10^8 rads. In every case, failure was caused by the formation of small holes in the membrane and resulted in a sudden increase in gas flow through the membrane and corresponding decreases in the separation factors. Since the separation factors had remained practically constant throughout the irradiation until failure occurred, the use of a value of 10^8 rads should result in a conservative estimate of the life of a membrane in a system used for separating radioactive species.

Several studies of the effect of irradiation on silicone rubber have been reported in the literature. In most of these studies, measurements were made of the changes in such physical properties as hardness and elasticity, or of the yield of gaseous fragments such as H₂, CH₄, etc.^{29,30} The results of these studies indicate that the physical properties of the membrane should be satisfactory to at least 10^8 rads, especially when the membrane is held firmly in a separations unit so that very little flexing due to pressure surges occurs. Robb²¹ reported that irradiation of silicone rubber membranes to 10^7 to 10^8 rads caused a 10 to 20% decrease in the nitrogen, oxygen, and CO₂ permeabilities, but also produced a 2 to 20% increase in separation factors. There are two reasons why Robb's data may not be applicable to the type of separations unit

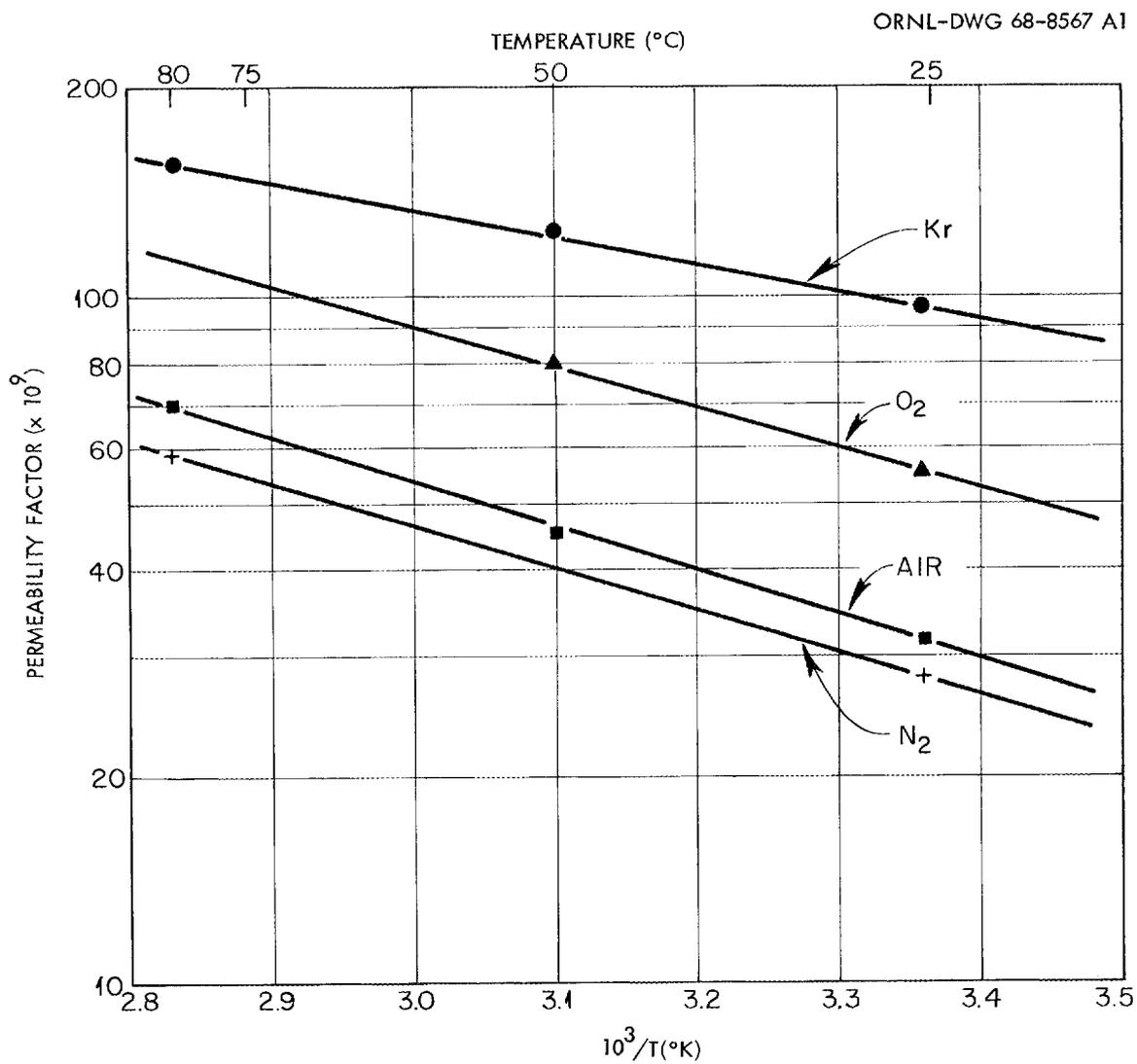


Fig. 17. Effect of Temperature on the Permeability Factors of Krypton, Oxygen, Air, and Nitrogen.

that we are considering. First, in our system the membrane would be bonded to mats and screens, and silicone rubber bonding materials would be used to seal these materials to a steel holder; any deterioration or change in size of these materials would affect the flow through the membrane. Second, the membrane in our system would be under stress because it would have been stretched about 20% before being bonded to the backing. Limited studies with elastomeric materials under stress have shown that irradiation tends to relieve the stress.³¹

5. DESIGN OF ENGINEERING-SCALE MEMBRANE UNIT

A subcontract was let for a 10-yd² multimembrane single-stage unit containing 45 sheets of 1- by 2-ft membrane to be prepared by the General Electric Company for evaluation by the Oak Ridge National Laboratory. A 6- by 6-in. unit that had satisfactory operating characteristics was fabricated. It contained a membrane surface equivalent to about 500 ft² per cubic foot of active volume. Design calculations given in this report (Sect. 6) are based on the assumption that full-size engineering membrane packages would have the same operating characteristics as the single membrane units used in our laboratory studies. A membrane unit was assumed to contain 500 ft² of membrane per cubic foot of volume.

