DESIGN OF FISSION GAS HOLDUP SYSTEMS*

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ABSTRACT

Recently the Harvard Air Cleaning Laboratory was asked to prepare a preliminary design for the fission gas holdup beds for the Fast Flux Test Facility. The staff of the Laboratory developed a set of simple equations for rapidly calculating the holdup efficiency, the temperature rise, and the pressure drop for each bed without the need for electronic computers. Because the methods used in this design may be of interest to other people in the field of nuclear safety, an outline of the approaches used in determining each of these factors is presented here.

Introduction

Recently the staff of the Harvard Air Cleaning Laboratory was asked to prepare a preliminary design(1) of a fission gas holdup bed for the Fast Flux Test Facility. After reviewing various possible designs, the staff recommended a simple adsorption holdup system consisting of a precooler and filter followed by two water-cooled adsorption beds. The three major factors to be determined in the design of these beds were: (1) the holdup efficiency of the adsorbent, (2) removal of decay heat from the beds, and (3) the pressure drop across the beds. Because the methods used in this design may be of interest to other people within the field of nuclear safety, an outline of the approaches used in determining each of these factors is presented here.

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1. Holdup Efficiency of the Adsorbent Bed

The initial step was to estimate the effluent concentrations of ^{133}Xe and ^{135}Xe, the two radioisotopes of interest. These estimates were calculated using the following equation:(2)

$$\frac{C}{C_o} = \exp\left\{-\frac{LV_s}{2(\varepsilon\gamma D_m + \lambda_p V_s d_p)}\left[\left(1 + \frac{4(\varepsilon\gamma D_m + \lambda_p V_s d_p)\rho K\lambda}{V_s^2}\right)^{1/2} - 1\right]\right\} \qquad (1)$$

where

C/C_o = the ratio of the output concentration to the input concentration of the radioisotope of interest.

and

d_p = mean adsorbent particle diameter, cm
D_m = molecular difusion coefficient for fission gas/carrier gas, cm^2/sec
K = effective adsorption coefficient, cm^3/gm
L = length of the adsorption bed, cm
V_s = superficial carrier-gas velocity, cm/sec
γ = tortuosity factor for interparticle diffusion, dimensionless
ε = fraction of adsorption bed consisting of interparticle void volume, dimensionless
λ = isotopic decay constant, sec^{-1}
λ_p = coefficient for axial dispersion, dimensionless
ρ = bulk density of the adsorbent, g/cm^3.

Equation 1 is a very general equation; its limitations are that 1) it assumes laminar flow of the carrier gas, which in turn implies that the modified Reynolds number is less than 100; 2) that the adsorption bed is well packed and 3) that the ratio of pipe diameter to adsorbent particle diameter is greater than 12. If these last two conditions are not met, channeling or wall effects may reduce the efficiency of the holdup bed, and it becomes very difficult to calculate the adsorption efficiency.

The effective adsorption coefficient may be calculated from Equation 2 where

$$K = \frac{\varepsilon}{\rho} + \frac{12D_p}{\lambda d_p^2}\left(K_o - \frac{\varepsilon}{\rho}\right)\left[\left(\frac{\lambda d_p^2}{4D_p}\right)^{1/2} \coth \left(\frac{\lambda d_p^2}{4D_p}\right)^{1/2} -1\right] \qquad (2)$$

and

D_p = diffusion coefficient for intraparticle diffusion, cm^2/sec
K_o = adsorption coefficient for a stable isotope, cm^3-g

The factor D_p can be calculated from the molecular diffusion coefficient as follows:

$$D_p = \frac{\gamma_p \varepsilon_p (1 - \varepsilon) D_m}{\rho K_o - \varepsilon} \qquad (3)$$

where

ε_p = fraction of the adsorbent particle volume consisting of macropore void volume, and
γ_p = tortuosity factor for intraparticle void volume

Equations 1 and 2 can be rewritten in terms of theoretical plate theory* permitting a simpler calculation for the effluent concentration. If the Height Equivalent of a Theoretical Plate, H, is defined as

$$H = \frac{\varepsilon \gamma D_m}{V_s} + \lambda_p d_p + \frac{d_p^2\ V_s (K_o - \varepsilon/\rho)}{60 \rho K_o^2 D_p} \qquad (4)$$

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*See comments on theoretical plate theory, given in _A Comparison of the Equations Used in the Design of Fission Gas Holdup Beds_, presented at this Conference.

and

$$\frac{V_s}{\lambda \rho K_o H} >> 1, \tag{5}$$

then the effluent concentration of fission gas is

$$C = C_o e^{-\frac{\lambda L \rho K_o}{V_s}\left(1 - \frac{\lambda \rho K_o H}{V_s}\right)}. \tag{6}$$

Equation 6 is a valid approximation if the dimensionless group $V_s/(\lambda \rho K_o H) >> 1$, and only in extreme cases, (i.e., an extremely low carrier gas velocity, an extremely short isotopic half life, or an extremely large adsorbent particle diameter) will this dimensionless group not be considerably greater than unity.

2. Removal of Decay Heat

The holdup beds should be designed so that the calculated temperature rises are small. Otherwise, slow destruction or even combustion (if the adsorbent is charcoal) of the adsorbent may occur. In the design calculations, the conservative assumptions were made that the centerline temperature could be calculated using the value of the adsorption coefficient for the temperature at the wall, and that the overall adsorption coefficient was equal to the value of the adsorption coefficient at the maximum centerline temperature. On the basis of these assumptions, the actual centerline temperature will be slightly below the calculated value, and the overall holdup time will be slightly greater than the calculated value.

