CALIBRATION AND INITIAL FIELD TESTING OF ^{85}Kr DETECTORS FOR ENVIRONMENTAL MONITORING AROUND A NUCLEAR FUEL REPROCESSING PLANT

by

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ABSTRACT

In order to measure ^{85}Kr in the environment around nuclear fuel reprocessing facilities, several types of commercially available detectors were calibrated in the laboratory and then field tested. Among the detectors evaluated were several sizes of flow-through ionization chambers (with vibrating-reed electrometers), thin-walled cylindrical GM tubes, single and double thin-window GM tubes, and β scintillation detectors. A laboratory facility for calibrating all types of external β detectors against standardized ionization chambers has been developed. Following calibration all suitable instruments were field tested in the environs of an operating nuclear fuel reprocessing plant to ascertain their limits of sensitivity, reliability, and applicability.

The most sensitive detector tested, a double window pancake-type GM tube, had a maximum sensitivity under field conditions of 1.8×10^{-8} µCi/cc. However, its window was extremely fragile. A more rugged, single window GM tube had a sensitivity of 3×10^{-8} µCi/cc. All successfully tested instruments are discussed with respect to appropriate environmental monitoring applications.

INTRODUCTION

Off-site surveillance around nuclear facilities is the responsibility of local and state agencies and Bureau of Radiological Health, U.S. Public Health Service. (At the site boundary the prime responsibility is that of the facility operator.) The needs of these agencies for field equipment capable of directly measuring airborne ^{85}Kr concentrations that are apt to appear in the nearby environment of an operating nuclear fuel reprocessing facility have led to studies of possible field detectors.

For the present study only the detection of ^{85}Kr was considered important. Aged nuclear fuel that undergoes chemical reprocessing contains insignificant quantities of ^{133}Xe and relatively small amounts of ^{3}H. Typical ^{133}Xe/^{85}Kr and ^{3}H/^{85}Kr activity ratios are $<10^{-4}\%$ and $<1\%$, respectively (1). Direct detection of ^{85}Kr in the environs of a reprocessing plant was considered feasible because short-term peak concentrations in excess of 0.01 pCi/cc were anticipated. ^{85}Kr concentrations below 0.01 pCi/cc require use of air sampling and laboratory analysis techniques. Air sampling methods used at a nuclear fuel reprocessing plant as a complement to direct measurements are discussed in a separate report (2).

Ionization chambers, in conjunction with vibrating reed electrometers, have been often considered for measuring ^{85}Kr with adequate sensitivity for environmental field surveys (3,4,5,6). The applicability of external detectors, such as GM and scintillation detectors, has also been investigated both theoretically (3,4), and experimentally (3,7,8). Differences between the various theoretical and experimental values for minimum detectable concentrations of ^{85}Kr have been noted. Therefore, a careful intercalibration and field test of all of the above detectors was needed before selection of detection systems appropriate for accurate measurement of ^{85}Kr in the environment around a nuclear facility would be possible.

The initial phase of the present study was a standardization of four commercially available flow-through ionization chambers for response to ^{85}Kr. Secondly, these standardized ionization chambers were used to monitor ^{85}Kr concentrations in a large volume calibration tank containing one of the external GM or scintillation detectors. In this manner the responses of the external detectors also were calibrated. An actual field test of the ionization chamber systems and the most sensitive of the external detectors was then performed at the Nuclear Fuel Services fuel reprocessing plant, Ashford, New York.

Based upon the field test conditions described and the activity levels measured, several choices of field monitoring systems are recommended. Because the ultimate choice of a particular system depends upon the goals of the monitoring program, including geographical, financial, and temporal factors, alternative systems are discussed.

CALIBRATION OF IONIZATION CHAMBERS FOR ^{85}Kr

Ionization Chamber Operation

Based upon a dimensional analysis approach, the relationship between the ionization current measured by a vibrating reed electrometer and a number of its constituent parameters may be represented by equation (1). This equation assumes use of an ionization chamber of volume, V_{std} (cc), which contains a gaseous β source of activity concentration S_V [(dis./sec.)/cc]:

$$I = \frac{Q}{T} = S_V \cdot V_{std} \cdot \bar{\bar{E}}_\beta \cdot \eta \cdot \frac{\varepsilon}{W} \tag{1}$$

where I = current (amp)

Q = charge (coulomb)

T = time (sec)

$\bar{E}_\beta$ = average energy liberated per β (ev/dis), 0.225 Mev for ^{85}Kr

η = efficiency = average energy absorbed per energy unit liberated

ε = charge per ion pair collected (coulomb/ion pair)

W = work done per ion pair formed (ev absorbed/ion pair)

The contribution of the 0.514 Mev γ from ^{85}Kr (0.004 abundance) has been assumed negligible.

Sensitivity has been taken to mean the level of current (above background) produced per unit activity concentration for a given isotope contained within an ionization chamber. From equation (1) it is apparent that sensitivity is a direct function of chamber volume V_{std} as well as η (efficiency). η is a non-linear function of volume and varies with the characteristics of the radiation, carrier gas, and chamber as shown in equation (2)*.

$$\eta = (1-e^{-\bar{\mu}\cdot\bar{r}}) + f_W \tag{2}$$

where $\bar{\mu}$ = average linear absorption coefficient for the average β energy and the carrier gas considered

$\bar{r}$ = average radial distance from point of decay to point of escape (or capture in wall)

f_W = contribution from secondary electrons produced in wall of chamber

For maximum sensitivity to be achieved, the factors contributing to background ionization current that have to be minimized are environmental γ rays, moisture, and alpha radiation from radon and its daughters. In table 1 background levels are presented for unshielded chambers and for the same chambers surrounded by a 2-inch thick lead house. In most cases two inches of lead shielding is quite effective, but the weight makes such a shield impractical for field use.

Moisture accumulation on chamber insulators, and resulting leakage currents, may be eliminated by placing a drying bed at the inlet when the chamber is used in the flow-through mode. In cases of high relative humidity in the environment, the entire chamber and electrometer preamp may be enclosed in a polyethylene bag containing an appropriate drying agent.

Table 1. Ionization chamber backgrounds.

Chamber volume (liters)	Background current, unshielded ($\times 10^{-15}$ amp)	Background current, 2" Pb shield ($\times 10^{-15}$ amp)
0.5	0.4	0.16
1.0	1.4	1.0
2.8	2.8	0.8
4.3	4.2	1.4

Excess α radiation background, due to radon and its daughters, is eliminated by using aged air (30 days) or by passing un-aged air through a radon holdup trap and a filter prior to the chamber. Previous work with activated carbon beds for rare gas adsorption (9,10) has led to selection and brief testing of beds suitable for the present use as a radon trap. The minimum detectable concentrations presented in this report for ionization chambers are dependent upon the use of such a trap. Data used for selecting appropriate quantities of carbon, and operating temperatures, for desired radon holdup times (and minimum ^{85}Kr holdup times) with a flow rate of $\sim$ 3 lpm are given in table 2.

Table 2. Radon trap test results.

Temperature (° K)	Carbon[a] Content (gm)	Carbon[a] Types	Kr holdup time, t_{Kr} (sec)	Rn holdup time, t_{Rn} (min)	t_{Rn}/t_{Kr}
298 ± 2	16	6GC	4.2	9	128
	20	BC	4.8	30	37
	20	FC	6.0	7	70
	125	6GC	45	90	120
	150	BC	22	58	164
	150	FC	61	93	90
274 ± 2	16	6GC	6.8	27	238
	20	BC	5.8	11	129
	20	FC	7.0	11	90
	125	6GC	67	293	262
	150	BC	54	230	256
	150	FC	45	223	297
196 ± 2	10	6GC	21	1800	5143
	20	BC	28	2910	6235
	20	FC	20	2040	6360

[a] Carbon identification (all coconut-base activated charcoals):

6GC = Union Carbide Columbia 6GC, Lot A 47-25, 10-24 mesh
BC = Barneby Cheney AC, Lot 7727, 6-10 mesh
EC = Fisher Coconut, Lot 7760, 6-14 mesh

Calibration Methods

The primary standards used for ionization chamber calibration were obtained from two independent sources: the National Bureau of Standards of the United States (NBS) and Le Commissariat a L'Energie Atomique of France (CEA). The specific activity of the ^{85}Kr (10.6 yr half-life) in the 8.41 ml NBS standard was 0.05 μCi/ml (± 4.3%) on the data of chamber calibration. The CEA standard used to check the NBS calibration had the specifications: specific activity = 8.2 x 10^{-2} μCi/ml (± 2%); ampoule volume = 36.11 ml; filling pressure = 12.65 cm Hg; and filling temperature = 21.7°C.

Similar transfer methods were employed for the NBS and CEA standards. The carrier gases used and the pressure equilibration times allowed were the only significant procedural differences.

The NBS standard was released from its ampoule into an evacuated part of the transfer system. Pure argon was admitted to mix with the krypton for several minutes before the combined gases were expanded into the evacuated 2870 cc ionization chamber. Since this expansion resulted in incomplete transfer, the procedure was subsequently repeated with the addition of argon until essentially all of the ^{85}Kr had been transferred into the ionization chamber. (Argon was used as the carrier gas because of its compatability, with a proportional counting system used for cross-checking results.)

The CEA ^{85}Kr standard was divided in the manifold shown in figure 1 so that known quantities of ^{85}Kr were available for several simultaneous calibrations. The three 1.8 liter tanks were γ-counted to verify their equality and to simultaneously provide a calibration of the NERHL 4" x 5" NaI scintillation system.

Proper selection of field potential for each ionization chamber used (to insure saturation current conditions) was verified before any ion current measurements were made. The potential supplied by a 270 volt battery was found adequate for most laboratory tests.

The initial direct calibration of the 2.8 liter ionization chamber with the NBS standard employed argon as the carrier gas. A comparative response test was required to compare the resulting calibration factor to the one obtained with the CEA standard which used air as the carrier gas. A sample of ^{85}Kr was expanded into an identical pair of evacuated 2.8 liter ionization chambers. Comparative ion current readings taken at exactly 1 atm STP were then used to convert the NBS calibration made with argon to the equivalent calibration for air.

For intercalibration of all sizes of ionization chambers, relative responses to the same ^{85}Kr concentrations had to be determined. Standards were split between different sizes of chambers and responses were compared to calculated concentrations for each chamber. Each chamber, containing a known fraction of a standard, was also γ-counted to simultaneously standardize the 4" x 5" NaI scintillation system for additional source geometries. For ^{85}Kr activities of ≥ 0.5 μCi the γ-counting method provided a rapid and accurate cross-check capability.

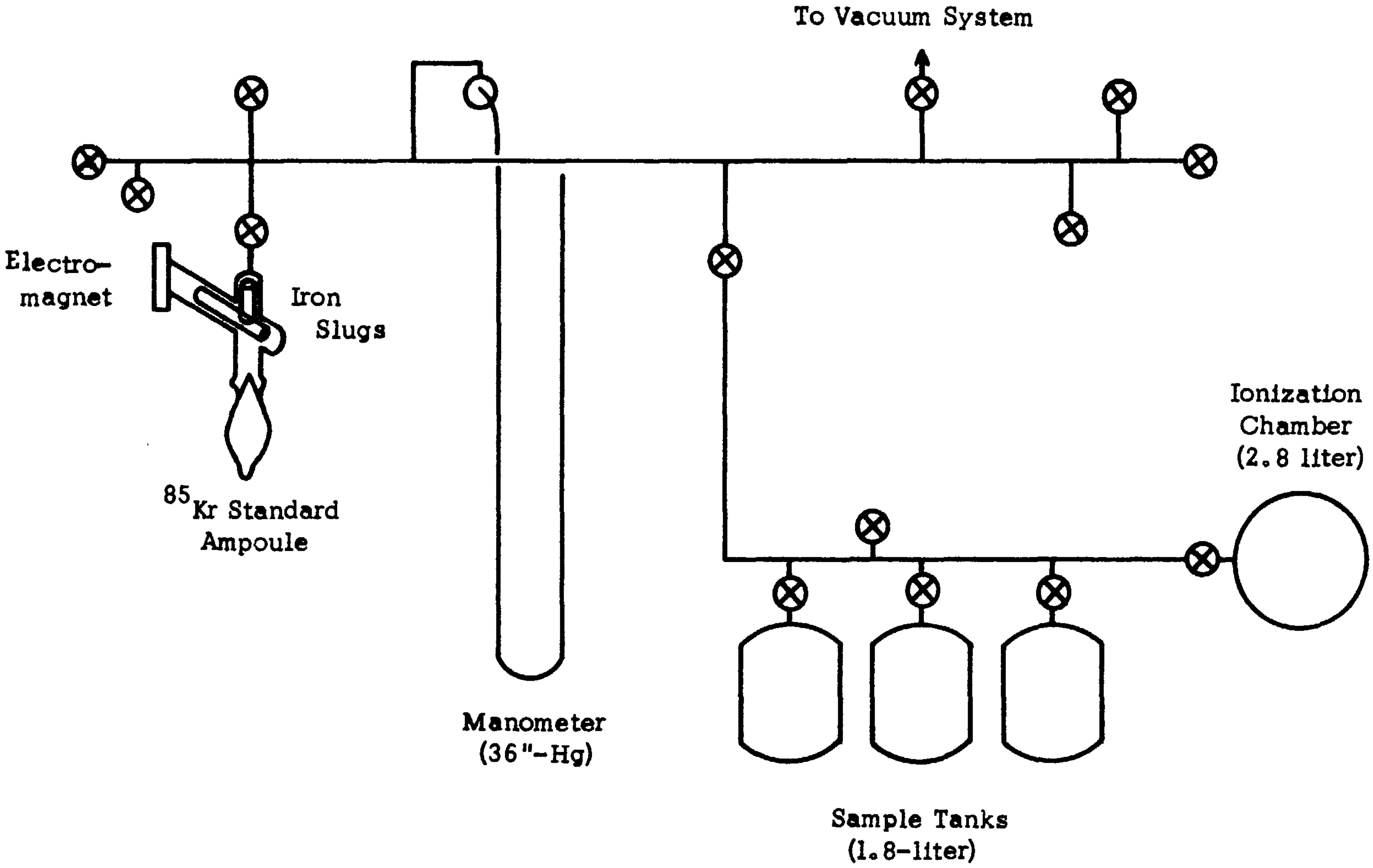

Figure 1. ^{85}Kr standard transfer manifold.

Results and Discussion

The most precise direct calibration of the 2.8 liter ionization chamber employed a CEA standard and the transfer method previously depicted. The 2.8 liter chamber calibration factor, $K_{2.8}$, corrected to STP conditions, is:

$$K_{2.8} = 22.2 \times 10^{-15} \text{ amp/pCi/cc} \pm 7.6\%$$

At 20°C it was:

$$K_{2.8}^{20^\circ C} = 20.5 \times 10^{-15} \text{ amp/pCi/cc} \pm 7.2\%$$

The calibration with an NBS standard in argon (at STP) resulted initially in a different value:

$$^{Ar}K_{2.8} = 30.2 \times 10^{-15} \text{ amp/pCi/cc}$$

However, the ion current in argon was found to be 1.5 times higher than in air for the same ^{85}Kr in air concentration. Thus, the comparable calibration factor for ^{85}Kr in air from the activity of the NBS standard is:

$$K_{2.8} = 20.4 \times 10^{-15} \text{ amp/pCi/cc} \pm 13.4\%$$

or

$$K_{2.8}^{20^\circ C} = 19.0 \times 10^{-15} \text{ amp/pCi/cc} \pm 13.0\%$$

The difference between the calibration factors found using the two different standards is within the quoted margins of error.