At the conclusion of this program, the General Electric Company had not been able to fabricate a 10-yd² unit that would withstand 150 psi of pressure (i.e., the pressure stipulated in the design).

6. CALCULATIONS OF THE COSTS OF MEMBRANE PLANTS FOR NUCLEAR INDUSTRY APPLICATIONS

Preliminary designs were made and capital costs were estimated for permselective membrane plants as applied to the nuclear industry. These estimates were made on the basis of data obtained with membrane supported on both sides (see Sect. 4.2.1) and were not updated to take advantage of the approximately 30% higher effective

permeabilities obtained with membrane supported only on one side. About one-half of the costs in these estimates is related to the effective permeability of the membrane unit.

The continuing improvement in membrane fabrication techniques will obviously decrease the cost of a membrane cascade. In June 1969, a new type of membrane, which gave a good nitrogen-oxygen separation factor and had a permeability about five times that of the silicone rubber membrane used in our experiments was under consideration at General Electric. General Electric anticipates that this new membrane will cost less to fabricate than the membrane we used and that it will soon be available for testing. There is, however, a limit to the decrease in the cost of a plant which can be obtained by improving the membrane. A large fraction of the cost is associated with the compressor-cooler, piping, and instrumentation required for each operating stage. This cost would remain constant regardless of the cost of the membrane; of course, a membrane material that resulted in an increased separation per stage would decrease the number of stages required.

The membrane cost used in these estimates was $\$10/\text{yd}^2$. This was General Electric's early estimate for the cost of membrane mounted in separation units when the construction of these units reached routine production scale. After our cost estimates had been completed, General Electric informed us that the cost of mounted membrane would probably be closer to $\$18/\text{yd}^2$ than to $\$10/\text{yd}^2$. Thus, the estimated costs reported here are probably about 20% low, assuming that the cost of the membrane is about 25% of the cost of a separations plant. Because of these uncertainties and the fact that no engineering-scale experiments have been conducted to provide a basis for plant optimization, the costs given below are only rough approximations. Our estimates do indicate, however, that the removal of noble gases from the off-gas from several types of nuclear facilities would not be prohibitively high. The plant designs and cost estimates were also valuable in planning the experimental program.

The three applications that were considered were the removal and concentration of the xenon and krypton from: (1) the cover gas that would blanket the molten

sodium of an LMFBR, (2) the gas from a reactor containment building following an accidental release of fission products, and (3) the off-gas from a nuclear fuel processing plant. In each of these applications, the assumption was made that in previous steps the radioactive iodine, particulates, and reactive gases such as sodium vapor, nitrogen oxides, etc., would have been removed from the gas. Thus the cost of removing these materials was not included in the estimates presented here.

6.1 Cost of Removing Xenon and Krypton from an LMFBR Cover Gas

For this study, the 1000-Mw (electrical) liquid-metal-cooled fast breeder reactor (LMFBR) designed by Babcock and Wilcox Company was used.³² The space above the sodium coolant in the reactor vessel will be filled with 25,000 ft³ of argon gas (Fig. 18). Since the fuel rods are to be vented to prevent increases in pressure, the inert fission product gases will accumulate in this cover gas. In order to decrease the hazard to operating personnel in case of accidental release of the gas, continuous removal of the fission product gases using a membrane separations plant has been considered. We assumed that the membrane plant would remove essentially all of the xenon and about 99% of the krypton from a stream of cover gas flowing at 10 scfm and would concentrate the radioactive gases by factors of 10, 100, or 500 for permanent storage.

The equilibrium activity of the cover gas is a function of the processing rate; data are given in Table 3 for gas feed rates (to the membrane plant) of 10, 1.0, and 0.01 scfm. The total activity of the gas would increase from 5.5×10^6 to 3.1×10^7 curies in the 25,000-ft³ gas space as the replacement rate decreased from 10 to 0.01 scfm. Xenon-133 would account for 80 to 95% of the total activity.

The data in Table 4 show the performance, size, and cost of membrane cascades for operation at a gas feed rate of 10 scfm and three concentrated gas withdrawal rates. The first, second, and third columns of the table give the results for recycling or venting 90, 99, and 99.8%, respectively, of the feed; the remaining gas would contain the concentrated noble gases. In each case, the activity of the decontaminated

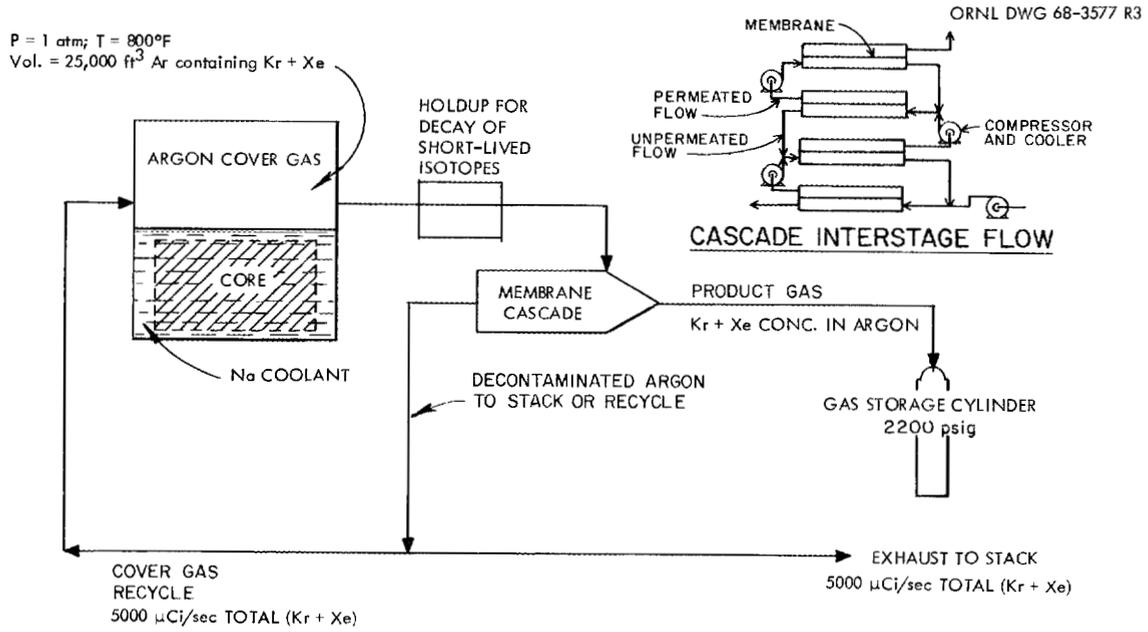


Fig. 18. Schematic Diagram for Removing Xenon and Krypton from the Argon Cover Gas of a 1000-Mw (electrical) Sodium-Cooled Fast Reactor.