The axial temperature distribution across the bed depends on the following heat balance(3):

$$k'' \frac{d^2 t_{av}}{dx^2} - C_p G \frac{dt_{av}}{dx} - \frac{2U}{r_o}(t_{av} - t_w) + q_o e^{-\alpha x} = 0 \tag{7}$$

where

C_p = heat capacity of the carrier gas, cal/°C-gm
G = superficial mass velocity, gm/cm^2-sec
k'' = effective axial thermal conductivity of the carrier gas + adsorbent, cal/cm-°C-sec
q = generation of heat per unit volume of bed at the inlet, cal/cm^3-sec
r_o = radius of the bed, cm
t_{av} = average radial temperature, °C
t_w = wall temperature
U = radial heat transfer coefficient, cal/cm^2-°C-sec
x = distance from inlet
α = coefficient of L in Equation 1, and is equal to

$$\alpha = \frac{V_s\left[\left(1 + \dfrac{4(\varepsilon\gamma D_m + \lambda_p V_s d_p)\rho K\lambda}{V_s^2}\right)^{1/2} - 1\right]}{2(\varepsilon\gamma D_m + \lambda_p V_s d_p)} \approx \frac{\lambda\rho K_o}{V_s}\left(1 - \frac{\lambda\rho K_o H}{V_s}\right) \qquad (8)$$

The factor, α, has units of reciprocal centimeters.

In Equation 7 the four terms represent, respectively, heat transfer resulting from (a) diffusion, (b) carrier gas movement, (c) conductivity through the walls of the bed, and (d) radioactive decay.

Integration of Equation 7 yields:

$$t_{av} - t_w = \frac{Q}{\dfrac{2U}{r_o} - C_p G\alpha - k\alpha^2}\left\{e^{-\alpha x} - e^{-\left(\sqrt{C_p^2G^2 + \dfrac{8kU}{r_o}} - C_pG\right)\dfrac{x}{2k}}\right\} \qquad (9)$$

The resulting equation enables the average bed temperature to be calculated as a function of the distance from the inlet.

It must be recognized that these heat transfer calculations depend on the modified Reynolds number

$$N_{Re} = \frac{Gd_p}{\mu} \tag{10}$$

where μ = the viscosity of the carrier gas, gm/cm-sec.

At low and intermediate Reynolds numbers, the radial heat transfer coefficient, U, can be calculated by the method of Yagi(4) and under these conditions the radial temperature profile across the bed would be expected to be parabolic, with the radial temperature, t_r given by

$$t_r = 2\left[t_{av} - t_w\right]\left\{1 - \left[\frac{r}{r_o}\right]^2\right\} + t_w \tag{11}$$

where

t_r = temperature at r, °C
r = distance from centerline, cm
r_o = radius of bed, cm

The centerline temperature is also the maximum temperature, and it follows directly from the above parabolic equation that

$$t_{centerline} = 2t_{av} - t_w \tag{12}$$

At higher modified Reynolds numbers the correlation of Colburn(5) can be used to calculate U. At these higher Reynolds numbers the temperature profile would be expected to be significantly blunter than the parabolic profile given by Equation 11, and the centerline temperature would be less than that given by Equation 12. We doubt that it would be efficient in terms of pressure loss to run a holdup bed at turbulent velocities, but it may be desirable to make calculations of what would result if such a procedure were to be used.

3. Calculation of the Pressure Drop

The pressure drop across the beds was evaluated using the well-known Kozeny-Carmen equation:

$$\Delta P = 180\ L\ V_s\ \mu\ (1 - \varepsilon)^2/\varepsilon^3\ d_p^2 \qquad (13)$$

where

ΔP = pressure drop, dynes/cm^2

Equation 13 should be used only for modified Reynolds numbers, N_{Re}, below 10. In the design calculations for the fast flux test facility, N_{Re} always remained below this value. Where values greater than 10 are encountered, a more general equation, such as that of Leva(6) should be used.

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SOME OBSERVATIONS ON NOBLE GAS PARTITIONING IN DYNAMIC AIR-WATER SYSTEMS

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ABSTRACT

Radioactive noble gases produced in fission would be released from reactor fuel elements which might fail from thermal stresses in the serious overheating incidents considered as design-basis accidents. Although in most design-basis accidents considered for reactor safety analysis iodine isotopes released prove to be the limiting isotopes, noble gas isotopes released in particular reactors and circumstances could contribute importantly to the dose to people at the site boundary. Suppression of steam following a serious meltdown in some water reactor designs is through quenching in a water system and the degree to which the noble gases remain in the water must be known to evaluate the significance of the noble gases released to the environment either in the water or in the air.

Experiments were conducted to help determine to what degree and how rapidly krypton-85 dissolved in water will disengage in a few dynamic water-air systems and from stagnant pools. Krypton-85 carried in inert krypton was dissolved in hot water contained in an aluminum vessel with a very small air space. After equilibration, the vessel was discharged in various ways and the disengagement rate noted. Rate of release from stagnant water in small vessels was also measured. The "immediate" release upon gravity draining ranged from small amounts to over 40%. In quiescent shallow pools release to air varied with the surface/volume ratio and temperature regime. During a 2-hour cooling period the krypton loss ranged from 14 to 43% of that initially present.

Liquid scintillation counting techniques were used to measure krypton-85 concentrations in the water phase. Methods and techniques are described.

This paper is based on work performed under U.S. Atomic Energy Commission Contract No. AT(45-1)-1830.

INTRODUCTION

To insure the protection of the environment during the operation of a nuclear reactor, various highly improbable situations are postulated and the distribution of biologically significant isotopes released under the conditions studied. Radioactive fission gases could escape from reactor fuel elements which might fail due to thermal stresses under these conditions. Although radioiodine is generally considered as the biologically limiting isotope in these exercises, the noble gas isotope could contribute significantly to the total hazard under some circumstances.

Steam generated following a loss-of-coolant in some light-water reactor designs is suppressed by quenching in a water system. A sequence of events for such a hypothetical situation leading to the generation of noble gases might be:

- An accidental loss of coolant to the reactor.
- Failure of emergency cooling provisions for a part of the fuel.
- Temperature increases in the uncooled areas resulting in the release of noble gases due to clad-failure and/or melting.
- A mixture of steam and noble gases or noble gases alone is swept out of the reactor through affected tubes.
- Final disposition of the coolant water may require eventual release to an open basin or a drain field.

If a significant portion of the active noble gas inventory could be carried out to the drain-field and released, such ground level release might constitute a radiation hazard.