The calibration factor found for the 2.8 liter chamber at 20°C and measured chamber response ratios were then used to determine the calibration factors for the 4.3, 1.0, and 0.5 liter ionization chambers. Table 3 lists all of the resulting calibration factors and their total error estimates.

Table 3. Ionization chamber calibration factors for ^{85}Kr in air.[a]

Chamber volume (liters)	Calibration factor ($\times 10^{-15}$ amp/pCi/cc)	Percent error (2s)
4.3	36.5	7.8
2.8 (#1)[b]	20.5	7.2
2.8 (#2)[b]	20.7	7.3
1.0	5.08	9.2
1.0 (V)[c]	5.71	13.4
0.5	2.30	13.5

a At 20°C, 76 cm Hg

b Both chambers of same manufacture (Applied Physics Corp.)

c Only chamber of different manufacture (Victoreen Corp.)

All relative errors are totals derived from twice the sample standard deviation of each measured quantity. The fact that total errors in calibration factors were lower at 20°C than at STP was indicative of an additional 2.6% error involved in the use of the air density correction curves. (The experiments were conducted at 20°C.)

CALIBRATION OF GM AND SCINTILLATION DETECTORS FOR ^{85}Kr

Calibration Facility Description

The NERHL facility (figure 2) for ^{85}Kr calibration of GM and other external β radiation detectors consists of a cylindrical 1.2 x 1.2 meter polyethylene tank with a transparent window/access port, a detector suspended at the tank's center, and a recirculating flow loop connected to an ionization chamber vibrating-reed electrometer monitoring system. This standardized monitor provides an accurate determination of ^{85}Kr concentrations in the continuously circulating gas mixture. As shown in the diagram in figure 3, the gas mixture is pushed by the leak-free peristaltic pump through a drying bed of silica gel or "Drierite," a carbon bed for radon removal, and a dust filter prior to reaching the ionization chamber and flowmeter. The carbon bed effectively holds up radon for many hours when refrigerated in a dry ice/alcohol bath (-78°C) and is used in all calibration tests where the ^{85}Kr concentration in the tank is less than 3 pCi/cc. The pressures in both the ionization chamber and flowmeter are monitored to correct readings to standard conditions.

For any radioactive source, detector response to a particular concentration is dependent upon the geometry of the source and its location with respect to the detector. Although an ideal laboratory approximation to an "infinite" cloud for ^{85}Kr is a tank or balloon with a diameter $\geq$3.6 meters, the 1.2 meter diameter NERHL calibration tank is a more practical geometry that can be related to an "infinite" cloud for calibration of field monitors.

To determine the ratio of the detector counting rate observed at the center of the NERHL calibration tank to the expected counting rate at the center of an "infinite" cloud for the same ^{85}Kr concentration, a theoretical β dosimetric model has been used. The ratio of the counting rates at the centers of finite and "infinite" clouds is equal to the ratio of the dose rates at the same locations, assuming: (1) the dose rate at a point is essentially the same as the kerma rate; and (2) the average kerma rate is proportional to the detector counting rate.

The β dose model of Loevinger, Japha, and Brownell (11) utilized here is valid for homogenious media of low atomic number with an arbitrary distribution of sources and is derived from an experimentally developed point source distribution for β emitters with a wide range of energies and spectral shapes. The equation derived by Loevinger, et al., (11) for the ratio of the dose rate at the center of a finite sphere to that at the center of an infinite sphere was utilized to calculate that a finite sphere with an equivalent volume to that of our cylindrical

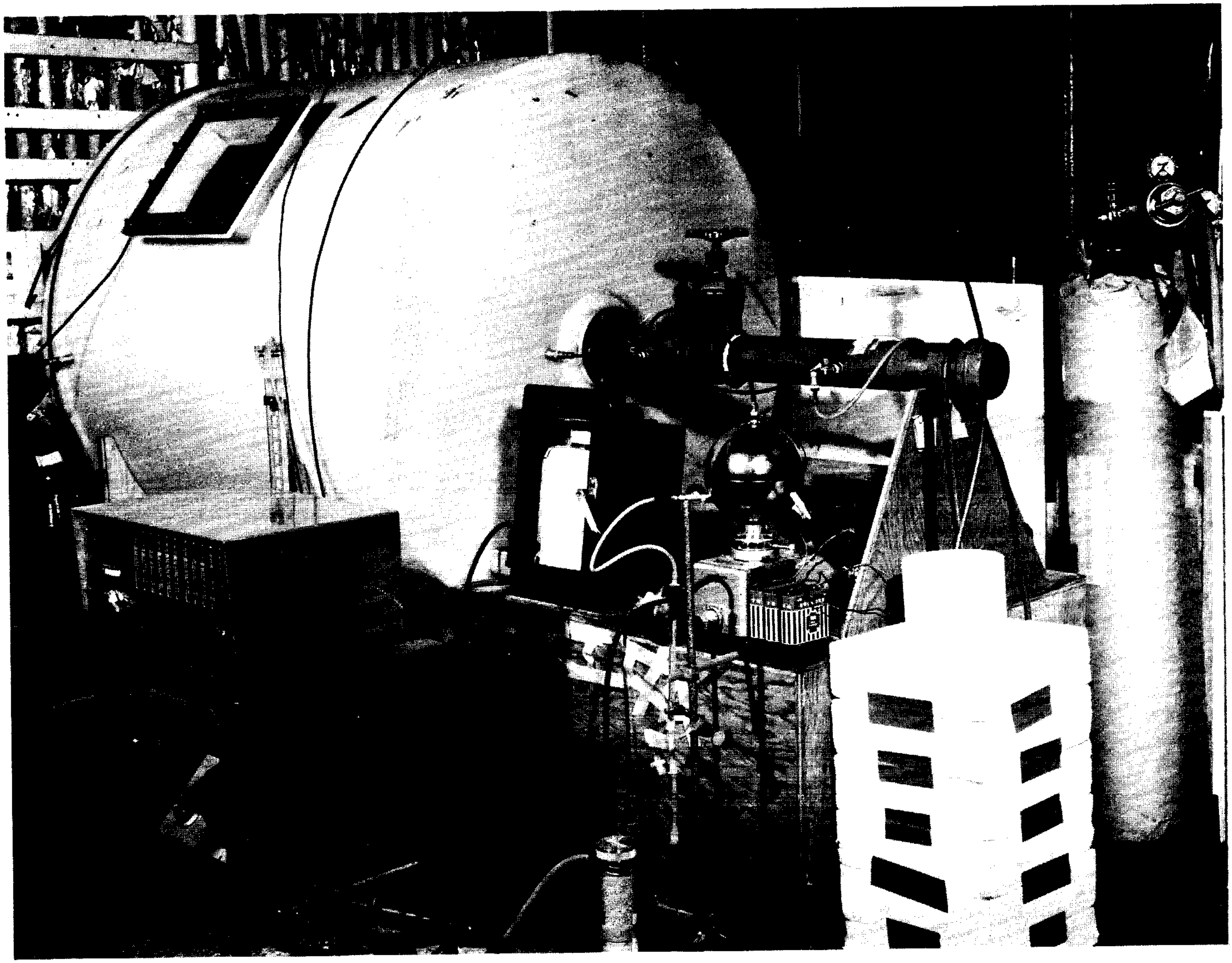

Figure 2. ^{85}Kr calibration facility at NERHL

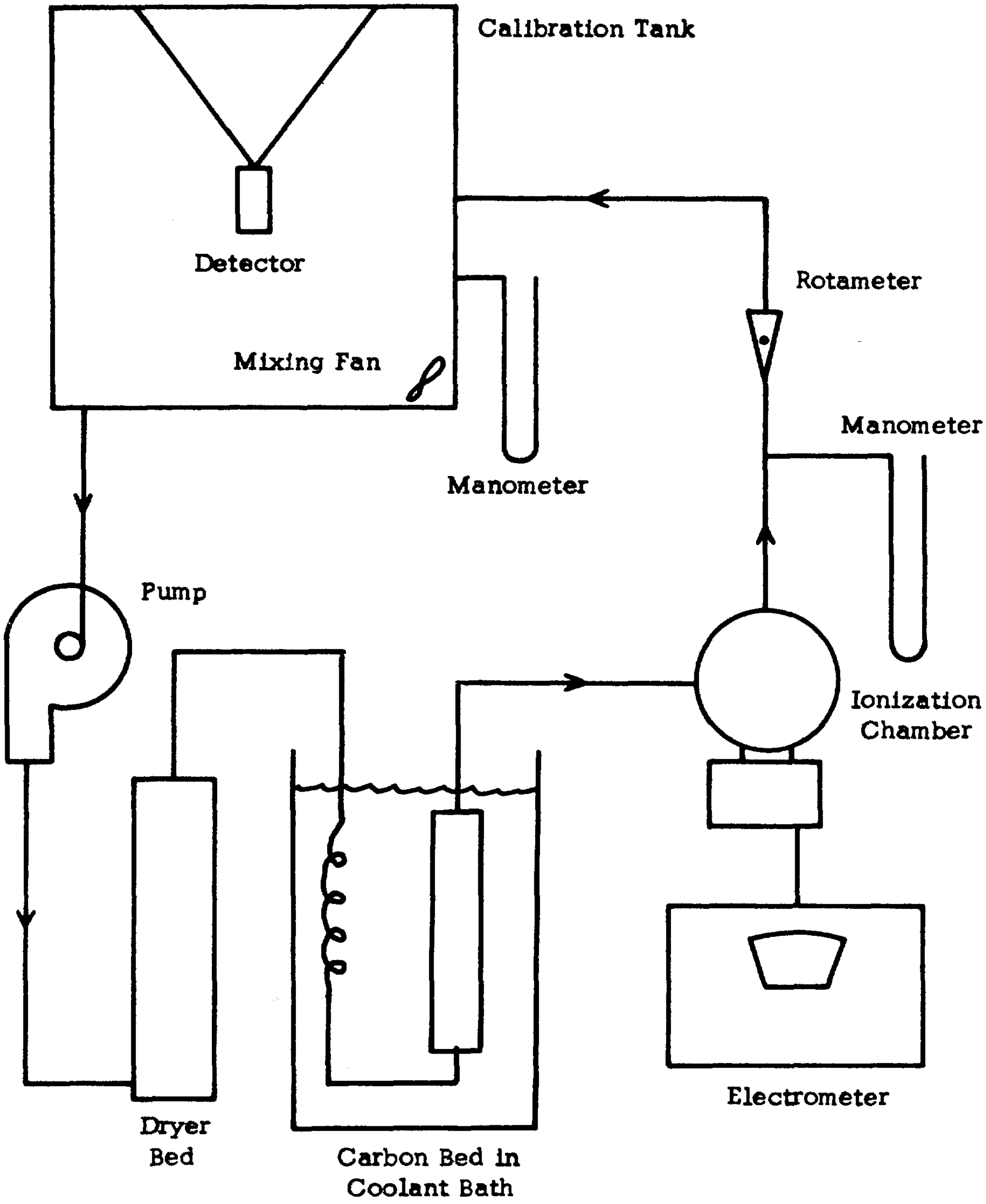

Figure 3. Diagram of ^{85}Kr calibration facility.

calibration tank has a central dose rate 0.808 times that of an "infinite" cloud of ^{85}Kr or 3.22 x 10^{-4} (rad/hr) / (pCi/cc). The validity of "equivalent volume" assumption was verified by comparing the predicted response pattern with measurements of detector response made at the center and ten other locations within the tank.

Instruments Calibrated

The various types of β detectors calibrated are presented below:

1) GM Detectors

Four different GM detectors were calibrated for their response to ^{85}Kr. These detectors, shown in figure 4, were classified according to their three basic configurations.

a) Cylindrical probe - 5" long x 1/2" diameter with ~ 4 π geometry.

b) Single end-window pancake detector - 2" diameter with ~ 2 π geometry.

c) Double end-window pancake detector - 2" diameter with ~ 4 π geometry.

A Picker Magnascaler III (model 5831A) scaler was used for all counting during calibration.

2) β Scintillator

A plastic (Pilot B) scintillator, 1.75" in diameter and 1/16" thick, in conjunction with a RIDL and amplifier single channel analyzer system was compared with the GM detectors listed above for relative sensitivity. An integral counting mode was employed.

3) Flow-through Ionization Chambers

As previously described, the calibration of the flow-through ionization chambers was accomplished by direct transfer of known ^{85}Kr standards. However, minimum detectable concentrations were determined in the calibration facility monitoring loop because of the low concentrations achievable, low external radiation background (~.01 mR/hr) comparable to typical field conditions, and the ability to make measurements with several instruments simultaneously.

In the calibration procedure the ^{85}Kr activity levels were varied from 1 to 100 pCi/cc while count rates were recorded to verify linearity of response vs. concentration. A large number of calibration points was obtained to improve the precision of the resulting calibration factors. Temperature and pressure checks were made periodically to allow ionization chamber readings to be corrected to standard conditions.