Table 3. Calculated Concentrations of Noble Gases Above the Sodium Coolant in the 1000-Mw (electrical) Reactor Designed by the Babcock and Wilcox Company

Blanket gas volume = 25,000 ft³

	Average Gas Feed Rate to Membrane Cascade (scfm)					
	10		1.0		0.01	
	Ci	atoms/ft ³	Ci	atoms/ft ³	Ci	atoms/ft ³
^{83m} Kr	9,800	0.140 × 10 ¹⁵	10,600	0.151 × 10 ¹⁵	10,700	0.153 × 10 ¹⁵
^{85m} Kr	39,800	0.134 × 10 ¹⁶	46,500	0.157 × 10 ¹⁶	47,300	0.160 × 10 ¹⁶
⁸⁵ Kr	43	0.311 × 10 ¹⁷	418	0.302 × 10 ¹⁸	4,310	0.312 × 10 ¹⁹
⁸⁷ Kr	70,000	0.681 × 10 ¹⁵	73,600	0.716 × 10 ¹⁵	74,000	0.720 × 10 ¹⁵
⁸⁸ Kr	108,000	0.232 × 10 ¹⁶	119,000	0.256 × 10 ¹⁶	121,000	0.260 × 10 ¹⁶
⁸⁹ Kr	9,660	0.396 × 10 ¹³	9,680	0.397 × 10 ¹³	9,680	0.397 × 10 ¹³
^{131m} Xe	16,300	0.360 × 10 ¹⁷	97,500	0.215 × 10 ¹⁸	216,000	0.478 × 10 ¹⁸
^{133m} Xe	89,400	0.379 × 10 ¹⁷	245,000	0.104 × 10 ¹⁸	302,000	0.128 × 10 ¹⁸
¹³³ Xe	4,470,000	0.434 × 10 ¹⁹	18,800,000	0.182 × 10 ²⁰	29,000,000	0.281 × 10 ²⁰
^{135m} Xe	62,200	0.127 × 10 ¹⁵	66,800	0.136 × 10 ¹⁵	66,900	0.137 × 10 ¹⁵
¹³⁵ Xe	356,000	0.251 × 10 ¹⁷	479,000	0.338 × 10 ¹⁷	498,000	0.352 × 10 ¹⁷
¹³⁷ Xe	33,900	0.182 × 10 ¹⁴	34,000	0.182 × 10 ¹⁴	34,000	0.182 × 10 ¹⁴
¹³⁸ Xe	258,000	0.562 × 10 ¹⁵	261,000	0.568 × 10 ¹⁵	261,000	0.568 × 10 ¹⁵
⁴¹ Ar	2,200	0.309 × 10 ¹⁴	2,200	0.309 × 10 ¹⁴	2,200	0.309 × 10 ¹⁴
Total Ci						
Kr	237,303		259,798		266,990	
Xe	<u>5,285,800</u>		<u>19,983,300</u>		<u>30,377,900</u>	
	5,523,103		20,243,098		30,644,890	

Table 4. Performance, Size, and Cost of Several Cascades of Permselective Membranes for Separating Krypton and Xenon from the Cover Gas of a Sodium-Cooled, 1000-Mw (electrical) Reactor

Gas feed rate to cascade = 10 scfm

	Concentrated Gas Withdrawal Rate		
	1 scfm	0.1 scfm	0.02 scfm
Cascade			
Number of enriching stages	9	15	20
Number of stripping stages	19	23	24
Membrane area, yd ²	4630	5020	5140
Cascade volume, ft ³	~ 9	~10	~11
Power requirement, kw	126	136	140
Largest compressor, hp	9.2	7.9	7.7
High-pressure side of membrane, psi	150	150	150
Low-pressure side of membrane, psi	0	0	0
Feed Gas			
Kr concentration, at. %	0.004	0.004	0.004
Xe concentration, at. %	0.136	0.136	0.136
Kr activity, Ci/ft ³	24.4	24.4	24.4
Xe activity, Ci/ft ³	542.6	542.6	542.6
Recycle (or Vented) Gas			
Kr concentration, at. %	0.47×10^{-5}	0.49×10^{-5}	0.46×10^{-5}
Xe concentration, at. %	0.53×10^{-9}	0.51×10^{-10}	0.25×10^{-10}
Kr + Xe activity, Ci/ft ³	0.029	0.030	0.028
Kr + Xe activity, μ Ci/sec	4350	4950	4657
Product Gas^a			
Kr concentration, at. %	0.04	0.4	2
Xe concentration, at. %	1.4	14	68
Ar concentration, at. %	98.6	85.0	30
Kr activity, Ci/ft ³	244	2440	12,200
Xe activity, Ci/ft ³	5426	54,260	271,300
Concentration factor, product/feed	10	100	500
Number of storage cylinders per week ^b	50	5	1
Installed cost, dollars	289,000	342,000	366,000

^aTo be stored.

^bStandard N₂ cylinders at a pressure of 2200 psi.

gas stream would be reduced to slightly less than 5000 $\mu\text{Ci}/\text{sec}$, a level that is acceptable for discharge to the atmosphere at the present time. However, it is likely that the decontaminated cover gas would be recycled to the reactor to eliminate the release of radioactive gases to the environment.

It is significant to note that the concentrated product may be stored in a very small volume. The number of conventional gas cylinders (at 2200 psi) required per week would be 50, 5, and 1, respectively, for the three product gas rates (1, 0.1, and 0.02 scfm) considered. The gas from one week's operation would produce about 3.2×10^4 w of heat. Blomeke and Perona,³³ who have studied the cost of shipment and storage of cylinders of concentrated radioactive noble gases, have concluded that this method would be practical to at least the year 2000.