The solubility of the noble gases in water at various temperatures has been studied.[1,2,3,4,5,6] The published information on the solubility of krypton is plotted in Figure 1 in cc Kr @ STP per 1000 grams of water at various temperatures. It is noted that the solubility as shown denotes the quantity of krypton which will dissolve per 1000 g. of water when the pressure of krypton is 1 atmosphere. In closed systems under equilibrium conditions krypton will distribute itself between the air and water to satisfy Henry's law constant. Partition coefficients have been calculated from solubility data and are shown in Figure 2 for xenon and krypton for temperatures from 0 to 50°C. Temperatures higher than 50°C are also of interest. The solubility of krypton and xenon is known to increase with temperature beyond about 100°C.

The equilibrium distribution is of interest since it represents the infinite-time conditions in a closed system. In an open system equilibrium will be reached when the noble gas in the liquid will come into a steady-state with the very small amount of naturally occurring noble gas in air, thus very little noble gas would be retained in the water. The equilibrium distribution of krypton and xenon for various air-water systems in closed systems is shown in Table I. These may be used as indicators of the long-term situation of noble gas and water systems.

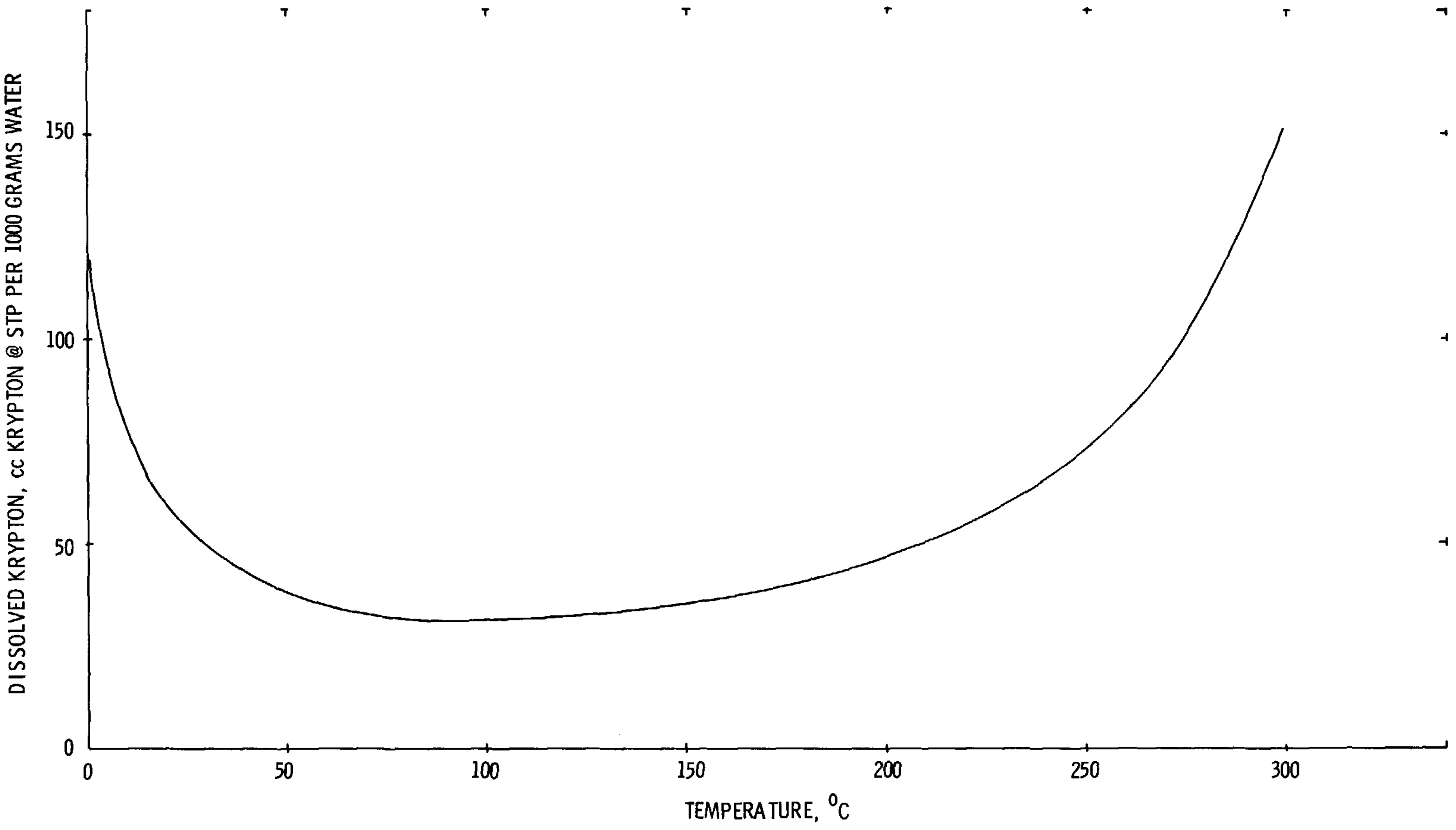

FIGURE 1

SOLUBILITY OF KRYPTON AT 1 ATMOSPHERE

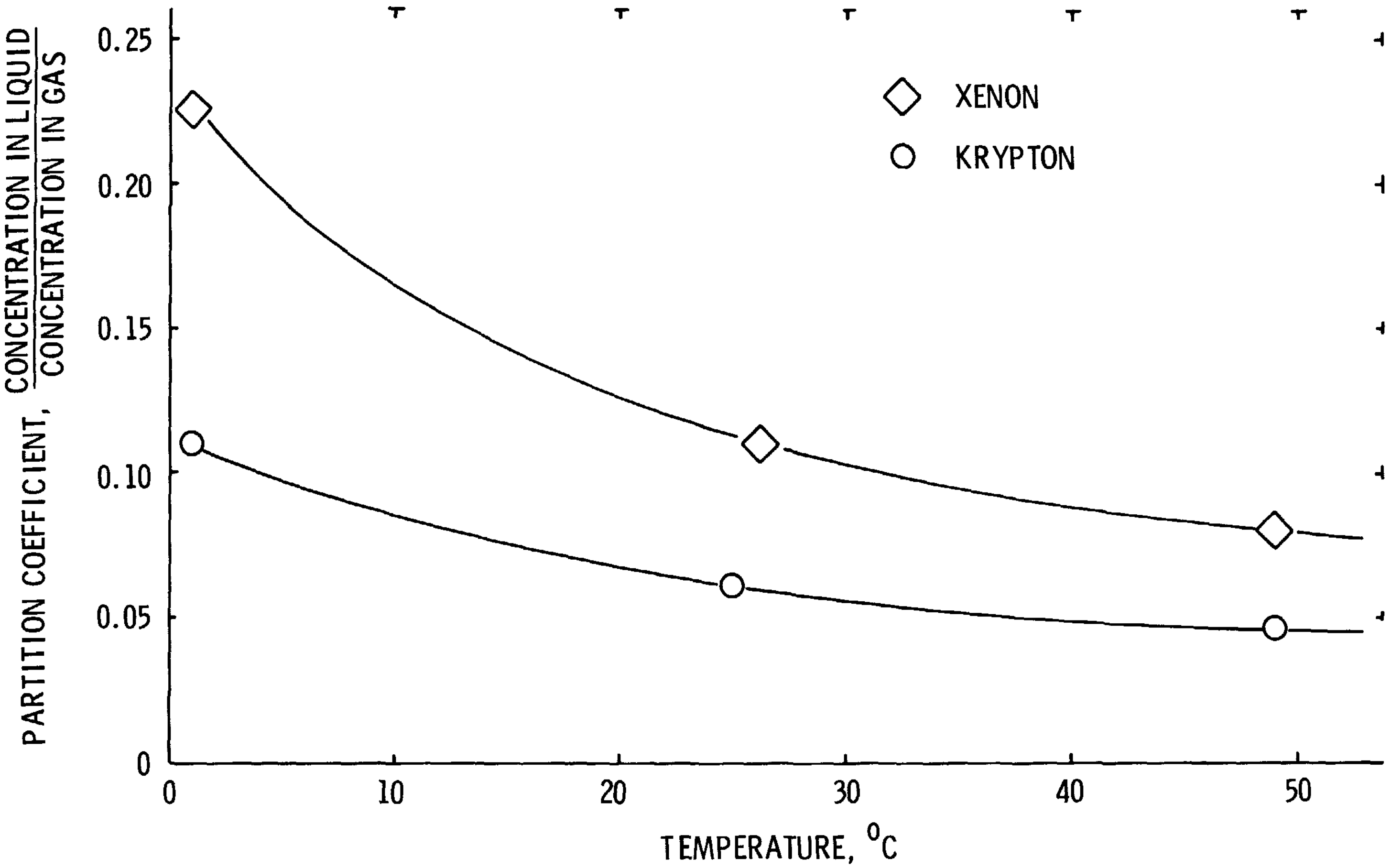

FIGURE 2

PARTITION COEFFICIENTS FOR XENON AND KRYPTON IN WATER

TABLE I

EQUILIBRIUM PARTITIONING OF KRYPTON AND XENON AT 50°C

Vol Air/Vol Water	Fraction of Xenon in Air Space	Fraction of Krypton in Air Space at Equilibrium
0.01	0.13	0.19
0.1	0.63	0.72
1	0.94	0.96
2	0.97	0.98
5	0.99	0.99
10	0.99	1.00
100	1.00	1.00

Knowledge of the equilibrium distribution as an index of the tendency of noble gas to enter or leave a water surface is of considerable worth, but does not solve the problem of the rate at which equilibrium is achieved. In a release of noble gas in a design basis accident the entry of the gas into the water system may occur under a wide range of temperature and pressures. The subsequent transport of the gas-water mixture to the final disposal point may occur in a very turbulent system. Subsequent disengagement when the water is discharged to a tank or basin will occur at a rate depending upon depth of fluid, temperature, air-water transfer rates, water impurities, and whether bubbles of gases are present.