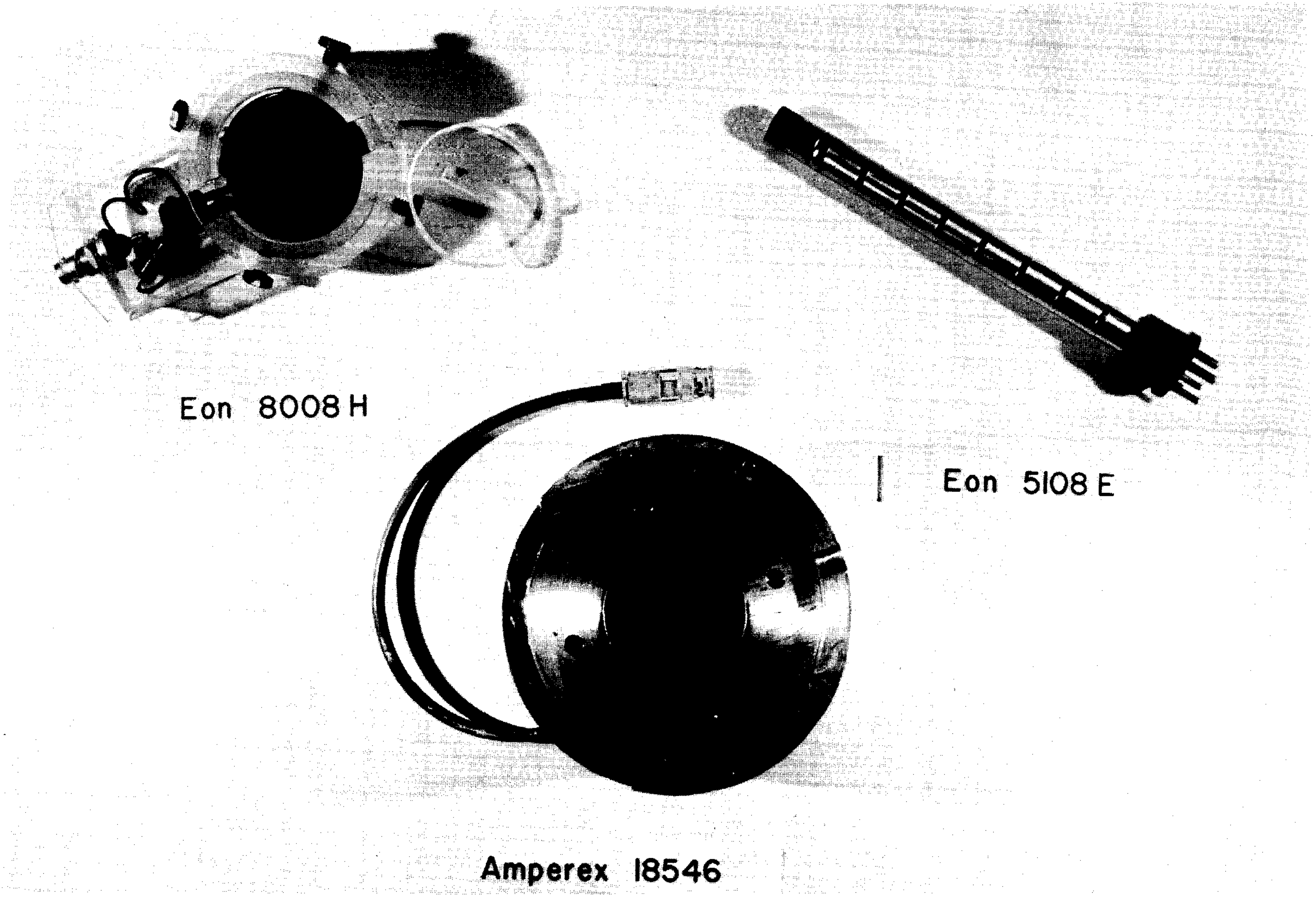

Figure 4. Calibrated GM detectors: double-window pancake GM in holder, single-window pancake GM/Al shield, and cylindrical probe, respectively

Derivation of Minimum Detectable ^{85}Kr Concentrations

The minimum detectable concentration (MDC) is defined here as the concentration corresponding to twice the total sample standard deviation s of the measurement. (This MDC is comparable to the "minimum significant measured activity" defined by Altshuler and Pasternak (12).

$$\mathrm{MDC} = \frac{2s}{C_{85}} \qquad (3)$$

where C_{85} = calibration factor for detector (cpm) / (pCi/cc)

s = total standard deviation of measurement (cpm)

The total standard deviation s is comprised of the standard deviation of the net count s_c and the standard deviation derived from the instrumental and procedural variations s_i. That is,

$$s = \sqrt{s_c^2 + s_i^2} \qquad (4)$$

where s_c is found from

$$s_c = \sqrt{s_g^2 + s_{b'}^2} \qquad (5)$$

s_g = standard deviation of the gross count

$s_{b'}$ = apparent standard deviation of the background

$$\text{when } s_{b'} = \sqrt{s_b^2 + s_{vb}^2} \qquad (6)$$

s_b = standard deviation of single background count

s_{vb} = standard deviation due to background level fluctuations

and s_i takes into account the error in the calibration curve and is evaluated from

$$s_i = \sqrt{\frac{\Sigma(x - \bar{x})^2}{n - 1}} \qquad (7)$$

where x = single measurement of standard activity

$\bar{x}$ = mean of several (n) measurements of standard activity

n = number of activity measurements

Thus, equations (3), (4), and (5) are evaluated to determine s so that MDC may, in turn, be determined from equation (1).

Calibration Results

Calibration factors (C_{85}) for net response to each type of detector to ^{85}Kr in air at 20°C have been determined for "infinite cloud" concentrations ranging from 0.05 to 50 pCi/cc. Figure 5 presents a comparative set of calibration curves for all the pulse-producing detectors tested. The obvious linearity of response vs. concentration made it unnecessary to obtain calibration data for concentrations near the minimum detectable limits for every detector. The mean calibration factors, C_{85}, obtained from the data plotted in figure 5 are given in table 4. The last column of this table lists the total errors for each calibration factor. For ^{85}Kr concentrations above 0.3 pCi/cc, the total calibration errors for these external detectors do not exceed 13.8%. Of this a 7.3% error is associated with the primary ionization chamber calibration.

Table 4. Calibration factors for external detectors in an "infinite cloud" of ^{85}Kr.

Detector type (brand and model)	Inherent geometry	Ave. Lab. background (cpm)	C_{85} $\left(\frac{\text{net cpm}}{\text{pCi/cc}}\right)$	Relative calibration error (2s)
2-window pancake GM (Eon 8008H)	~ 4 π	50	720	13.4%
1-window pancake GM (Eon 8001T)	~ 2 π	45	362	12.4%
(Amperex 18546)	~ 2 π	75	481	13.8%
Clindrical Probe GM (Eon 5108E)	~ 4 π	66	402	13.2%
(LND 719)	~ 4 π	70	477	12.2%
β Scintillator (Pilot B)	~ 2 π	54	316	12.6%

The second single-window pancake GM detector listed in table 4 (Amperex 18546) is identical to that used by Ludwick, et al., (7) in a 63-detector network for ^{85}Kr tracer studies. He reports a calibration factor equivalent to 550 cpm/pCi/cc for one of these detectors, but has found the factor to vary slightly from unit to unit. Thus the difference from the value given in table 4 is not considered to be more than detector to detector variation.

To provide a guide for selections of appropriate ionization chambers for various ^{85}Kr monitoring applications, a table of minimum detectable concentrations (MDC) is presented in table 5. Values in table 5 are given for both shielded and unshielded chambers. The values listed are based upon the following assumptions:

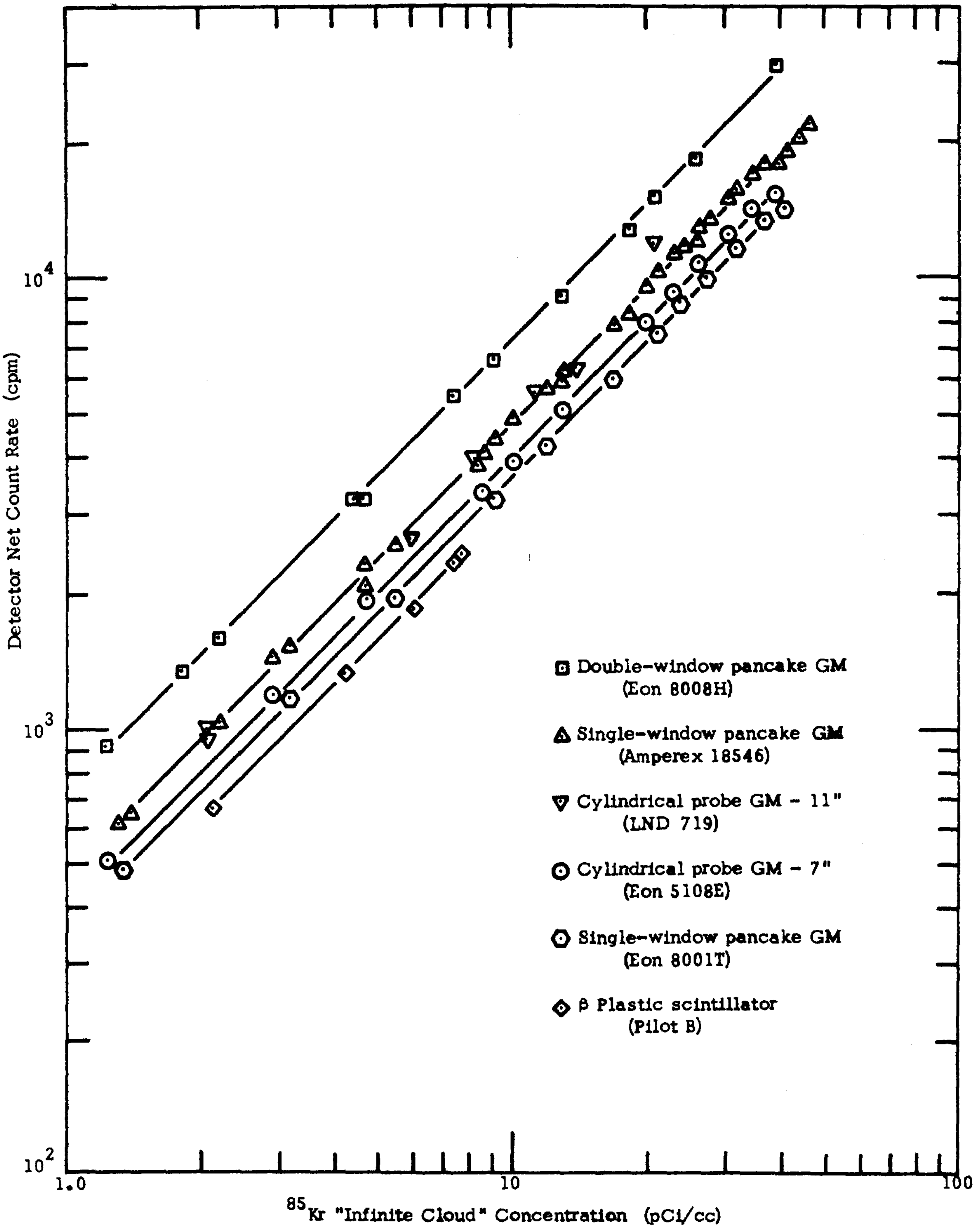

Figure 5. Comparative calibration curves for external β detectors.

1) Air entering the chamber is dry and radon-free.

2) The calibration factor obtained for 20°C, 76 cm Hg applies (table 3).

3) Sampled ^{85}Kr concentration is not changing rapidly (i.e., a 15 minute reading is allowed).

Table 5. Minimum detectable concentrations for ^{85}Kr in ionization chambers.[a]

Chamber volume (liters)	MDC ^{85}Kr chamber unshielded (pCi/cc)	MDC ^{85}Kr chamber/2" Pb shields (pCi/cc)
0.5	$1.3 \cdot 10^{-1}$	$1.5 \cdot 10^{-1}$
1.0	$1.9 \cdot 10^{-1}$	$1.5 \cdot 10^{-1}$
2.8	$3.9 \cdot 10^{-2}$	$3.1 \cdot 10^{-2}$
4.3	$3.0 \cdot 10^{-2}$	$2.3 \cdot 10^{-2}$

[a] Cary-Tolbert design (Applied Physics Corp.)

Equations (3) through (7), given earlier, were applied to data obtained for all of the external detectors tested to calculate the minimum detectable concentrations for each one. These MDC's are listed in table 6. The maximum times assumed to be available for each count were 4 hrs for sample and 30 min for background--30 min background was chosen to minimize magnitude of s_{vb} in equation (6). Short count (10 min sample and 10 min background) values are also given for comparison. Total instrumental errors were assumed to be negligible when scalers were used to record count data. Use of ratemeters with chart recorders, instead of scalers, will reduce sensitivity according to the additional levels of error introduced.

Conclusions on ^{85}Kr Calibration

The calibration curves presented indicate the linearity and precision of detector responses over the range of ^{85}Kr "infinite cloud" concentrations of interest (0.05 to 50 pCi/cc). Comparative curves for 5 different GM detectors and a thin plastic scintillator showed that the best GM detector was a factor of 2.3 times more sensitive than the scintillator. When 4 hrs was the maximum counting time available for a sample count, and 30 min was available for its appropriate background, ^{85}Kr concentrations as low as 0.007 pCi/cc were detectable in the laboratory. Increased variability of field backgrounds were expected to reduce sensitivity measurably, to 0.02 pCi/cc for similar counting periods. Thus, for these long counting times all of the GM detectors would be capable of detecting ~1/7 of the 10CFR20 guideline for the general population (13)[1]. For a 20-minute total counting

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[1] 3×10^{-7} µCi/cc (submersion)

Table 6. Minimum detectable ^{85}Kr concentrations for calibrated external β detectors*.

Count Time Bkgnd/Sample	Laboratory MDC (pCi/cc)		Field MDC (pCi/cc)	
	Long Count[a] 0.5/4 hr	Short Count[b] 10/10 min	Long Count[c] 0.5/4 hr	Short Count[d] 10/10 min
Detector Type (Model)				
2 window pancake GM (Eon 8008H)	.007	.012	.020	.012
1 window pancake GM (Amperex 18546)	.011	.024	.042	.027
(Eon 8001T)	.014	.025	.040	.025
Cylindrical Probe (LND 719)	.011	.024	.043	.024
(Eon 5108E)	.013	.024	.046	.028
β Scintillator (Pilot B)	.016	.029	.045	.029

* Notes on counting conditions:

(1) All values assume the MDC = $2s/C_{85}$.

(2) Total instrument errors are assumed to be negligible in each case.

(3) The magnitude of relative background variations ($2s_{vb}/B$, where B = background count rate) assumptions for count intervals are denoted by the following:

Subscript	Relative Background Variation($2s_{vb}$)
a	4.8%
b	9.8%
c	27.4%
d	11.8%

(4) 0.3 pCi/cc MPC (air) 10CFR20 for general population.(13)

time, 10 min sample and 10 min background. due to a smaller value for s_{vb}, all the detectors could measure <1/10 this guideline field level.

It should be noted that the minimum detectable activities presented here are the ^{85}Kr concentrations detectable when the count accumulated over a specified time interval is read out at the end of that time interval, and is then compared with an appropriate background measured for a similar interval. Since maximum sensitivities depend strongly upon background levels and their fluctuations, background data acquired for each type of detector are as important as data for relative response to ^{85}Kr. (This fact is demonstrated by the relationship between the single window pancake-type GM tube and the first cylindrical probe GM tube. The former has a lower minimum detectable limit due to its lower background, even though the latter has the higher relative response to a given concentration of ^{85}Kr.)

^{85}Kr FIELD MONITORING TESTS

Test Conditions

A field trip to the Nuclear Fuel Services reprocessing plant, Ashford, Cattaraugus County, New York in June 1969 permitted testing and evaluation of several calibrated instruments. The following discussion concentrates upon this evaluation and the test results that illustrate important characteristics of each detector with respect to environmental monitoring applications.

A summary of these findings is also included in the broader concurrent field trip report "An Investigation of Airborne Radioactive Effluent from an Operating Nuclear Fuel Reprocessing Plant," (2) which gives details of the composition of the stack effluent, the location of the environmental monitoring stations, and interpretation of sampling and monitoring results.

The detector field tests were conducted during two separate fuel dissolution cycles. The ^{85}Kr activity discharged from the stack for each tonne of fuel dissolved average 5×10^3 curies (2). (The plant was designed to process one tonne/day.) This activity was monitored at the stack by both the GM stack monitor normally operated by the plant and a one liter flow-through ionization chamber system standardized at the NERHL laboratory. These source data, in addition to plant and field meteorological data, enabled projections of plume location and corresponding selection of four field monitoring stations during each dissolution cycle. (See figure 6.)