The costs of the various membrane plants do not differ widely.³⁴ For example, a plant for concentrating the original volume of gas by a factor of 10 would cost \$289,000, as compared with \$366,000 for a plant providing a concentration factor of 500. This is due to the small equipment at the concentrating end of the cascade.

Our data on the effect of irradiation on membrane life (Sect. 4.5) indicate that the membrane in a plant such as that described in Table 4 would have only a very short life if the cover gas from an LMFBR were fed directly to the separations plant. Most of the activity in the gas would be the result of short-lived isotopes of xenon and krypton; consequently, the activity of the gas would decrease rapidly with time. If the cover gas were retained for 20 days (either in a storage tank or on absorbents), the life of the membrane in the last concentrating stage of the cascade would be about 110 days, assuming that the membrane received a cumulative dose of 10^8 rads prior to failure (Fig. 19). Retention of the cover gas for 30 days would increase the membrane life to about 6 years. Further economic studies will be required before the optimum balance between the cost of replacing membrane units and the cost of retaining the cover gas can be determined. When this balance is determined, the total cost of gas retention and the separations plant can be estimated.

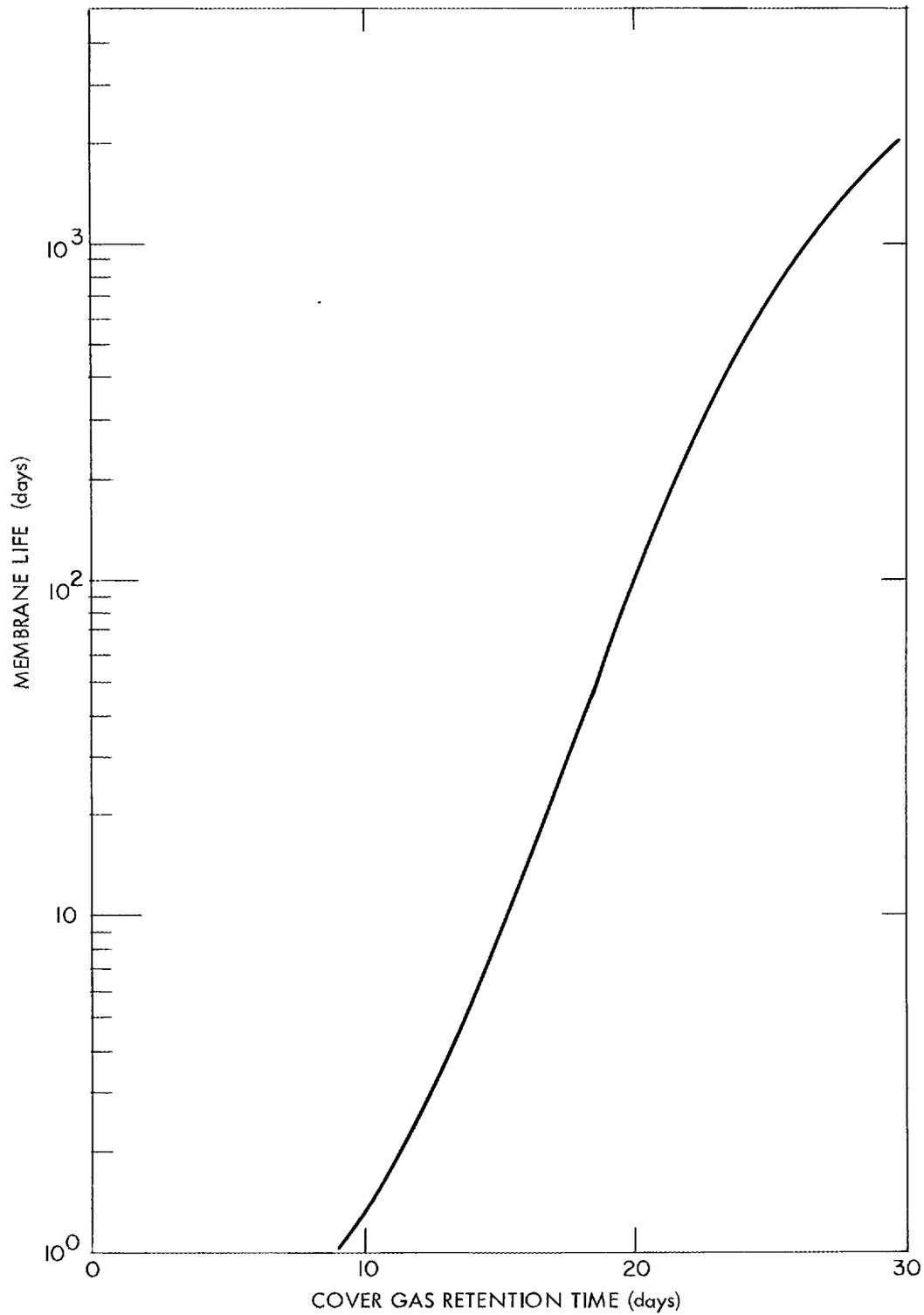


Fig. 19. Variation of Membrane Life with Holdup Time of Cover Gas from a Sodium-Cooled Power Reactor. Basis: Irradiation of membrane to 10^8 rads.

6.2 Cost of Removing Noble Gases from a Reactor Containment Building

In order to estimate the costs of membrane plants for removing radioactive noble gases following a nuclear accident, we selected a maximum credible loss-of-coolant accident involving an advanced water-cooled reactor with the following characteristics:³⁵

Power, Mw	
Thermal	3200
Electrical	1000
Flux, neutrons $\text{cm}^{-2} \text{sec}^{-1}$	3×10^3
Fuel loading	
Metric tons of uranium	100
Grams of uranium	10^8
Fuel enrichment	
^{235}U , %	2.3
moles	10^4
atoms	6×10^{27}
Containment shell volume, ft^3	3×10^6
Time to accident (at end of fuel life)	
Days	625
Seconds	5.4×10^7
Fuel irradiation, Mwd/metric ton	20,000