We have been concerned with this problem and have up to the present time conducted some experiments to help understand the rates at which krypton enters and leaves simple water systems. This work may also have application to aeration-deaeration problems.

SUMMARY

The absorption and release of krypton gas in dynamic air/water systems was monitored by liquid scintillation of the labeled Kr concentration in the water. Ten milliliters of Kr gas at STP (37.4 mg) was injected into ∿ two liters of tap water held at the desired temperature. Dissolution was slow (∿ 90 min)and complete dissolution was obtained in only the room temperature experiment. The rate at which Kr disengages was shown to be a marked function of agitation, temperature and geometry of the system. As much as 42% was lost during gravity draining through a 1/2" valve. Lesser amounts were lost during less turbulent transfers. A loss of ∿ 14.5% per unit of surface to volume ratio was found from unagitated, small pools during a 2-hour cooling cycle. Much smaller losses are anticipated from deeper vessels. Losses from quiescent isothermal pools also appear to vary with surface to volume ratio.

EXPERIMENTAL

The absorption and release of krypton gas by water was examined by monitoring the Kr concentration in the liquid phase during Kr/water contact and the subsequent exposure of the liquid to air. Pure Kr gas labeled with ^{85}Kr was used and the Kr concentration in water determined by liquid scintillation counting. Ten milliliters of Kr gas at STP (37.4 mg) were injected into approximately 2 liters of tap water held at the desired temperature in a 3" OD × 20" long aluminum absorption vessel. The apparatus is diagrammed in Figure 3. During most of the runs, the vessel was aligned horizontally with the closed end tilted upwards to trap the Kr gas during the injection. The other end was sealed with a water filled 1/2" ODT. Ambient pressure was maintained by displacement of water during the injection. After the gas injection, the second ball valve was closed and the vessel manually shaken to enhance gas/water contact. The Kr concentration in the water was monitored by periodic extraction of liquid samples via the silicone rubber sealed sampling ports. Initial difficulties in obtaining valid samples were eliminated by repetitively "pumping" the liquid in and out of the syringe.