The ^{85}Kr detectors utilized at these field stations included two single-window pancake GM tubes (Amperex 18546 and Eon 8001T) and two ionization chambers (4.3 and 2.8 liters) with vibrating-reed electrometers. Since evaluation of instrument performance was not the only goal of the field tests, detectors with the poorest MDC levels (Eon 5108E and

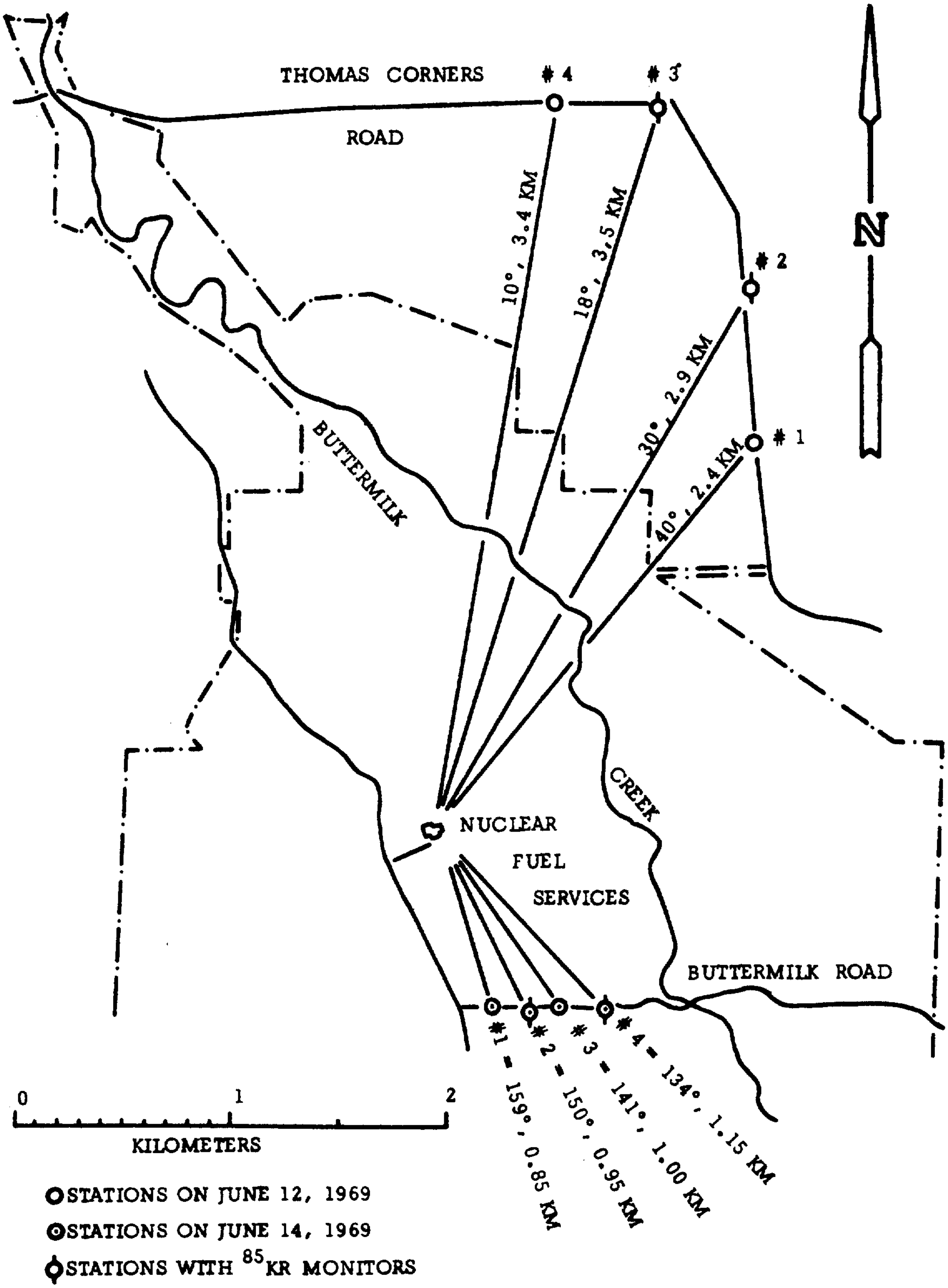

Figure 6. Location of environmental monitoring and sampling stations.

β scintillation) were not used in favor of those that would yield data most useful for plume characterization. Two double-window pancake detectors (Eon 8008H) had ruptured windows (cause unknown) and replacements were not available in time for the field tests. The second cylindrical probe detector (LND 719) was calibrated and tested at the laboratory after the field trip.

Typical field sensitivities for each detector were evaluated after accumulation of field background data, not only at the monitoring sites, but also at an additional site several miles from the plant property. Extraneous elevations in observed backgrounds due to power line noise or level fluctuations were avoided by thoroughly cross-checking backgrounds obtained with different combinations of power supplies, regulators, and line filters.

Test Results

GM Detectors

All the GM detectors tested under field conditions operated satisfactorily without problem and provided adequate sensitivity for characterizing ^{85}Kr activity levels in the plume passing over the monitoring site during the fuel dissolution process. One field system employed a portable recording ratemeter with a 40-second time constant and 2.5 inch-wide chart for its printout. The total error was $\leq$ 18% for ^{85}Kr concentrations above 0.1 pCi/cc using this system, compared with a total error of $\leq$ 14% for the other field systems which used scalers to record counts for a preset time interval.

A typical plot obtained from a single-window GM tube-recording ratemeter combination is shown in figure 7. This figure shows that the concentration levels reached 1 to 2 pCi/cc for the time intervals that the plume passed over the on-site monitoring station (see figure 6). Comparable results were obtained when GM counts were recorded every 3 minutes from a scaler. Data taken as 10-minute scaler counts gave less information about peak levels, but provided adequate integral values for computing average concentrations. Table 7 lists these average ^{85}Kr concentrations observed at each monitoring station during the two fuel dissolution runs. The dosimetric significance of these levels is discussed elsewhere (14).

Backgrounds were measured for 10 minutes prior to following each dissolution run. Backgrounds measured in the field were essentially the same as those measured in the NERHL calibration tank.

The most sensitive detector tested in the field (MDC = .025 pCi/cc) was the single window pancake-type GM tube with the 3.5 mg/cm^2 window (Amperex 18546). The other single window pancake-type detector (Eon 1008T) had slightly less sensitivity for ^{85}Kr in spite of its thinner 1.4 mg/cm^2 window.

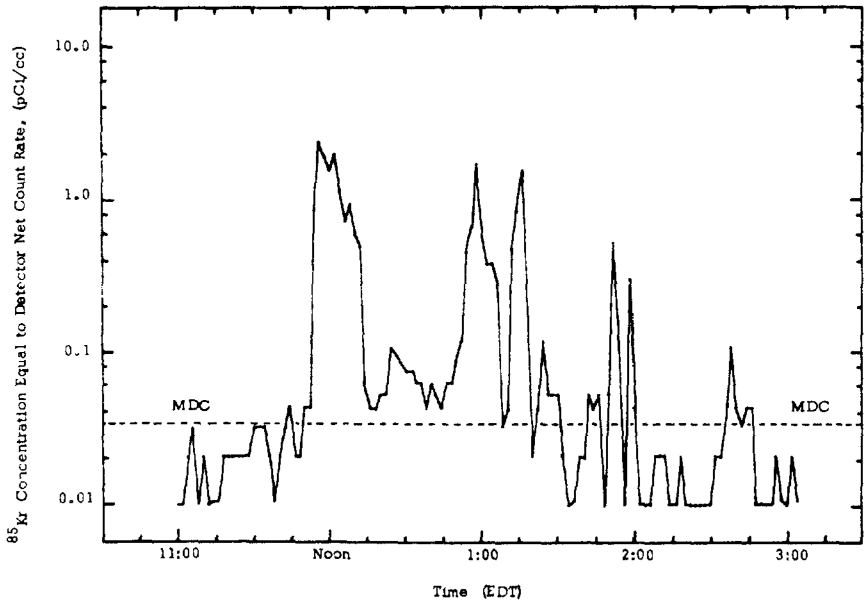

Figure 7. Typical field GM-ratemeter plot for fuel dissolution period (on-site).

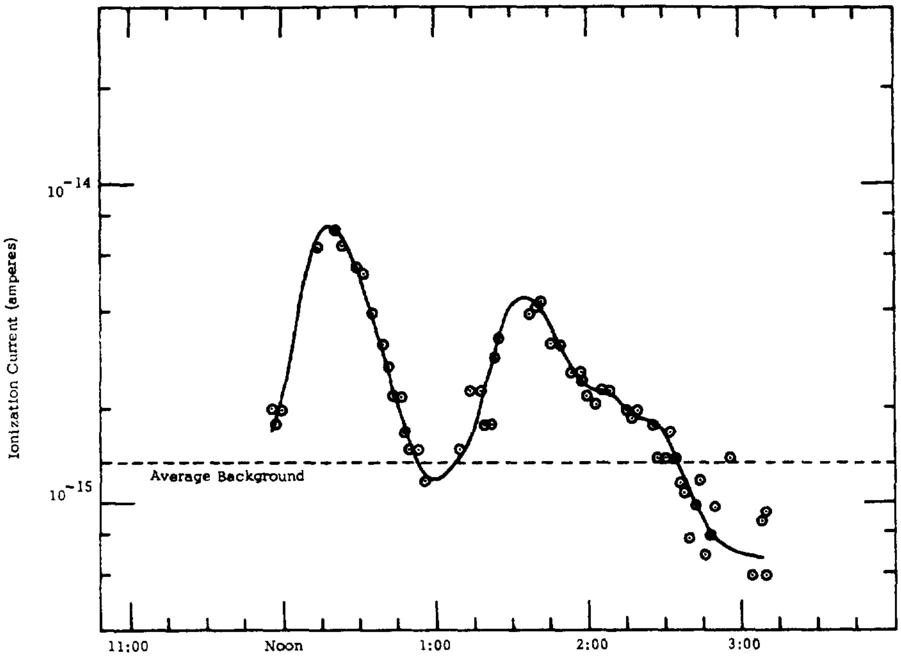

Figure 8. Response of 2.8 liter ionization chamber field monitor during fuel dissolution period (on-site).

Table 7. Average ^{85}Kr concentrations at field monitoring stations.[a]

Date[b]	Data averaging time (min)	Measurement interval (hrs:min)	Avg. ^{85}Kr conc. (pCi/cc)
6/12	2[c]	3:20	$6.4 \cdot 10^{-2}$
6/12	10[d]	2:32	[e]$1.7 \cdot 10^{-2}$
6/14	3[d]	2:42	$4.8 \cdot 10^{-1}$
6/14	2[c]	2:42	$2.8 \cdot 10^{-1}$

[a] Averages are expressed for measurement interval given. Levels returned to background after 3 to 4 hours following the start of fuel dissolution. Since there is no more than one dissolution cycle per day, 24-hr averages are ~ 1/8 of the values given in this table.

[b] On 6/12 field monitors were outside the site boundary; on 6/14 they were on-site (figure 6).

[c] From ratemeter record.

[d] From scaler.

[e] Underestimate--monitoring started 38 minutes after the commencement of fuel dissolution.

The cylindrical probe with a 30 mg/cm^2 wall (Eon 5108E) was only used for brief background tests in the field. Though its relative response to ^{85}Kr was slightly higher than that of the 1.4 mg/cm^2 single window pancake GM during calibration, its higher background response diminished its maximum sensitivity and resulted in its relegation to back-up status for the field tests. However, extended field testing in the immediate vicinity of our laboratory during rainy, as well as clear, weather with this type of cylindrical probe has proven that its durability is a strong argument favoring its choice for future field use, especially for measurement periods exceeding a day. The second cylindrical probe calibrated (LND 719) has slightly greater sensitivity than the first (Eon 5108E) due to its greater active length; and its durability characteristics seem about the same in the mock field tests carried out near the laboratory since the field trip. In contrast, the double window GM detectors, another of which has ruptured for no apparent reason since the field trip, cannot presently be recommended for use outside the laboratory.

Ionization Chambers

Figure 8 shows the response of one of the 2.8 liter ionization chambers used as an environmental monitor during the same dissolution and at the same location as that for which GM data have been presented in figure 7. The smoothing and flattening of the ionization chamber response curve appeared to be due primarily to the size of the radon traps used in these monitoring systems. Post-field-trip testing has indicated (table 2) that the 130 gm activated carbon bed used in the field system was much too large for its intended purpose. The time for a 1-minute wide (FWHM) pulse of ^{85}Kr activity to produce its peak response in the 2.8 liter ionization chamber after travelling through 130 gm of carbon at -78°C was $\sim$ 27 minutes. Attempts to relate levels of ionization chamber readings to inputs of activity were fruitless when the response time of the system was this long. Further data indicated that 20 gm of charcoal at -78°C (table 2) will effectively hold up ^{222}Rn 34-48 hrs, while affecting the passage of ^{85}Kr slightly. Even with this small carbon bed, however, the integrating nature of the flow through chamber itself may make it extremely difficult to relate its response to the rapidly fluctuating ^{85}Kr levels that are transported to it by the wind.

The calibrated 1.0 liter ionization chamber used for checking the calibration of the existing stack effluent monitor (in the plant), on the other hand, operated quite satisfactorily. This smaller ionization chamber system, with a 130 gm carbon bed operated at 37°C, yielded much faster response ($<$45 sec time constant) than that of the field monitoring systems. Changes in the stack concentration of ^{85}Kr were not rapid compared to this response time (after the initial 10-minute rise at the commencement of the fuel dissolution process), and the ^{222}Rn background was insignificant compared to the external γ radiation background (1-2 mR/hr) at the stack monitoring location. Thus the stack monitoring ionization chamber's readings were both accurate and relevant, when background corrections were made for all significant changes in the external radiation field.

It should be noted that although the ionization chamber systems can be made to operate in the field, the degree of care, number of precautions, and amount of operator training required to obtain usable data for environmental levels, and the questionable nature of the data obtained when the field levels passing the instrument are fluctuating rapidly, all weigh heavily in favor of using simpler systems for this purpose. In addition, with the proper choice of counting conditions, several of the GM systems tested can detect lower concentrations of ^{85}Kr than a 4.3 liter ionization chamber.

Errors and Minimum Detectable Concentrations

The total errors, in the field measurements made with GM detectors, $\leq$ 18%, consist of the total calibration errors, the variations of background, the counting errors, and instrumental errors (such as chart alignment, readability of scale, electronic noise and drift). Ionization current averaging errors are controlled by the electrometer system's time constant rather than by "counting time." The importance of making appropriate temperature, pressure, and external background variation corrections for ionization chambers to avoid introduction of additional errors is evident and must be considered in field usage, especially for stack monitoring applications.

The minimum detectable activities presented in tables 5 and 6 have been found to represent those in the field, but attention must be paid to assumptions and conditions specified to obtain each set of figures, especially external γ radiation levels.

CONCLUSIONS AND RECOMMENDATIONS

Detector Sensitivity

All the detection systems tested under field conditions provide adequate sensitivity for characterizing environmental ^{85}Kr activity levels from the plume of a nuclear fuel reprocessing plant during a fuel dissolution process. The most sensitive detector field tested is a single window pancake-type GM tube (Amperex 18546) with a MDC of .025 pCi/cc. The double window pancake GM (Eon 8008H), tested only in the laboratory, appears to have about twice the maximum sensitivity of the field tested detectors, but probably cannot endure field conditions. For short term measurements, however, even the least sensitive GM detector tested has adequate sensitivity for measuring the 1.0 to 10 pCi/cc levels that can occur at a monitoring site momentarily crossed by the plume during a 3-hour fuel dissolution period.