Under these conditions, the concentrations of krypton and xenon in the containment shell immediately after the accidental release would be about 100 and 650 ppm, respectively. Since most of the xenon and krypton would be nonradioactive, these concentrations would not decrease appreciably with time. After a period of 1 day, the activity of the xenon would be about 150 times that of the krypton, and the total activity in the containment shell would be more than 2×10^8 Ci (3.5×10^5 w). However, because of the relatively short half-life of the xenon (the half-life of the most abundant radioisotope, ^{133}Xe , is 5 days) and the long half-life of much of the krypton (10-year ^{85}Kr), the total activity would decrease rapidly until, after about 45 days, the ^{85}Kr would become the limiting radioactive isotope. The activity level (due to krypton) would remain at about the 10^6 -Ci level for several years. Analyses have shown that, because of the more rapid decay and more

effective removal of xenon, the decontamination of the gas is always limited by the activity of the krypton it contains.³⁵

A system for removing the noble gases from the reactor containment building has been designed by Blumkin.³⁶ In this system, the gases are continuously cycled through a membrane plant, effecting the removal of a fraction of the noble gases on each cycle. After 7 days, nearly all of the xenon and 99% of the krypton would be removed, and the activity in the containment building would be reduced to a level acceptable for discharges to the atmosphere. This process would require 27,840 yd² of membrane in eight stages; the estimated capital cost is about \$1,100,000. Later considerations have indicated that there would be little incentive for removing the noble gases from the reactor building so rapidly. A smaller plant that would remove the noble gases within 35 days would have to be only one-fifth as large as the plant just discussed and would cost about \$300,000.

The exposure of the membrane in the last concentrating stage of a cascade for removing noble gases from the reactor containment building was calculated as a function of decay time before processing (Table 5). If the gases in the containment shell were allowed to decay for 30 days and were subsequently removed by a membrane plant during the next 7 days, the integrated exposure to the last stage would be about 1.2×10^7 rads. After a decay of 60 days, the exposure would be only about one-tenth of this value. Since the radiation exposure is nearly directly proportional to the processing time, the exposure would be only about 6×10^7 rads if a 35-day processing period was used.

These calculations indicate that irradiation would not appreciably affect the membrane during the removal of the noble gases from a reactor containment building at the processing schedules considered. Considerably shorter decay times and longer processing periods would be acceptable from the point of view of the irradiation of the membrane.

Table 5. Noble Gas Activity in the Shell, and Irradiation Exposure^a of the Membrane in the Last Concentrating Stage During Removal of Noble Gases from Nuclear Containment Shell

Basis: Size - 3200 Mw (thermal)
 Flux - 3×10^{13} neutrons $\text{cm}^{-2} \text{sec}^{-1}$
 Fuel life - 625 days
 Fuel load - 100 metric tons
 Fuel enrichment - 2.3% ^{235}U
 Fuel irradiation - 20,000 Mwd/ton
 Containment volume - $3 \times 10^6 \text{ ft}^3$

	Decay Time Before Processing		
	30 days	60 days	120 days
Kr activity in shell, Ci	9.0×10^5	8.95×10^5	8.86×10^5
Xe activity in shell, Ci	2.0×10^7	8.0×10^5	1.0×10^3
Initial Kr dose rate to membrane, rads/min	2.78×10^2	2.78×10^2	2.71×10^2
Initial Xe dose rate to membrane, rads/min	9.72×10^3	3.82×10^2	4.79×10^{-1}
Initial total dose rate, rads/min	9.99×10^3	6.59×10^2	2.71×10^2
Integrated dose during a 7-day processing period, rads	1.22×10^7	1.07×10^6	5.89×10^5

^aCalculated for the last stage of the cascade, where the noble gas concentration is 100 times higher than the feed.

6.3 Cost of a Permselective Membrane Plant for Processing Off-Gas from a Fuel Reprocessing Plant

In the aqueous processing of reactor fuels, the fuel is usually dissolved in nitric acid. Therefore, the dissolver off-gas contains nitrogen, oxygen, water vapor, nitrogen oxides, xenon, and krypton. If the water vapor, nitrogen oxides, and other chemically active gases were removed, the remaining gases could be treated in a cascade of permselective membrane stages to markedly reduce the concentration of radioactive noble gases and thereby make discharge of the cleaned gas to the atmosphere practical. The concentrated noble gases could be collected and stored indefinitely.

The curves in Fig. 20 show the relationship between cost and plant size as determined by the volume of dissolver off-gas to be treated per minute. These data were calculated using the costs for the two applications reported above rather than from a plant designed for this particular application. A 5-metric ton/day plant was assumed to generate about 100 scfm of off-gas (see Table 6). Costs (Fig. 20) are given for achieving off-gas decontamination factors (DF's) of 10, 100, and 1000; all values are based on a concentration factor (CF) of 100 for the recovered noble gases. For comparison, the estimated costs for a plant for adsorbing noble gases in chlorofluoromethanes are included.³⁷ These costs are for fully equipped, operable plants but do not include allowances for building space or for head-end treatment facilities to remove nitrogen oxides, water, etc.

Because of the delay between the discharge of fuel from the reactor and reprocessing, DF's greater than 100 are probably unnecessary, using present-day release standards; for longer-cooled fuel (more than 60 days), DF's of 10 may be sufficient. Under these conditions, the cost of a gas-separation system for a 5-metric ton/day reprocessing plant is in the range \$280,000 to \$420,000. A plant to reduce the level of activity in the off-gas by a factor of 1000 would cost about \$620,000.

Calculations have been made of the irradiation exposure that would be received by a membrane cascade used to remove the noble gases from the off-gas from a LMFBR fuel reprocessing plant. Exposures received during the processing of 30-day-cooled