After the Kr concentration stabilized (normally 2 hours), the vessel was aligned vertically, vented and the water discharged. Several methods of gravity draining were employed. In 4 experiments, the water was allowed to drop to the bottom of a 4-liter beaker approximately 12" from the valve. In 6 experiments, the water was drained via a 1/2" ODT to the bottom of a beaker -- very slowly in 3 cases. In 3 runs, the water was left in the vessel. Liquid samples were taken after venting, immediately after draining and at intervals during the exposure of the liquid interface to air. In 7 of 9 experiments, cooling of the liquid accompanied exposure. In 1 case (run 10), the water temperature was maintained for the initial 2 hours of exposure. Run 12 was at ambient temperature.

Since the heavier noble gases have an appreciable solubility in the aromatic hydrocarbons used as a solvent in the liquid scintillator solution, liquid scintillation counting has been used to monitor low concentrations of radioactive noble gases.[7,8,9] Scintillator solutions also exhibit a good solubility for water without significant loss of counting efficiency and were especially useful for this study.

The procedure for measuring aqueous samples containing ^{85}Kr was as follows.

1. An aqueous sample was extracted from the solution to be analyzed, using a standard needle and syringe.

2. A 1 ml sample was delivered to the bottom of a 25 ml precooled screw cap borosilicate vial filled to the top with the liquid scintillator -- 100 g napthalene, 6 g 2,5-diphenyloxazole and 0.6 g 1,4-bis[2- (5-napthazole)] benzene in 1 liter of pure dioxane. The vial overflowed upon slow injection of the sample. A tight-fitting cap which allowed no air bubbles was quickly placed on the vial. Excess scintillator fluid was removed with acetone, followed by a water rinse and the vial dried using cheesecloth.

3. The sealed vials were held at about 5°C during pipetting and during

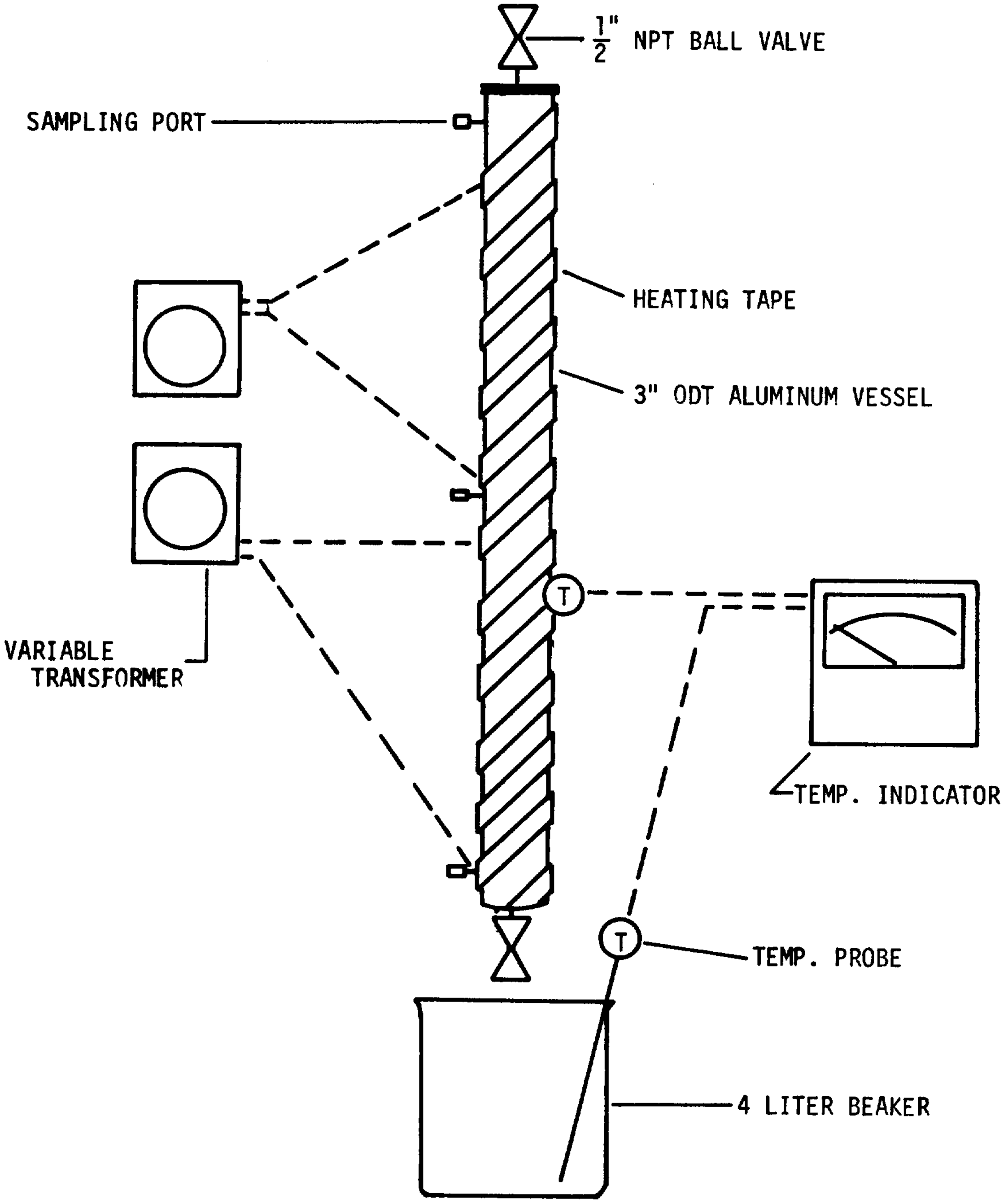

FIGURE 3

KRYPTON ABSORPTION VESSEL

counting. The vials were allowed to sit 30 minutes in the refrigerated counter instrument before the count. The instrument was a Nuclear Chicago, Mark I, 3-channel liquid scintillation spectrometer. A series of 1 to 10 minute counts was averaged to arrive at the counting rate of each sample. Using tritium (0.0186 Mev beta) as a source, the method has a counting efficiency of ∿ 18% and would indicate that for an energetic beta as ^{85}Kr (0.67 Mev) the counting efficiency is in excess of 75%. Background activity is automatically subtracted using the levels actually determined during the counting cycle. The lower detection limit is approximately 100 cpm.