Detector Reliability

The thick-walled (30 mg/cm^2) cylindrical probes were the most durable of the detectors tested. Their ability to withstand mild shock and rain imply reliability for long-term field monitoring applications. Under the same field conditions the single and double-window tube pancake tubes, though more sensitive, may suffer from frequent window failures. These latter detectors are available with either 1.4 or 3.5-4 mg/cm^2 windows. The thicker window is recommended for field use. Its choice results in a mere 5% degradation in window transmission from the 95% value quoted for ^{85}Kr β particles impinging upon the 1.4 mg/cm^2 window. The increased durability is certain to compensate the user for the slightly lowered sensitivity of the heavier windowed model.

The ionization chambers that have been field tested can be operated as field monitoring systems; but these systems require experienced operators. Wind, humidity, radon background, mechanical shock, and inadequately regulated power and rapidly fluctuating ^{85}Kr levels are the major field problems that have to be overcome to obtain reliable data.

Choice of Detector for Field Monitoring

Long-term (weeks to months) environmental monitoring would demand the most sensitive detectors and systems that could endure the environment with a minimum of attention. The choice at present is between the single windowed pancake tube (Amperex 18546) and the thicker walled (30 mg/cm^2) cylindrical probes (Eon 5108E or LND 719) which, though slightly less sensitive, is certainly the most durable of the detectors evaluated.

Choice of Detector for Stack Monitoring

In a separate phase of the field study a 1.0 liter ionization chamber monitoring system has been successfully used to measure the ^{85}Kr concentration in the plant's stack effluent monitoring loop. However, no particular improvement over conventional stack noble gas monitors consisting of GM or plastic scintillator detectors in a large cavity was evident. In fact, the rapid response, ease of replacement, and relative insensitivity to high humidity conditions of these latter detectors probably offer significant advantages over ionization chambers for routine stack monitoring operation. It was concluded that field ionization chamber systems for ^{85}Kr detection have their chief value when used for in-line calibration of existing ^{85}Kr monitors of other types.

Choice of Counting Times

In a field situation there are short periods of high activity in the vicinity of the detector interspersed with long periods during which only background is observed. The dose imparted by the activity causing these peaks in counting rates can account for 90-95% of the total ^{85}Kr dose at that location. These peaks of activity can be most precisely evaluated if counting and printout periods are kept short. An ex post facto analysis of the recorded data reveals the duration and magnitude of the obvious peaks of activity, as well as the background and its fluctuations for similar time intervals. Integration of the counts corresponding to the activity peaks and subtraction of the appropriate backgrounds allows conversion to integrated concentration values. These integrated concentration levels can then be averaged over any longer time period during which no ^{85}Kr activity is present (table 7, footnote a). This measurement procedure results in much smaller total relative errors than would be attainable with a smaller number of long counting periods.

GM and other external pulse-generating detectors provide the user with great flexibility in the choice of counting (or averaging) periods. The shortest practical measurement periods are recommended, since they can provide the precision necessary to resolve peak levels occurring for short intervals. Sensitivity or precision may suffer slightly if a counting period is chosen to match a multiple (either a fraction or an integer) of the period used for averaging the value of a meteorological factor (such as wind speed or direction), but the resulting data actually describe the behavior of the ^{85}Kr plume for the period of dosimetric significance. Thus, a properly operated GM detector system in conjunction with adequate meteorological and source strength data appears to be the optimum combination for obtaining meaningful environmental monitoring results that can be translated into reliable estimates of ^{85}Kr dose commitments.

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DISCUSSION

WOODRUFF: It would seem to me that these detectors are not specific to Krypton-85, but would also be sensitive to any beta emitter or even a gamma emitter. Is this a problem, or does the Krypton-85 activity so dominate the situation that you don't worry about the others?

SMITH, DG: Your last comment is correct. There is so much Krypton-85 that when there was not Krypton-85 being eluded we couldn't detect anything above a normal outdoor background with these detectors. We did take other gas samples in the stack and analyze them in our laboratory to ascertain the relative concentrations of tritium in the stack and Krypton-85 in the stack for this period. As a matter of fact, the Tritium in the stack was only about 10% of the total Tritium release per day predicted by the safety report (so we are now looking for the other 90%).

MAECK: I may have missed the point, but what's the significance of the Krypton level? Is it above maximum permissible levels? Is it below and if it's below, how far is it below?

SMITH, DG: It is far below. We made some dose estimates based on these two days' data which would lead you to conclude that if you were standing at the site boundary the increase in dose per person over background might be over 10 to 12 mr per year. (Correction: 0.3 to 3.2 mrem/year. See References 2 and 6.) So, from a hazard standpoint, we're beginning to feel that we can say that there's really no problem. But, there is continued public pressure to get the measurements and to prove that there is no problem. You can do this most precisely by measuring each activity peak that is eluded, integrating these events over a year, showing that you have measured (at the stack environment) all the Krypton that has come out for a year, and indeed it does not exceed your projections of the annual value. Therefore, the study area that might be most interesting is use of Krypton-85 from the fuel reprocessing plant for meteorological studies. You've got a built-in tracer, and since you don't have a health problem, and that tracer is going to be eluded daily, you have a very good set-up for checking out your meteorological predictions in hilly country.

SIMENS: Following up on your last remarks, what's the greatest distance from the source once you've taken measurements?

SMITH, DG: About three kilometers.

SIMENS: Do you feel like you can go further than that?

SMITH, DG: Yes, not a lot further, maybe about five.

WILHELM: You showed the slides with the brownish plumes of nitrogen oxide and you told us you drew some gas in the monitor. Did you have some corrosion problems with your monitoring?

SMITH, DG: I didn't show the slide of our sampling train and stack monitoring system. We had filters, carbon beds, a scrubber, and a drier bed preceding the ionization chamber so that we could clean up the air to essentially pure air and Krypton. Air samples were taken downstream of this ionization chamber.

WILHELM: This is a thing which I have been working on for a long time. Are you absolutely sure that the Krypton doesn't stick to the charcoal?

SMITH, DG: We experimented with different sizes of adsorption systems to find out what size wouldn't perturb the response of the ionization chamber in the stack. Now, for that first burst of activity, let's say the first fifteen minutes of that dissolution period, our ionization chamber did lag slightly in its readings, but after that, the chamber readings, on the integrated samples, and the response of the plant's GM detector were almost identical.

WILHELM: By the way, could you give me a number for the concentration of NO_2 and N_2O_4, respectively in the off-gas?

SMITH, DG: No, I really don't know the concentration. I think it varies greatly over a period of time, because the temperature of the bath is not constant. When the operator decides that the Krypton isn't the fuel isn't being dissolved rapidly enough, he periodically charges this bath with more steam to raise the temperature. And when you saw that Krypton-85 monitor's curve, you saw some fluctuation, it wasn't just an exponential drop off. There were some little dips and peaks in it. This is the result of changing the bath temperature which would affect the rate of ellution of the Nitrogen-dioxide.

WILHELM: I wonder what the peak concentration could be in the off-gas?

FIRST: Judging from the color of the plume in the photograph, and comparing it with plumes of nitric acid plants, I would estimate the concentration to be 1% by volume. It may be more of a problem to residents than the Krypton!

QUESTION: If your primary objective is simply to establish a dose rate over an extended period of time, it seems that perhaps there are other ways it could be investigated to give you an integrated dose such as a thermaluminescent dosimeter set up somewhere around the site. Have you considered this as a substitute system?

SMITH, DG: Yes, New York State has asked us whether we could test the applicability of TLD's to this type of measurement. And there really hasn't been a lot of work done on the beta response of TLD systems. There have been a few studies most of them at much higher dose rates. When you get down to environmental conditions and environmental levels, I don't think anybody has really identified the limit of detectability for Krypton-85 -- at least not any published study that I have seen. We did do some work at our laboratory on this problem a year and a half ago and the results were so discouraging that I don't think they ever came out with a publication. But, they might have been able to see concentrations that were continuously up around 10^{-6} and 10^{-5} micro curies/cc. You might have noted from the diagram of field concentration of Krypton-85 vs time (Figure 7) that our peak field concentrations near the site boundary were only 2×10^{-6}; and that's for a fifteen minute period, once a day, less than two hundred days a year. Thus, I think that we are talking about something far below the TLD's limits of sensitivity, with the possible exception of $CaSO_4$ TLD's that would be changed and read daily.

WATSON: You mentioned a dose rate in roentgens per hour; would you elaborate on that unit since Krypton-85 is primarily a beta emitter.

SMITH, DG: Would you repeat that question, I don't quite follow what you want.

WATSON: You mention a dose rate estimate based on your measurements in r/hr.

SMITH, DG: I'm sorry, I was careless, that was rad/yr.

WATSON: Roentgens per hour or 5/yr, the time base is not important to the question.

SMITH, DG: Rem per year.

WATSON: Rem per year. And was this to the total body or to the skin?

SMITH, DG: Well, it's total body immersion, with dose rate at skin surface calculated for beta radiation. The gamma was comparatively insignificant.

WATSON: Isn't the beta insignificant to the total body also?

SMITH, DG: Well, there is a public health service report called "A Review of the Radiological and Environmental Aspects of Krypton-85" (BRH/NF 69-16). It was published last September. And it goes into a full discussion of that point and the modifications of the 10 CFR 20 guideline for total body immersion situation where the isotope is a beta emitter. We were assuming that total body was a point receiver for this calculation. But if you want a more refined calculation you would take advantage of that fact that it is not the point and that the depth dose at 1 mm $\simeq$ 0.08% of the beta surface dose. In this latter situation the gamma dose is more important than the beta dose: gamma dose at 1 mm $\simeq$ 0.9% of the beta dose (see Reference 6).

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

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ABSTRACT

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

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

INTRODUCTION

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

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

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

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

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

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

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

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

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

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

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

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

THE SELECTIVE ABSORPTION PROCESS

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

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

PILOT PLANT

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

Plant Description

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

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

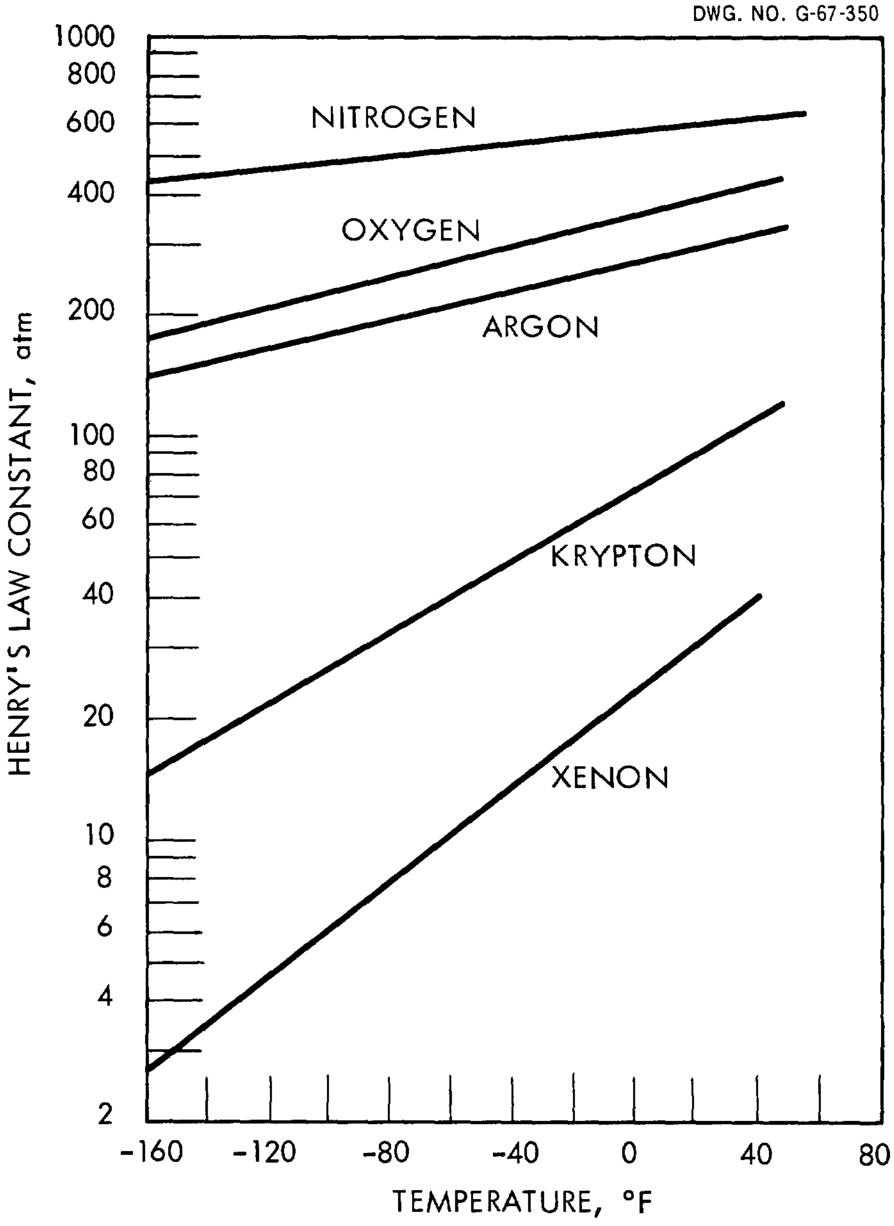

Figure 1

RELATIVE SOLUBILITIES OF GASES IN REFRIGERANT-12

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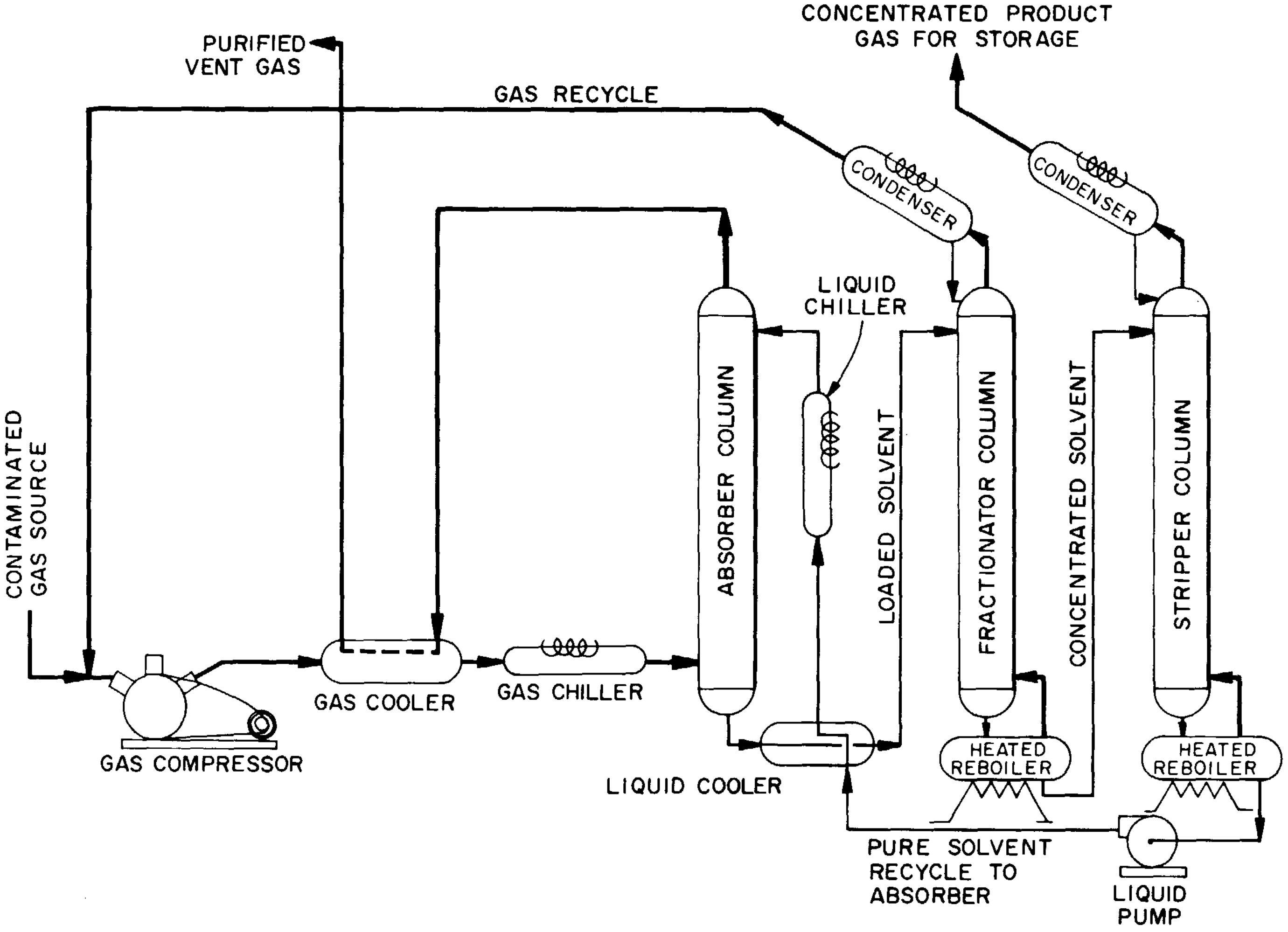