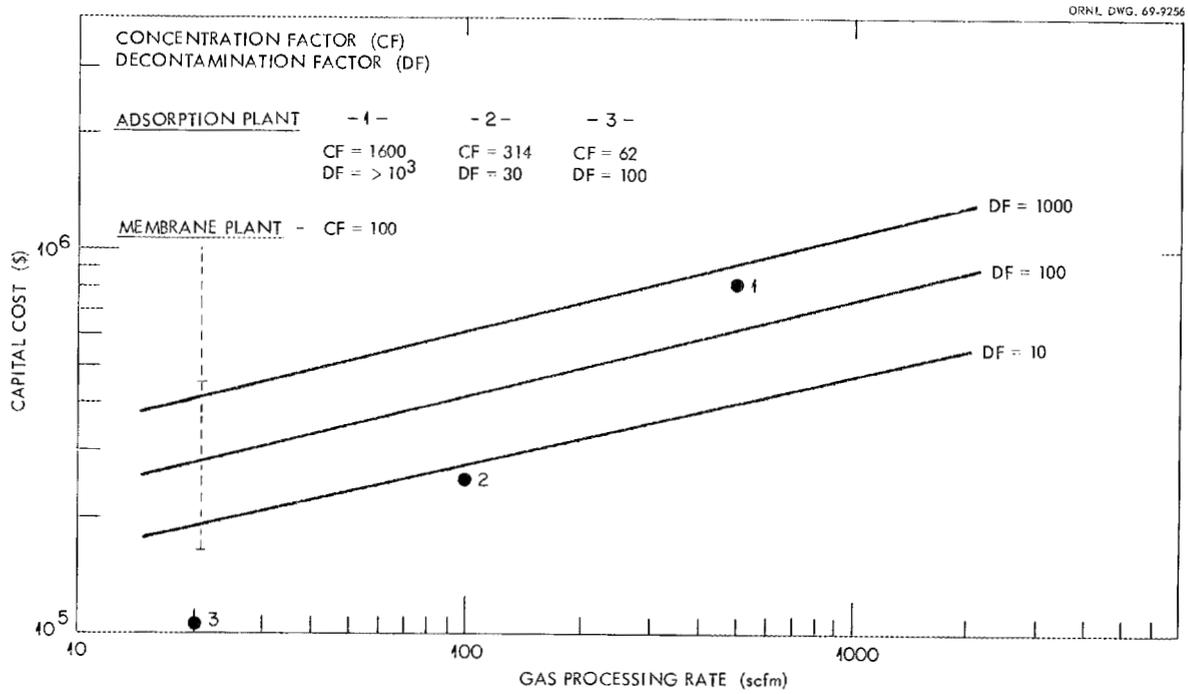


Fig. 20. Estimated Capital Costs for Removing Noble Gases from Off-Gas of a 5-metric ton/day Reactor Fuel Processing Plant.

Table 6. Noble Gas Activity in the Off-Gas from a Fuel Reprocessing Plant,³⁸
and Exposure of the Membrane

Basis:	Reactor Fuel	Processing Plant	
	LMFBR (Atomics International oxide reactor ^a) Burnup - 80,000 Mwd/metric ton Irradiation time - 540 days Composition - mixed core and blanket	Rate - 5 metric tons of fuel per day Decay time - 30 days Off-gas flow - 100 ft ³ /min	
		Reactor Fuel	
		30-day-cooled	60-day-cooled
⁸⁵ Kr, Ci/ton fuel		3.395 x 10 ⁴	2.383 x 10 ⁴
^{131m} Xe, Ci/ton fuel		1.477 x 10 ⁴	3.134 x 10 ³
^{133m} Xe, Ci/ton fuel		2.958 x 10 ⁴	3.503 x 10 ⁻³
¹³³ Xe, Ci/ton fuel		1.935 x 10 ⁵	3.742 x 10 ³
Off-gas, scfm		100	100
Concentration factor, top stage		100	100
Concentration factor, second stage		43.5	43.5
Membrane exposure, top stage, rads/day		3.99 x 10 ⁶	5.74 x 10 ⁵
Membrane exposure, second stage, rads/day		1.74 x 10 ⁶	2.50 x 10 ⁵

fuel would be the most stringent requirements expected for a fuel reprocessing plant in the near future. Under the proposed operating conditions, if the membrane were replaced after receiving a radiation dose of 1×10^8 rads, the 7 yd^2 of membrane in the last concentrating stage would need to be replaced about every 58 days; other stages would need to be replaced at longer intervals. About 50 years would be required to give the membrane at the feed stage an equivalent exposure. Only the last five stages would be needed to be replaced, due to irradiation exposure, at intervals of less than two years. The total membrane replaced in these stages over a period of two years would be about 630 yd^2 and would cost about \$3150 per year. If the only cause of failure was irradiation, the prorated cost of replacing the membrane in the feed stage plus all concentrating stages would be about \$10,000 annually.

If the fuel were allowed to decay for 60 days prior to processing, the irradiation exposures would be only about one-seventh of those encountered with 30-day-cooled fuel. In this case, the replacement cycle for the top stage of the concentrating section would be longer than one year.

7. REFERENCES

1. C. M. Slansky, H. K. Peterson, and V. G. Johnson, "Nuclear Power Growth Spurs Interest in Fuel Plant Wastes," *Environ. Sci. Technol.* 3(5), 446-51 (1969).
2. J. J. de Nunno, F. D. Anderson, R. E. Baker, and R. L. Waterfield, Calculation of Distance Factors for Power and Test Reactor Site, TID-14844 (Mar. 23, 1962).
3. G. W. Keilholtz, "Removal of Noble Gases from Off-Gas Streams," *Nucl. Safety* 8(2), 155-60 (1966).
4. J. B. Robertson, Behavior of Xenon-133 Gas After Injection Underground, IDO-22051, U. S. Geological Survey, Waste Resources Division, Idaho Falls, Idaho (July 1969).
5. L. A. Weller, The Adsorption of Krypton and Xenon on Activated Carbon - A Bibliography, MLM-1092, Mound Laboratory, Miamisburg, Ohio (1959).