An estimate of the level of ^{85}Kr labeling was determined by counting a series of air dilutions of the Kr/^{85}Kr source. Aliquots containing from 0.595 to 14.7 μg Kr in 0.1 to 0.25 cc air were injected into glass vials fitted with a rubber septum. Initially, some gas was probably lost during the injection due to the pressure induced in the liquid, already at greater than ambient pressure, by the extra gas volume. During subsequent runs, the vials were inverted during injection of the gas and liquid rather than gas was forced from the container.

RESULTS

Absorption

The maximum Kr concentrations detected during the 11 experiments are tabulated in Table II. A concentration of 18.1 μg Kr/cc would indicate complete absorption of the Kr injected and is well below saturation at the temperatures used (182 to 203°F). None of the 10 experiments at elevated temperatures attained this concentration. Handling problems may have caused less gas to be injected in 7 of 10 experiments giving low results. Concentrations ranged from 70 to 80% of maximum for the other 3 runs. Complete dissolution was indicated for the single run (No. 12) at ambient temperature.

Under the conditions used in these experiments, dissolution of Kr gas by water at elevated temperature was slow. Under static conditions (single gas space above the liquid 0.043 ft^2 interface), the Kr concentration did not attain a near stable value in 2 hours. With manual shaking, a quasi-stable concentration could be obtained in approximately 90 minutes.

Release

Three procedures were followed in draining the water from the absorption vessel during these experiments. Kr loss varied with the degree of disturbance to the liquid surface and the surface area exposed. The results are listed in Table III.

Gravity-Draining from Absorption Vessel -- Liquid disturbance and film breakup was greatest in this group. The 1/2" ball valve was opened and the liquid allowed to drain at its own rate into a 4-liter beaker. Only 5 to 10 seconds were required to empty the vessel. Losses ranged from 20 to 42% -- 36 to 42% in 4 of 5 experiments. Liquid disturbance was less in the next

TABLE II

DISSOLUTION OF KRYPTON IN WATER

(2.06 liter water in aluminum 3" ODT × 20" vessel)

Run No.	Water Temperature During Absorption °F	Contact Time min.	μg Kr/cc Water
1	182	90	7.0†
2	182	120	7.2†
3	185	120	7.2†
4	195	120	3.8†
5a	196	120	14.5
6	194	170	13.1
7	197	150	10.9*
7a	203	120	10.2*
8	199	120	8.9*
10	196	120	13.4
12	70	150	18.0

† Leak in plastic gas reservoir caused dilution of Krypton source.
* Sampling port on source cylinder not purged prior to use.

TABLE III

KRYPTON LOST FROM WATER DURING GRAVITY DRAINING OF ABSORPTION VESSEL

Run No.	Kr Conc. μg/cc	Water Temp.* °F	Kr Lost %
12" Free Fall to 4 Liter Beaker via 1/2" NPT Opening			
1	6.9	182	40
2	6.1	182	36
3	6.9	185	42
4	3.8	198	36
5a	13.7	99	20
Expelled Under Surface of Liquid After Initial 1/4" Free Fall Period, Full Flow			
6	12.8	194	5
7	10.8	197	13
7a	10.4	203	11
Expelled under Surface of Liquid After Initial 1/4" Free Fall Period, Restricted Flow			
8	8.7	199	n.d.
10	13.4	193	2
12	18.0	74	1

*Temperature of water in vessel prior to drain.

series of experiments. Water was drained from the absorption vessel through a 1/2" ODT extending to approximately 1/4" of the bottom of the container. Under these conditions, approximately 20 seconds were necessary to empty the absorption vessel. Losses ranged from 5 to 13%. In the last 3 experiments, flow from the absorption vessel was restricted to maintain a smooth liquid surface in the container during draining. Approximately 1 minute was required to empty the container. Losses were under two percent.

Exposure of Liquid Interface to the Air -- The water containing the dissolved Kr gas was exposed to air under a variety of circumstances. Loss of dissolved Kr was monitored during cooling, on extended exposure in containers of various surface to volume ratios and at ambient and elevated temperatures.

The loss of dissolved Kr from water during the initial 2 hour cooling period for various surface to volume ratios is tabulated in Table IV. No significant variation is evident using containers whose surface to volume ratios ranged from 2.32 to 2.78 ft^{-1}. Losses ranged from 25 to 43% -- predominantly above 35%. Only when the surface to volume ratio was reduced to 0.6 ft^{-1} (run 5a) was there a significant drop in loss. The average loss per unit of surface to volume was 14.5% for the 2 hour cooling cycle. An equivalent loss in a large quench tank 60' in diameter containing 50 ft. of water (approximately 10^6 gallons) would release only 0.3% of the dissolved Kr during this period. (See Table V for the Physical Characteristics of Containers Considered in Study.)

Loss of Dissolved Kr from Water Under Differing Thermal Conditions -- Loss of dissolved Kr from water under differing thermal conditions was viewed by experiments in the 3" OD × 20" high aluminum absorption vessel. Losses were lowest in the ambient temperature run -- 7%. Twice as much Kr was lost in the same period during a water cooling cycle -- a decrease from 196° to 100°F, and 5 times as much was lost if heat was added through the walls to maintain an elevated temperature, 196°F. Results are shown in Table VI.

Kr losses from quiescent, standing pools of water with varying surface to volume ratios are shown in Figure 4. The values shown for the 3" diameter absorption vessel and 6" diameter beaker are from a run at room temperature and all values could be used. The remaining values were taken from cooling-cycle tests and the initial values are not plotted. The time in which one half the Kr was lost varied from approximately 38 hours using a s/v of 0.6 ft^{-1} (3" diameter absorption vessel) to 11 hours using a s/v of 0.6 ft^{-1} (6" diameter beaker) and indicated a rough correlation between Kr loss and surface to volume ratio.