Figure 2

KRYPTON-XENON ABSORPTION PROCESS PILOT PLANT
SCHEMATIC FLOW DIAGRAM

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

Process Flow

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

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

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

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

TEST RESULTS

In Phases I and II, the pilot plant was intentionally operated over a wide range of processing conditions to define, for each refrigerant solvent, the process capabilities and to establish parametric dependencies. In all, 34 pilot plant tests were conducted with refrigerant-12[14] and 40 tests were conducted with refrigerant-11[15]. Xenon was not used in the first two phases of the project since it is felt that a plant designed and operated to remove krypton from the process gas will easily remove at least a comparable amount of xenon, because xenon is more soluble than krypton in the refrigerants. Tests are, however, tentatively planned with xenon during the Phase V work. A summary of the first and second phase test conditions and results is given in table I. In each and every test, the krypton concentration in the absorber feed was deliberately forced to a level high enough to yield at least a detectable quantity (5 to 10 ppm*) of krypton in the off-gas. Consequently, some of the experimental runs were conducted with a relatively high absorber feed krypton concentration. While krypton removals to below detectable limits are impressive and, in fact, sometimes resulted in situations where the feed concentration was inadvertently allowed to drop too low, such removals do not provide quantitative information necessary for the exact analysis of column performance. As previously discussed, the lower concentration limits may be investigated later during Phase V of the scheduled program where tracer experiments are planned. No difficulties are anticipated in attaining good performance at these lower concentration levels.

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

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

TABLE I

SUMMARY OF PILOT PLANT TESTS

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

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

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

MASS TRANSFER PARAMETERS

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

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

1. The procedures should not be overly complex and should be equally adaptable to either the refrigerant-11 or the refrigerant-12 data.

2. Of the various methods considered, the ones selected should be those which afford the best overall match of the actual pilot plant separation data.

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

Because each has some advantages, two basic models were used in the determination of stage heights. In both cases, the models were used with the run data to compute, for each test, the number of krypton stages in the absorber column; these numbers of stages were next divided into the packing height, 9 feet, to obtain the stage heights. The stage height values were then correlated using operating conditions to form parameter groupings.

Differential Stage Approach

An equation of the form

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

where Z = required column height, inches;

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

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

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

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

where k = gas-liquid equilibrium coefficient;

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

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

y = gas phase mole fraction of absorbing component;

x = liquid phase mole fraction of absorbing component; and

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

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

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

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

where k = gas-liquid equilibrium constant;

T = absorption temperature, °F; and

P_{Total} = total pressure, atmosphere.

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

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

TABLE II

PARAMETERS FOR GAS-LIQUID EQUILIBRIUM COEFFICIENTS

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

of an average L/G ratio, however, while making the model more attractive for this system, does present another problem in the design of a column. This is because the known gas and liquid flows at the start of the design are the feed flows, and there is no a priori way to establish what the average will be. For this reason, correlations were developed using the experimental data for each refrigerant to predict the average L/G ratio based upon the known feed L/G ratio:

For refrigerant-11

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

and for refrigerant-12

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

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

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

For refrigerant-11

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

and for refrigerant-12

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

where H_{OG} = stage height, inches;

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

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

P = absorption pressure, atmosphere; and

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

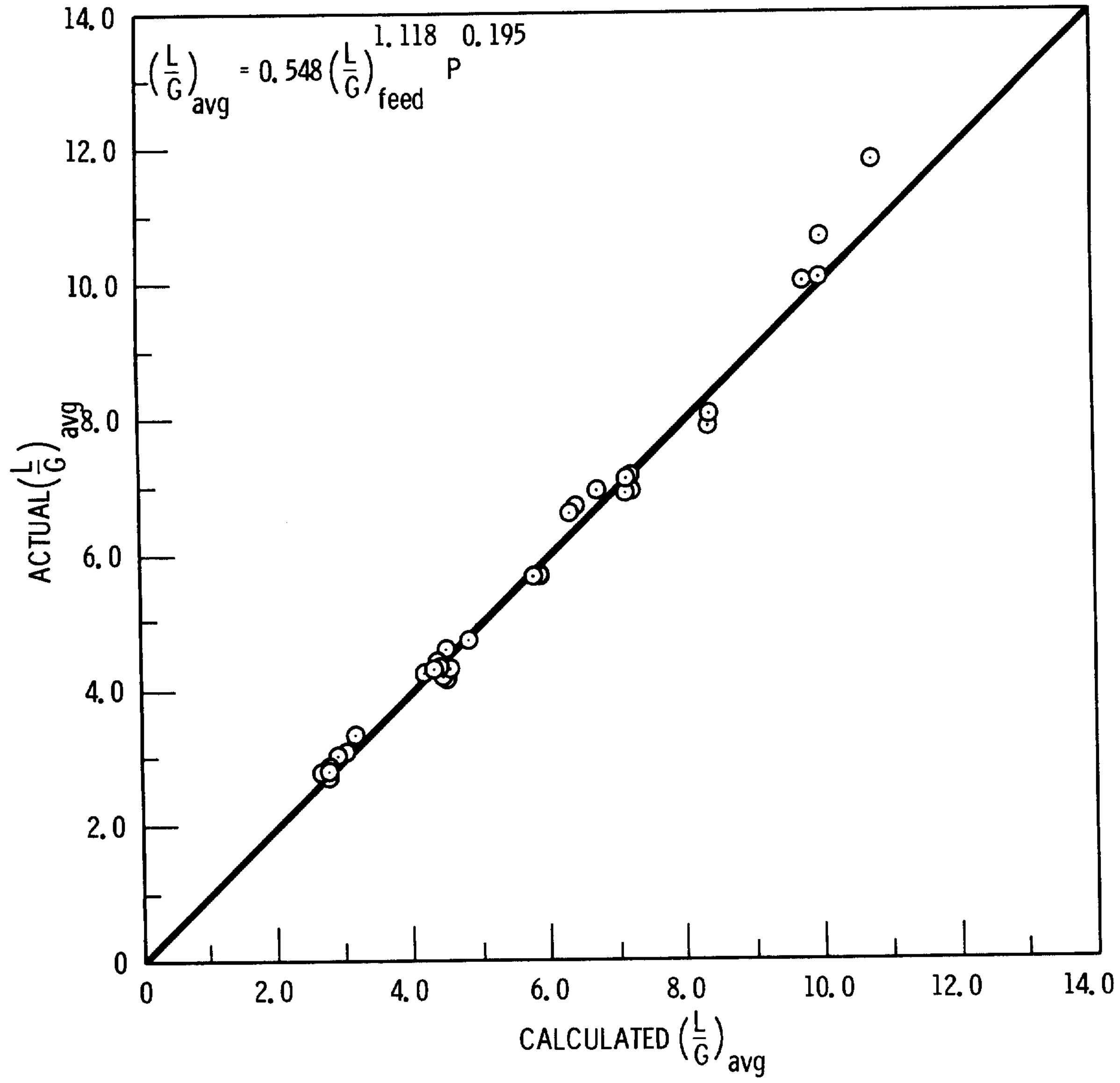


Figure 3

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

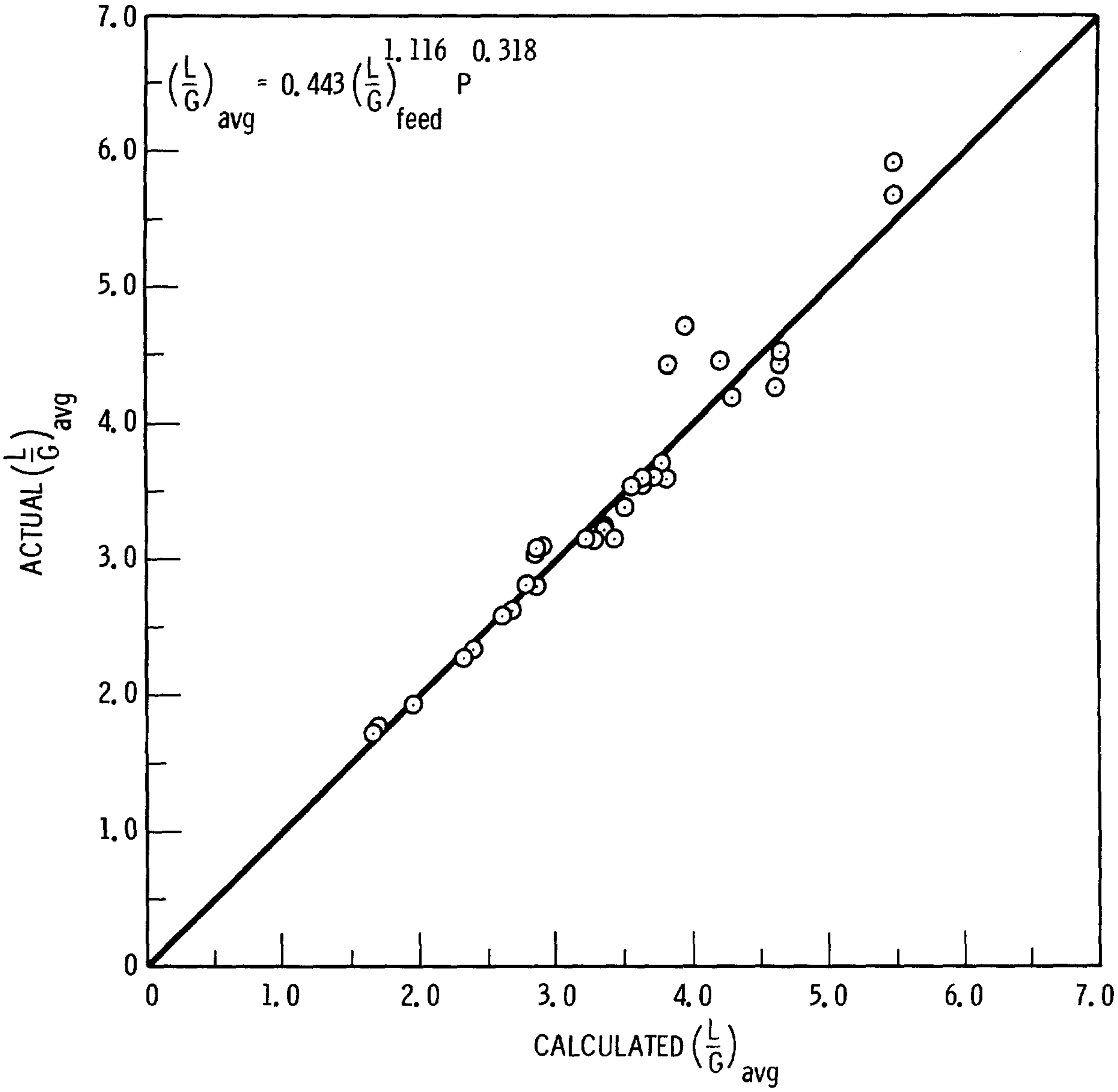


Figure 4

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

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

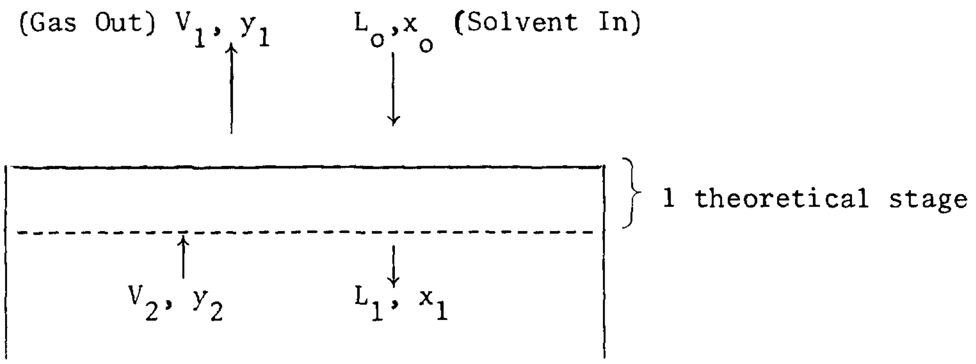
$$\alpha = \exp\,(2.0394 - 0.008253\ T)$$

where T is in °F.

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

Plate-to-Plate Approach

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



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

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

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

and the solvent in stream 1 is:

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

where subscript f refers to solvent.