6. C. M. Slansky, H. K. Peterson, and V. G. Johnson, "The Production and Waste Management of Krypton-85 in Nuclear Power Industry in 1970 - 2000 A.D.," Idaho Nuclear Corporation (to be published).
7. J. R. Merriman et al., "Concentration and Collection of Krypton and Xenon by Selective Adsorption in Fluorocarbon Solvents" (SM-110/25), p. 303 in the Proceedings of the Symposium on Operating and Developmental Experience in the Treatment of Airborne Radioactive Wastes, International Atomic Energy Agency, August 1968.
8. R. F. Taylor and G. P. Wall, "Development of a Production Process for Radio-Krypton Recovery by Fractional Absorption," *Progr. Nucl. Energy, Ser. IV* 5, 307-45 (1963).
9. Vijay Mohan Bhatnagar, Clathrate Compounds, pp. 103-107, S. Chand and Co., Delhi, India, 1968.
10. J. Slivnik, "Recovery of Xenon and Krypton in the Treatment of Gaseous Radioactive Wastes " (SM-110/24), p. 315 in Proceedings of the Symposium on Operating and Developmental Experience in the Treatment of Airborne Radioactive Wastes, International Atomic Energy Agency, August 1968.
11. R. H. Rainey, W. L. Carter, S. Blumkin, and D. E. Fain, "Separation of Radioactive Xenon and Krypton from Other Gases by Use of Permselective Membranes" (SM-110/27), p. 323 in the Proceedings of the Symposium on Operating and Developmental Experience in the Treatment of Airborne Radioactive Wastes, International Atomic Energy Agency, August 1968.
12. J. K. Mitchell, "On the Penetrativeness of Fluids," *J. Roy. Inst.* 2, 101-8, 307-21 (1831).
13. J. K. Mitchell, "On the Penetration of Gases," *Am. J. Med. Sciences* XIII, 100-112 (1833).
14. Proceedings of Symposium, Membrane Processes for Industry, Birmingham, Ala. May 19-20, 1966.

15. R. W. Roberts, The Effect of Polymeric Structure Upon Gas Permeation, Ph.D. Thesis 62-2410, State University of Iowa (1962).
16. S. A. Stern, "Industrial Application of Membrane Processes: The Separation of Gas Mixtures," Proceedings of Symposium, Membrane Processes for Industry, Birmingham, Ala., May 19-20, 1966.
17. N. Lakshminarayanaiah, "Transport Phenomena in Artificial Membranes," *Chem. Rev.* 65(5), (1965).
18. Karl Kammemeyer, "Silicone Rubber as a Selective Barrier," *Ind. Eng. Chem.* 49(10), 1685-86 (1957).
19. R. M. Barrer and H. T. Chio, "Solution and Diffusion of Gases and Vapors in Silicone Rubber Membranes," *J. Polymer Sci., Pt. C*, No. 10, 111-38 (1965).
20. C. J. Major, "Investigation of Unique Gas Permeability Cell System to Remove CO₂ and Other Noxious Gases from Space Cabins," N 65-29624, Department of Chemical Engineering, University of Iowa, for National Aeronautics and Space Administration (1965).
21. W. L. Robb, Thin Silicone Membranes and Their Permselective Properties and Some Applications, Report 65-C-031, General Electric Company (1965).
22. J. M. Holmes, private communication to D. E. Ferguson (October 1965).
23. R. N. Ricles, "Molecular Transport in Membranes," *Ind. Eng. Chem.* 58(6), 19-35 (1966).
24. Samuel Blumkin, A Method for Calculating Gradients for Multicomponent Systems Involving Large Separation Factors, K-OA-1559 (1968).
25. S. H. Jury, Analysis of Fractionation of Gas Mixtures Using Dimethyl Silicone Rubber Membranes (to be published).
26. S. A. Stern and W. P. Walawender, "Analysis of Membrane Separation Parameters," *Separation Sci.* 4(2), 129-59 (1969).

27. H. P. Briggs, General Electric Company, personal communication.
28. R. M. Barrer, "Diffusion in Elastomers," Kolloid-Z. 120(1), 177-86 (1951).
29. A. Charlesby, Atomic Radiation and Polymers, pp. 297-311, Pergamon, New York, 1960.
30. A. E. Chapiro, Radiation Chemistry of Polymeric Systems, Interscience, New York, 1962.
31. J. W. Boon, "Elastomeric Material," pp. 245-88 in Radiation Effects on Organic Materials, ed. by R. O. Bolt and J. G. Carroll, Academic, New York, 1963.
32. Babcock and Wilcox Company, 1000-MWe LMFBR Follow-on Study - Task II and III Final Report, Vol. 1-5, 13AW-1328 (February 1969).
33. J. O. Blomeke and J. J. Perona, Management of Noble Gas Fission Product Wastes from Reprocessing Spent Fuels, ORNL-TM-2677 (Nov. 22, 1969).
34. S. Blumkin, Permselective Membrane Cascades for the Separation of Xenon and Krypton from Argon, K-OA-1622, Rev. 1 (1968).
35. R. H. Rainey, Criteria for Noble-Gas Removal Using Permselective Membranes, ORNL-TM-1822 (1967).
36. S. Blumkin to D. M. Lang, Separation of Krypton from Air by Means of a Permselective Membrane, K-OA-1552, Rev. 1 (Nov. 28, 1967).
37. J. R. Merriman and J. H. Pashley, Engineering Development of an Adsorption Process for the Concentration and Collection of Krypton and Xenon: Fourth Summary Progress Report, July through December, 1968, K-1786 (April 1, 1970).
38. K. Buttrey, O. R. Hilling, P. M. Mager, and E. H. Ottewitte, "LMFBR Task Force Fuel Study," NAA-SR-Memo 12604 (Jan. 10, 1968).

ORNL-4522
 UC-10 — Chemical Separations Processes
 for Plutonium and Uranium

INTERNAL DISTRIBUTION

- | | |
|-------------------------------------|---------------------------------|
| 1. Biology Library | 61. D. G. Jacobs |
| 2-4. Central Research Library | 62. R. J. Kedl |
| 5. ORNL — Y-12 Technical Library | 63. G. W. Keilholtz |
| Document Reference Section | 64. D. M. Lang (Y-12) |
| 6-22. Laboratory Records Department | 65. S. A. Levin (Y-12) |
| 23. Laboratory Records, ORNL R.C. | 66. H. G. MacPherson |
| 24. E. S. Bettis | 67. W. C. McClain |
| 25-34. R. E. Blanco | 68. J. R. Merriman (K-25) |
| 35. J. O. Blomeke | 69. J. P. Nichols |
| 36. W. J. Boegly, Jr. | 70. J. H. Pashley (K-25) |
| 37-40. S. Blumkin (K-25) | 71. J. J. Perona |
| 41. R. E. Brooksbank | 72-76. R. H. Rainey |
| 42. W. H. Bridges | 77. M. W. Rosenthal |
| 43. F. N. Browder | 78. Jerome Roth |
| 44. K. B. Brown | 79. Dunlap Scott, Jr. |
| 45. W. E. Browning | 80. M. J. Skinner |
| 46. J. R. Buchanan | 81. A. N. Smith |
| 47. W. L. Carter | 82. E. G. Struxness |
| 48. W. B. Cottrell | 83. D. A. Sundberg |
| 49. K. E. Cowser | 84. D. B. Trauger |
| 50. D. J. Crouse | 85. W. E. Unger |
| 51. F. L. Culler | 86. E. Von Halle (K-25) |
| 52. J. T. Day | 87. A. M. Weinberg |
| 53. D. E. Fain (K-25) | 88. M. E. Whatley |
| 54. D. E. Ferguson | 89. R. G. Wymer |
| 55. L. M. Ferris | 90. P. H. Emmett (consultant) |
| 56. J. H. Gibbons | 91. J. J. Katz (consultant) |
| 57. R. W. Glass | 92. J. L. Margrave (consultant) |
| 58. J. M. Googin (Y-12) | 93. E. A. Mason (consultant) |
| 59. J. M. Holmes | 94. R. B. Richards (consultant) |
| 60. A. R. Irvine | |