TABLE IV

VARIATION IN LOSS OF ABSORBED KRYPTON WITH SURFACE/VOLUME RATIO OF STANDING POOL DURING A 2-HOUR COOLING CYCLE

Run No.	Krypton Conc. μg Kr/cc Water	Surface/Volume Ratio, ft^2/ft^3	Percent Absorbed Krypton Lost
1	4.2	2.78	36
2	4.6	2.78	39
3	3.9	2.78	25
4	2.5	2.78	43
5a	12.6	0.6	14
6	11.2	2.78	37
7	10.6	2.32	35
7a	8.5	2.32	29
8	7.8	2.35	35

TABLE V

PHYSICAL CHARACTERISTICS OF WATER POOLS

	Diameter	Area	Depth	Volume Of Water	Surface To Volume ft^2/ft^3
Quench Tank	60'	2827 ft^2	50	∿ 10^6 gal	0.0212
Open Basin	350'×350'	1.225×10^5 ft^2		varies	
Aluminum Absorption Vessel	2.81"	6.2 in^2	20"	2.03 liters	0.6
4-liter Beaker	6"	28.2 in^2	5-3/8"	2.03 liters	2.78
2-liter Beaker	5"	19.65 in^2	5-3/8"	1.67 liters	2.32
1-liter Beaker	4"	12.57 in^2	5-3/8"	1.05 liters	2.35

TABLE VI

VARIATION OF LOSS OF ABSORBED KRYPTON WITH TEMPERATURE REGIME

(3" ODT Absorption Vessel, Surface/Volume 0.6 ft^{-1})

	Kr Conc. μg Kr/cc Water	Water Temp. °F	Percent Absorbed Krypton Lost
During 2-hour Cooling Cycle	6.2	196	14
During 2-hour At Elevated Temp. (Heat Added)	12.1	194-196	35
During 2-Hours At Ambient Temp.	18.0	70	7

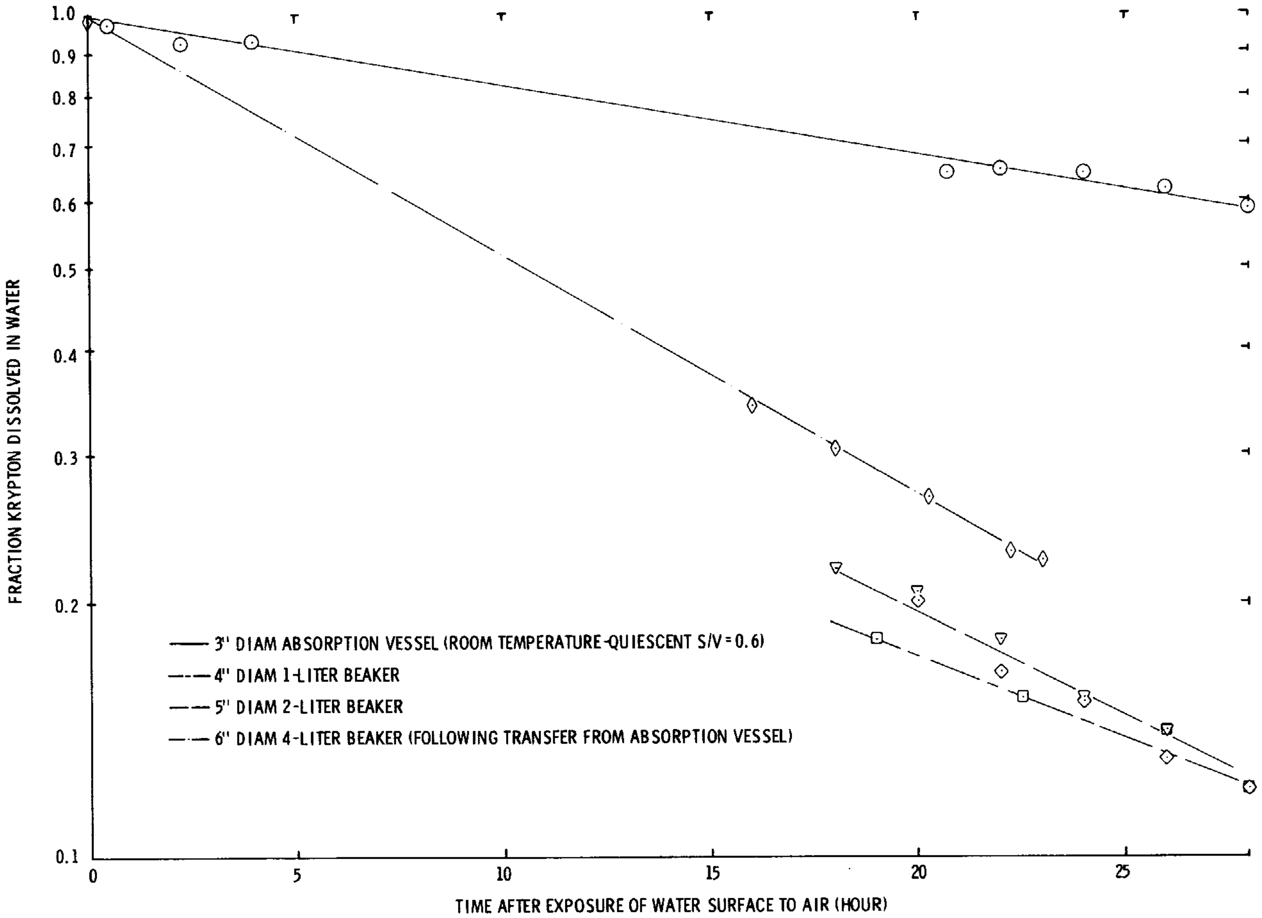

FIGURE 4

VARIATION OF Kr RELEASE RATES BY SURFACE/VOLUME RATIO

CONCLUSIONS

A few general observations can be made based upon the limited experimental study conducted.

- Dissolution of krypton gas in water at elevated temperatures is slow for a single vapor/water interface.