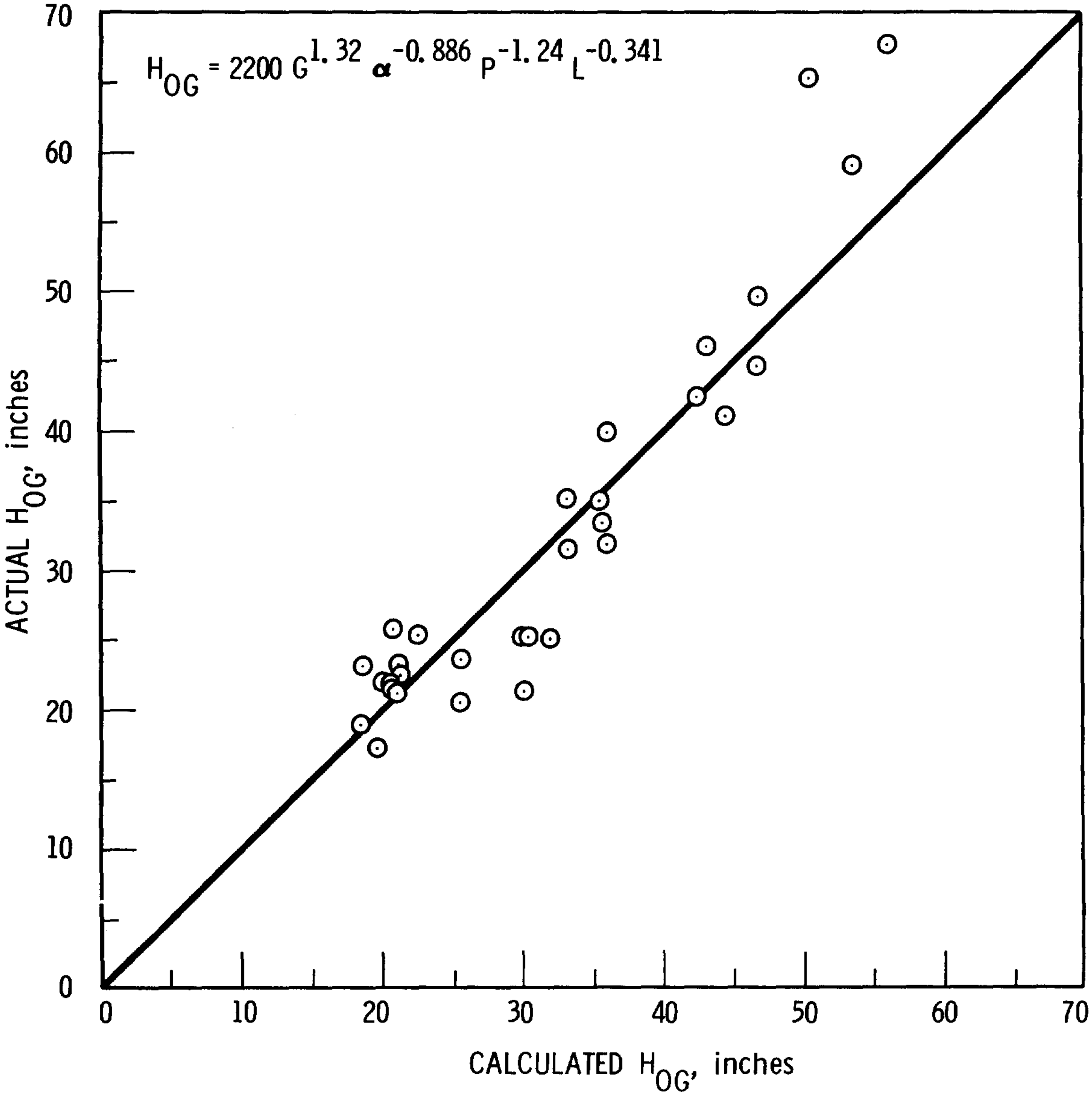


Figure 5

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

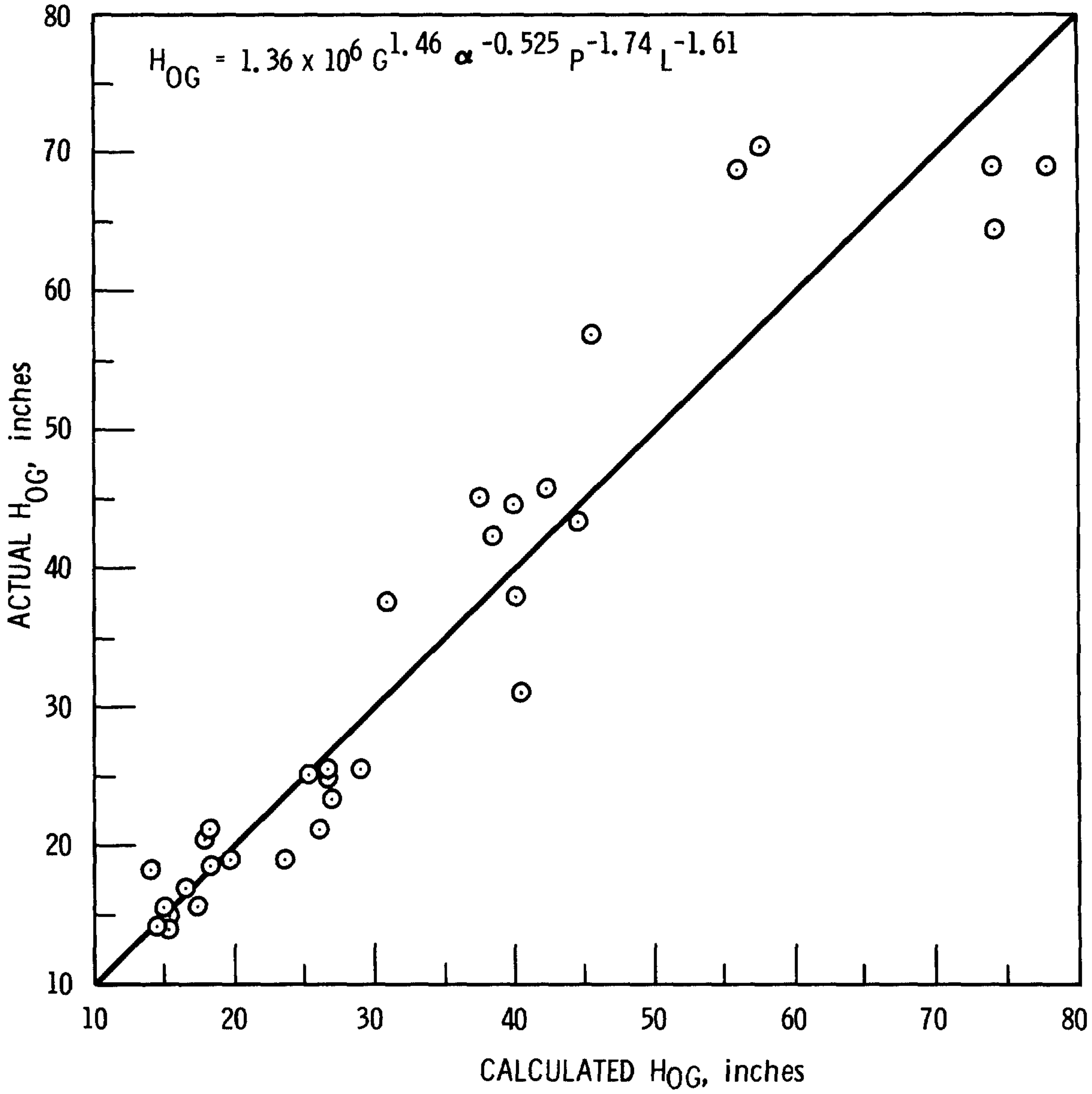


Figure 6

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

A solvent balance about the stage is:

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

and an overall balance shows that

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

Thus:

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

or

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

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

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

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

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

or

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

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

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

For refrigerant-11

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

and for refrigerant-12

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

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

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

Comparison of Approaches

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

PLANS FOR FUTURE WORK

Phase III

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

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

2. Experimental confirmation of these predictions.

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

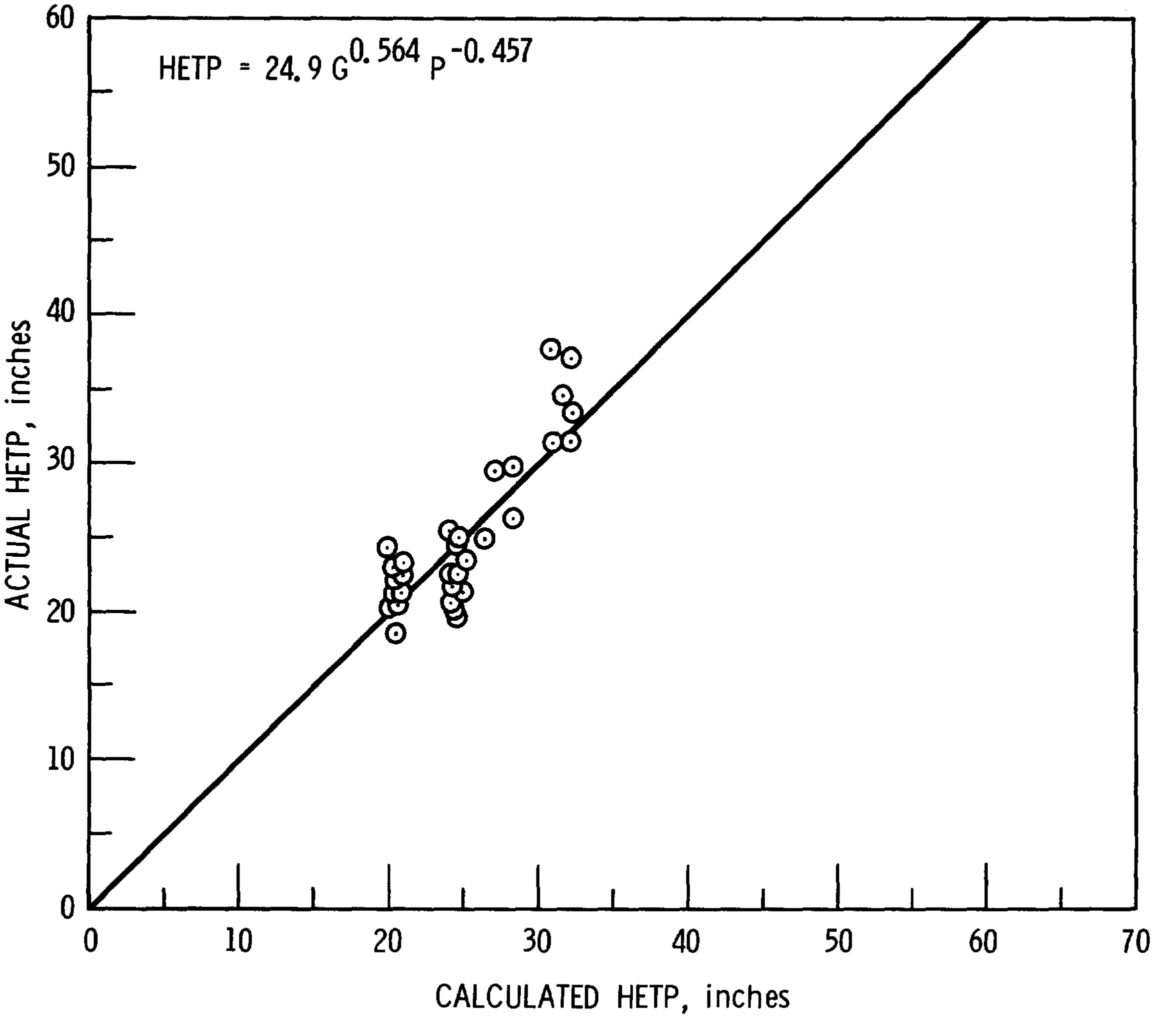


Figure 7

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

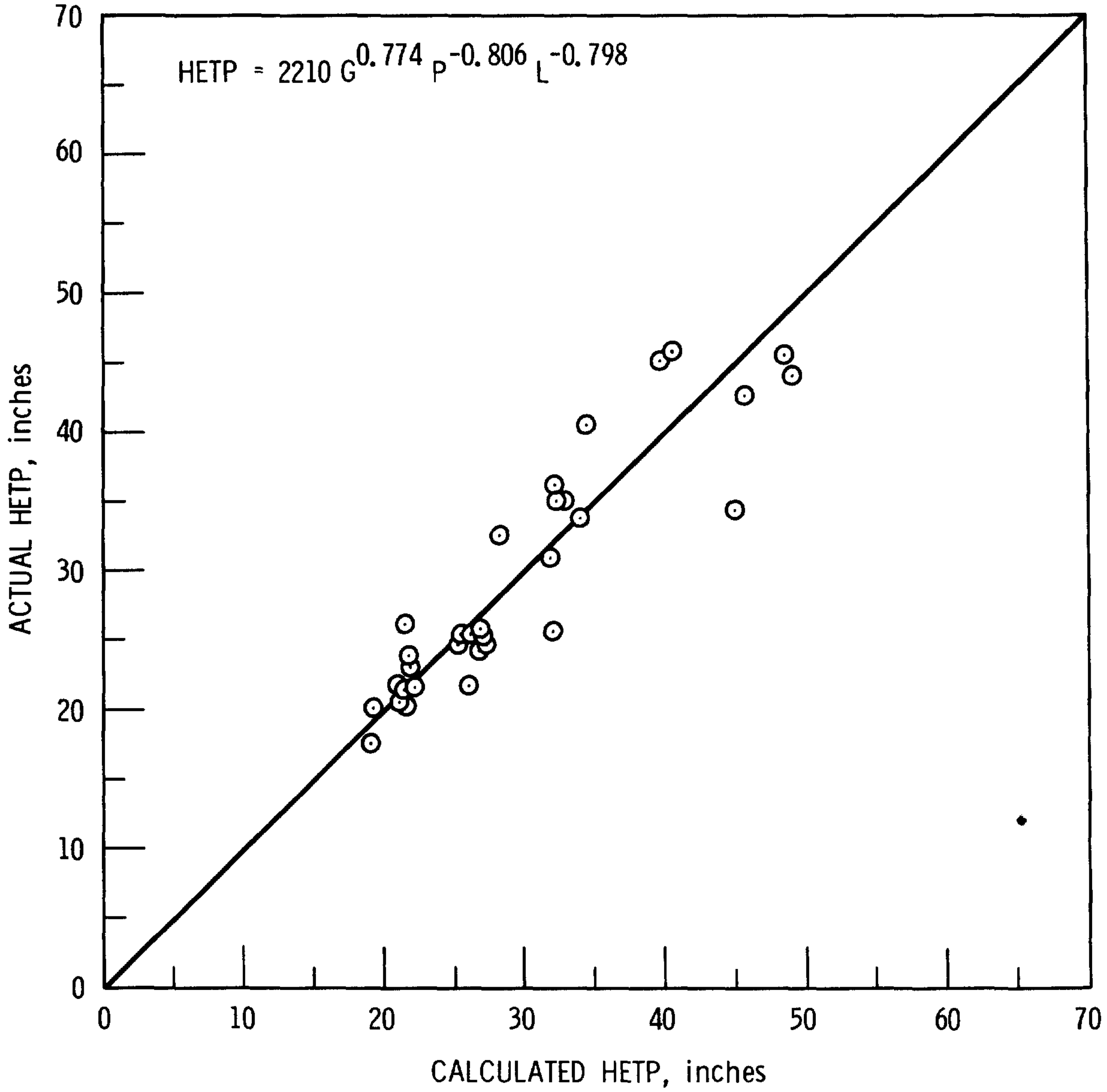


Figure 8

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

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

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

Phase IV

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

Phase V

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

OUTLOOK FOR APPLICATION OF THE ABSORPTION PROCESS

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

BWR Systems

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

PWR Systems

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

Fuel Reprocessing Plant

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

Vented Fuel LMFBR

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

LWR Accident Case

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

CONCLUSION

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

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

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

ACKNOWLEDGEMENTS

The authors are pleased to recognize several other employees of the Process Systems Development Department of the ORGDP for their efforts in the design, construction, and operation of the pilot plant. Mr. K. E. Habiger developed the computer simulation of the absorption process that provided component flow rates necessary for the initial equipment design calculations. Mr. D. L. Burkett, operations supervisor for the department, was responsible for the construction phase of the project and helped initiate and maintain pilot plant operation. The many skills of the chemical operators and maintenance personnel working for the department are also gratefully acknowledged.