EXTERNAL DISTRIBUTION

- AEC, Idaho Operations Office, P.O. Box 2108, Idaho Falls, Idaho 83401
95. K. K. Kennedy
- AEC, Oak Ridge Operations, Oak Ridge, Tennessee 37830
96. C. S. Shoup
97. Laboratory and University Division
98. Patent Office
- AEC, Oak Ridge Operations, Site Representative, ORNL
99. H. W. Behrman

AEC, Washington, D.C. 20545

- 100. C. B. Bartlett
- 101. W. G. Belter
- 102. D. J. Donoghue
- 103. W. H. McVey
- 104. H. A. Nowak
- 105. A. F. Perge
- 106. A. J. Pressesky
- 107. W. H. Regan
- 108. H. Schneider

Allied Chemical Nuclear Products, Inc., P.O. Box 35, Florham Park, N.J. 07932

- 109. R. I. Newman
- 110. A. Schneider
- 111. E. M. Shank

Argonne National Laboratory, 9700 South Cass Ave., Argonne, Ill. 60440

- 112. R. C. Vogel
- 113. D. S. Webster

Battelle Memorial Institute, Pacific Northwest Laboratory, FFTF Drive,
P.O. Box 999, Richland, Washington 99352

- 114. C. J. Foley

Babcock and Wilcox Co., Atomic Energy Division, P.O. Box 1260, Lynchburg,
Virginia 24505

- 115. Harry Honig

CVI Corporation, Box 2138, Columbus, Ohio 43216

- 116. Harold Parish

E. I. Du Pont de Nemours and Co., Savannah River Plant, Aiken, S.C. 29801

- 117. L. H. Meyer
- 118. C. H. Ice
- 119. C. M. Patterson
- 120. E. B. Sheldon
- 121. Harold Hull

Dow Chemical Company, Rocky Flats Division, P.O. Box 888, Golden,
Colorado 80401

- 122. D. L. Ziegler

Environmental Health Research and Training Center, Room 1108, Mayo Building,
School of Public Health, University of Minnesota, Minneapolis, Minn. 55455

- 123. C. P. Straub

General Electric Company, 175 Curtner, Ave., San Jose, California 95125

- 124. R. G. Barnes

General Electric Company, Vallecitos Laboratory, Pleasanton, Calif. 94566

- 125. W. H. Reas

General Electric Company, Nuclear Energy Division, 310 De Guigne Drive,
Sunnyvale, California 94086

- 126. G. D. Hoggatt

- General Electric Company, Medical Development Operations, Bldg. 5,
Schenectady, N.Y. 12300
127. J. J. Kasglaw
128. W. J. Ward III
- Environmental Technology, Inc., Schenectady, N.Y. 12300
129. Angelo Dounancas
- Gulf Energy and Environmental Systems, Inc., Box 608, San Diego,
California 92100
130. L. H. Brooks
- General Electric Company, Midwest Fuel Recovery Plant, Route 1, Box
219B, Morris, Ill. 60450
131. R. W. Lambert
- Idaho Nuclear Corporation, Idaho Falls, Idaho 83401
132. J. A. Buckham
- Idaho Nuclear Corporation, Nuclear Reactor Testing Station, Idaho Falls,
Idaho 83401
133. G. F. Offutt
- Johns Hopkins University, 513 Ames Hall, Baltimore, Maryland 21218
134. Abel Wolman
- Los Alamos Scientific Laboratory, P.O. Box 1663, Los Alamos, N.M. 87544
135. C. W. Christenson
- Mound Laboratory, Bldg. A, Room 155, Miamisburg, Ohio 45342
136. S. Freeman
- Nuclear Fuel Services, Inc., Wheaton Plaza Bldg., Wheaton, Md. 20902
137. W. H. Lewis
- Nuclear Fuel Services, Inc., P.O. Box 124, West Valley, N.Y. 14171
138. R. T. Smokawski
- Iowa Electric Light and Power Co., Cedar Rapids, Iowa 52420
139. Dave Flanagan
- WADCO, Inc., P.O. Box 1970, Richland, Washington 99352
140. C. R. Cooley
- Syracuse University, Syracuse, N.Y. 13210
141. S. A. Stern
- University of California, Berkeley, California 94700
142. W. J. Kaufman
- University of North Carolina, Chapel Hill, N.C. 27514
143. H. C. Thomas
- University of Texas, Austin, Texas 78712
144. E. R. Gloyna
- Vanderbilt University, Nashville, Tennessee 37203
145. F. L. Parker

WRSP0, Atomic Energy Division, Phillips Petroleum Company, Idaho Falls,
Idaho 83401

146. W. L. Slagle

147. G. O. Bright

Atlantic Richfield Hanford Co., Attn: Document Control, P.O. Box 250,
Richland, Washington 99352

148. R. E. Tomlinson

Nuclear Institute "Jozef Stefan," Ljubljana, Yugoslavia

149. J. Slivnik

Union Carbide Corporation, New York, New York 10017

150. J. A. Swartout

151-286. Given distribution as shown in TID-4500 under Chemical Separations
Processes for Plutonium and Uranium category (25 copies - NTIS)