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DISCUSSION

SIMENS: I was wondering, the data show that the minimum of feed concentrations of Krypton that you have used so far are about 40 ppm. What would be the result of going down to about 2 ppm of feed concentration?

MERRIMAN: In our best judgment, good removal can still be achieved. There are several reasons why we feel this is true. First of all, nothing in the theory would suggest that, so long as vigorous solvent stripping is maintained, adsorption would decline with concentration. Second, we did cover three decades of krypton concentration in the feed, and statistically this did not have any significant effect on the krypton removals that we observed. Third, the British did some work many years ago using a different, lower capacity solvent, but they did have concentrations in the one-part-per-million range. If you make compensations for the differences in absorption properties of the solvents, it appears that their removals were consistent with ours. However, we do have plans to do some tracer level tests at concentrations even below one or two parts per million to wrap this point up. We hope to get into these within the next few months. I would like to emphasize again that all of the evidence that we have indicates that the performance will hold up, even for very low concentrations.

FIRST: You mentioned that the unit that you have been working on is economical for this purpose. Would you care to give us an estimate of the cost of a unit for a thousand megawatt power station?

MERRIMAN: Of course, I would be a little reluctant to give you a "firm quotation" at this time, but a ball-park estimate for a plant that would give a pretty good decontamination factor, say of up to 1000, might be $175,000 for a boiling water reactor. If you want to economize a little bit and just put in a system that would give a decontamination factor of about 100 to 300 or something like that, you could possibly cut out the fractionator column and have just an absorber column followed by a stripper system. This would cut the cost down to maybe $125,000. There have been some other estimates made of the costs of systems for reactor stations, and I believe these are generally consistent with the two numbers that I gave you, so it doesn't appear to be a very high cost system. I should emphasize, however, that our cost estimates are based on conceptual studies, rather than detailed engineering considerations.

WITT: In order to back you a little farther into the corner in preparation of being shot, could we ask if that number is just equipment or equipment and installation?

MERRIMAN: The estimates I gave were for installed costs of the equipment and auxiliaries, such as refrigeration systems and instrumentation. These are strictly estimates of the capital costs of the plant, and we have never made any estimates of operating costs. Also, costs of building modifications were not included either.

WITT: Then what principle air flow rate did you have your eye on with that number, was it 20 cfm or 50 cfm?

MERRIMAN: 60 scfm.

QUESTION: You mention some British work on the absorption process?

MERRIMAN: Yes. It was a process that used a slightly different flow sheet, in that the gas feed was injected into the middle of a column which contained an absorption section and a fractionating section. The solvent used was carbon tetrachloride, which has a much lower capacity for noble gases than refrigerants; the packing used was Raschig rings; and the temperature was approximately room temperature. This work was done by Taylor and Wall and McIlroy in the late 1950"s. They have published quite extensively on it. I would be happy to give you some references.

WITT: Could you offer us any estimate on hydrogen-oxygen hazards in this process treatment if you should get such into the process feed at this point?

MERRIMAN: We haven't worked with hydrogen yet. What we would first do would be to use one of our computer programs to estimate just what concentrations would exist in various sectors of the process and check to see whether any are in the explosive region. If so, we would have to take a hard look to see if there would be any way to avoid this, because it would represent a hazard.

WITT: Do you have plans along this line?

MERRIMAN: Yes, we do plan to conduct some hydrogen-krypton separation tests.

FRANCIS: In line with our work in looking at nuclear process plants, -- power plants, pardon me -- we have estimated some decontamination factors which are in excess of the ones reported here by an order of magnitude, using cryogenic distillation methods. We now have some work in progress which we think will be available in about the end of October. And if you would like to share in that date or any others here would like to I'd be happy to receive your inquiry some time.

MERRIMAN: I should mention again that it is perhaps a little misleading to judge the absorption process solely on the basis of some of the decontamination factors I have shown. We were limited in our ability to detect krypton. We used a gas chromatograph, and we actually conducted several runs which were not reported, the reason being that we couldn't measure the decontamination factors: They were considerably greater than a thousand, but how much greater, we couldn't measure. Then again, our absorber is just a 9-foot-tall column, and we confined this formal presentation to the values that we could measure in this system with some precision. With the absorption process, you can just about achieve whatever decontamination factor you need by adding more absorber stages, or lowering the temperature, or raising the pressure, or increasing the L/G ratio, or some conbination of these actions.

SIEGLER: You mentioned that your costing was based on about a 60 cfm plant. How sensitive is the operation of this type of a facility to variation in its flow rate? What happens for example, if the flow rate goes to 100 cfm. Can it handle upsets like this?

MERRIMAN: You could design it to handle upsets like that. The problem is that if you design it very closely around 60 and you did upset it to around 100, you might flood the column. What we would propose to do in a case where there was some probable variation, would be to design a system with a conservative diameter and perhaps even with a control system with which you could maintain a constant column feed by recycling some of the vent gas back through, as necessary. When there was a burden from a nuclear station to the process, we would bleed in feed from the nuclear process and adjust our vent flow and our product flow accordingly.

A COMPARISON OF EQUATIONS USED IN THE DESIGN OF FISSION GAS ADSORPTION BEDS*

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ABSTRACT

The radioactive isotopes of krypton and xenon are the most difficult fission products to contain, and measurable quantities of these isotopes may be released from nuclear reactors and fuel reprocessing plants. One method of removing the shorter lived isotopes of these materials is to pass the waste gas stream through an adsorption holdup bed. If the time of holdup is long compared to their half lives, the process of radiodecay will remove these isotopes. In this paper, a comparison is made of the various equations which have been developed for evaluating the efficiency of fission gas holdup beds. It is shown that under conditions favorable for high efficiency, each of these equations leads to the same simple approximate solution. This fundamental similarity is shown to be due to the probabilistic nature of mass transfer. The limits of applicability of the approximate equation is examined and it is suggested that, in many cases of engineering design, the approximate equation will be sufficiently accurate.

Introduction

Of all fission products, isotopes of krypton and xenon are the most difficult to retain in nuclear facilities. Fortunately, because these isotopes are chemically inactive, once released they do not concentrate in body tissues. However, releases of even small amounts of radioactive substances can create problems, and in any case engineering safeguards must be adequate to maintain predetermined emission standards. One common engineering safeguard is the use of adsorption beds in which the holdup time of these isotopes is long in comparison with the halflife of the isotopes under consideration. Such a process can be effective against all fission produced noble gases except the 10.76 year krypton-85. At the Harvard School of Public Health, we have been studying the design of fission gas holdup beds and the factors which affect their performance.

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In this paper, we shall show how the theoretical plate concept, as commonly used in chemical engineering practice, can be used in the design of fission gas holdup beds. In a more general way we show that under conditions of optimum design for a fission gas holdup bed, the various theories which have been proposed for the design of holdup beds lead to essentially the same result.

Comparison of Theoretical Models

1. Browning's Theoretical Chamber Model

Let us begin with the theoretical chamber model of Browning(1,2). In this model it is assumed that the holdup bed consists of finite sections, and that in each section there is rapid and complete mixing of the gases before they pass onto the next section. Although the physical basis for this model can be severely criticized, the model itself can describe with surprising accuracy the breakthrough curves observed following pulse inputs of fission gases. Further, if in place of an adsorption bed, a series of flowthrough holdup tanks is used, then the theoretical chamber model can fit almost exactly the experimental conditions.

Now let us examine what this model predicts. Assume that there is a constant concentration, C_o, of a fission gas in the input to a holdup bed and we need to calculate the steady state effluent concentration of fission gas, C. Recently,(3) it was shown that the theoretical chamber model predicts that

$$C = C_o e^{-Z\lambda t_b} \tag{1}$$

where

t_b is the ideal holdup time, sec, and is most easily calculated from the product of mk/V, where m is the mass of adsorbent, k is the bulk adsorption coefficient, and V is the flow of carrier gas.

Z is the efficiency factor, dimensionless.

λ is the isotopic decay constant, sec^{-1}.

The factor, Z, gives the effect of imperfect mass transfer on the efficiency of the holdup bed. For the theoretical chamber model:

$$Z = \frac{N}{\lambda t_b} \ln\left(\frac{\lambda t_b}{N} + 1\right) \qquad (2)$$

where

N is the number of theoretical chambers.

Only when the dimensionless ratio,

$$\frac{N}{\lambda t_b},$$

is large in comparison to unity will the bed have an efficiency factor near unity. Under the condition that

$\frac{N}{\lambda t_b} >> 1$,

Equation 2 reduces to

$$Z \approx 1 - \frac{\lambda t_b}{2N} . \qquad (3)$$

It will be shown that Equation 3 bears a close relationship to models based on the concept of a theoretical plate.

2. Burnette's Theoretical Plate Model

Now let us examine the first theoretical plate model proposed for the design of fission gas holdup beds, namely the modification by Burnette *et al.*(4), of the mass transfer model of Hougen and Marshall(5). In this model the adsorption of fission gases is assumed to be limited by a film surrounding the adsorbent granules. This model can describe certain types of adsorption; but for the adsorption of fission gases, the model is not especially good because the rate of adsorption is limited by intraparticle diffusion rather than by an external film(6). Yet the breakthrough equation of Burnette, like that of Browning, can be made to fit the observed breakthrough curves with a high degree of accuracy. The reason for these unexpectedly good results will be examined later in this paper. First we will examine the result predicted by Burnette's model. In particular, his model predicts that the ratio of effluent concentration to the input concentration, C/C_o, is also given by Equation 1, with the factor Z now defined by

$$Z = \frac{1}{1 + \frac{\lambda t_b}{N}} . \tag{4}$$

If $\frac{N}{\lambda t_b} >> 1$, Equation 4 reduces to

$$Z \simeq 1 - \frac{\lambda t_b}{N} \tag{5}$$

which, with the assumption that one theoretical plate is equivalent to two theoretical chambers, is identical to Equation 3.

3. Diffusion Controlled Mass Transfer

A more recent development in the analysis of fission gas adsorption beds began with the model of Madey(7) based on interparticle molecular diffusion. We have extended this model to include the additional effects of eddy diffusion and intraparticle diffusion, thus including all mechanisms of mass transfer thought to be important in the design of fission gas holdup beds.(6,8)

This model can be rewritten in terms of theoretical plate theory through the following definitions

$$H_1 = \frac{d_p^2 V_s (k - \varepsilon/\rho)}{60 \rho k^2 D_p} \tag{6a}$$

where

H_1 = the height equivalent of a theoretical plate (HETP) due to intraparticle diffusion, cm
d_p = diameter of an adsorbent granule, cm
D_p = intraparticle diffusion coefficient, cm^2/sec
k = bulk adsorption coefficient, cm^3/gm
V_s = superficial carrier gas velocity, cm/sec
ε = fractional interparticle void volume, dimensionless
ρ = bulk density of the adsorbent, g/cm^3.

and

$$H_2 = \lambda_p d_p \tag{6b}$$

where

H_2 = HETP resulting from eddy diffusion
λ_p = coefficient for eddy diffusion, dimensionless

and

$$H_3 = \frac{\varepsilon \gamma D_m}{V_s} \tag{6c}$$

where

H_3 = HETP resulting from interparticle molecular diffusion, cm
D_m = the coefficient for molecular diffusion, cm^2/sec
γ = the tortuosity factor for interparticle molecular diffusion, dimensionless.

The overall height equivalent of a theoretical plate, H, is simply the sum of the HETPs from the mechanisms discussed above, or:

$$H = H_1 + H_2 + H_3 \tag{7}$$

and the number of theoretical plates, N, is equal to

$$N = L/H \tag{8}$$

where

L = the length of the bed, cm.

If the somewhat tedious calculations are followed through, then from Equation 6 of Reference 6, it follows that for

$$\frac{N}{\lambda t_b} >> 1, \quad Z \approx 1 - \frac{\lambda t_b}{N} .$$

Thus again for the case of an efficient adsorption bed (efficient meaning here that

$$\frac{N}{\lambda t_b} >> 1$$

so that the loss of efficiency due to the mechanisms of mass transfer is small), Equation 5 permits a rapid calculation of the theoretical efficiency of the adsorption bed.

Analysis of Results

Each of the above models leads to the same asymptotic expression for Z as

$$\frac{N}{\lambda t_b} >> 1.$$

Why? The answer follows from the fact that each model assumes a series of random molecular motions, and the breakthrough curve predicted by each model approximates a normal Gaussian curve as the number of random motions increases. If it is assumed that the breakthrough curve of a stable isotope is indeed a normal Gaussian curve with a maximum at time, t_b, and a standard deviation of

$$t_b \sqrt{2/N}$$

then the fraction of a radioactive isotope passing through the bed is given by

$$C/C_o = e^{-\lambda t_b \left(1 - \frac{\lambda t_b}{N}\right)} \quad (9)$$

if $\frac{N}{\lambda t_b} >> 1$.

Equation 9 is a simplification, but when it is in error, it errs on the conservative side. Therefore, this equation may prove useful in rapid analysis of the efficiency of fission gas holdup beds.

The main point of interest here, we believe, is that in the design of fission gas holdup beds, as long as the dimensionless group

$$\frac{N}{\lambda t_b} >> 1,$$

then all the equations discussed here lead to essentially the same result.

Appendix: A note on the definition of HETP.

The HETP (Height Equivalent to a Theoretical Plate) as calculated by Equations 6-a,b,c, is consistent with the defination of HETP given in standard chemical engineering references, such as the Chemical Engineers' Handbook. This definition differs by a factor of two from the standard definition of HETP in gas chromatography. In general:
1 HETP in gas chromatography = 2 HETP in chemical engineering.

Both definitions of HETP can be nondimensionalized by dividing the HETP value by the mean particle diameter.

The chemical engineering definition of a dimensional HETP was used here because this report was written for engineering design. The nondimensionalized gas chromatographic HETP was used in an earlier report(8) comparing fission-gas adsorption with the mechanisms of gas chromatography.

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DISCUSSION

KOVACH: In the derivation of these equations and their experimental proof, do you know if yourself or anyone else used actual gas concentrations under conditions which are expected in the effluent of nuclear reactors?

UNDERHILL: Our calculations apply to a nuclear reactor effluent in which there is a much greater concentration of inert gas than radioactive fission gas. I believe that it is possible to prove mathematically in such a case that the assumption of a linear isotherm is correct. Our method of analysis, which uses statistical moment theory, is extremely powerful; we have recently found that it gives an exact answer to such a difficult problem as calculating the effect of the pressure drop across a gas chromatography column.

KOVACH: The problem we have in reconciling the experimental data to the derived equation is that we have some experimental data which we obtained from some Russian workers which shows that neither the diffusion nor the external mass transfer controls the process, but the decay rate. This is at least in the 25° to -100°C range and in the general velocity and concentration ranges that we are using. So you get an exponential function from the decay rate and you can actually plot by checking the MEV through the adsorption bed.

UNDERHILL: What temperature was that again?

KOVACH: 25°C + to -100°C. They believe that if you go to cryogenic conditions you will obtain mass transfer controlled diffusion.