Even with much greater interfacial areas in a packed-column, Wood and Caputi[6] found greater times required to attain equilibrium concentration at slightly elevated temperatures -- 4 hours at 0° and 24°C, and 5 hours above room temperature. Thus, it appears that solubility and rate decrease with increased temperature to approximately 80°C.

- Significant quantities of dissolved krypton can be lost rapidly from water under a variety of circumstances.

In these experiments, increasing the surface to volume ratio increased Kr losses. This was indicated in both standing pools and during gravity draining from the absorption vessel. Internal circulation of the liquid with surface renewal and increased surface activity also appear to increase Kr losses as indicated by the varying loss under differing temperature regimes.

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DISCUSSION

SCHINDLER: On your first slide you show that the solubility of Krypton pulp in water increased with higher temperature. What is the reason for this?

MISHIMA: The graph presented on Krypton solubility is just the published data. Some indications of the mechanisms for the solubility of Krypton in water can be found in the first two references in the paper. I don't feel qualified to discuss this.

THE DEVELOPMENT OF A LONG-LIVED, HIGH-EXPANSION FOAM FOR ENTRAPPING AIR-BEARING NOBLE GAS

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ABSTRACT

The development of a long-lived foam with many potential uses is one of the benefits realized from the noble gas confinement studies carried out by Douglas United Nuclear, Inc.

Under the concept of long-lived, high-expansion foam control, the escaping gases would be passed through a foam generator that would encapsulate the contaminated air. Radioactive decay and slow permeation of the gases through the foam would restrict the final release of the gases to within acceptable radiation control limits.

This paper describes the successful quest for a high expansion foam (300 to 1 expansion ratio) with the ability to withstand time (120 days or more) without the loss of internal structural integrity. The technique developed of blowing the foam with a flooded impingement plate, thus requiring no nozzles or devices prone to plugging, has proven to be quite reliable and successful.

A description of facilities and instrumentation, as well as presentation of data from tests performed on a small bench top facility used to evaluate some 250 odd foam candidates to the large facility used to successfully encapsulate quantities of 5,000 cubic feet of air-bearing, tagged noble gas at various ppm per cubic foot of air, is made.

The foam development work and techniques employed appear useful for controlling industrial gaseous emissions, dust suppression, gas scrubbing of reactor containment vessels and even possibly in agriculture as an insulator for the prevention of frost damage.

This work was performed under USAEC Contract AT(45-D-1857)
by Douglas United Nuclear, Inc.

I. INTRODUCTION

Reactor containment vessels and/or confinement exhaust systems are the usual last-ditch engineered safeguards which are provided to protect the public from the inadvertent release of radioactive fission products. In the event of imperfect performance of these safeguards following a major reactor accident, a serious hazard to the public could result from the release of noble gases. In addition, the performance of confinement systems, which are designed to control and limit the rate of fission product releases but do not provide near-absolute containment, would be greatly enhanced if an economical method for trapping noble gases could be developed.

The purpose of the Noble Gas Confinement Study was to investigate, on a development scale, a method of controlling the releases of chemically inert, gaseous fission products (xenon and krypton) which would occur as a result of fuel melting accidents by encapsulation in a high-expansion foam.

II. DISCUSSION

All nuclear reactors which operate at more than nominally zero power level are equipped with a series of safeguards which prevent dangerous releases of radioactivity to the environs. These safeguards are conventionally: (1) a highly reliable nuclear control system, (2) a highly reliable primary coolant supply system, including primary and backup supplies, and (3) a containment or confinement structure which contains or controls the radioactive release should the other safeguards fail.

While present-day safeguards provide a highly effective defense in depth against radioactive releases, research continues in an effort to refine and improve this protection. Such work is aimed at both improving the effectivenss of the existing concepts in coping with the total spectrum of hypothetical reactor accidents, and at developing additional safeguard concepts to improve the depth of protection provided. The Noble Gas Confinement Study falls into both categories, in that it could evolve a means for maximizing the reduction in radioactive releases achieved by existing containment and confinement systems, or an added safeguard which provides protection in the event of containment or confinement structural failure.

The majority of radioactive products generated within the reactor core are amenable to relatively straightforward control measures. Particles containing fission products which are solids at ambient temperatures can be filtered, and most of the gaseous and dissolved species can be controlled by physico-chemical means - ion exchange, absorption, chemical precipitation. The inert gases, however, are largely unaffected by such measures. The actual content of radioactive noble gases, even in a large power reactor core, is only roughly one cubic foot under STP conditions. However, the radioactive species are mixed with thousands of cubic feet of nonradioactive noble gas isotopes, and would probably be further diluted in very large volumes of air, steam, and possibly hydrogen upon release from a stricken reactor core. Hence, the problem of noble gas control is to either entrap the entire volume of gases containing the noble gas containment, or to resegregate and trap the noble gas by some means.

A. Conceptual Description

The foam method of noble gas control visualizes the continued exhausting of escaping gases through a filtration system, and then passage through a foam generator which will encapsulate and hold the contaminated air for a period of time. Radioactive decay and slow permeation and release of the gases through the foam structure would provide, hopefully, several orders of magnitude reduction of the high radiation source, which otherwise would drift uncontrolled as a potential health hazard.

A number of investigators have been engaged in a search for materials which would generate foams capable of containing the noble gases for extended periods of time. Efforts have been directed toward modifying the high-expansion foams used in fire-fighting with various additives to extend the normally short life of these foams. Some success had been reported in the past with the use of animal protein in the generation of foams with improved stability and life. Upon project inception, foam life in high expansion foams was, to the best of our knowledge, limited to one or two hours at the most.

The desired foam formulations now available exhibit the ability of flowing freely, and of having the capability of holding water in the cell wall. Additional tests on water retention by exposure to high temperature, which could result from exposure to sunlight or heat generated due to the radiactive decay processes which may occur in confined air volumes, will be investigated at some future date.

B. Technical Background

Technical information directly applicable to the problem of producing a long-lived foam had not been found, either in literature searches or through industrial and laboratory contacts. Work in other laboratories had been directed at foam encapsulation of air within a confined space, and was largely aimed at encapsulating radioiodine, which exhibits solubility and chemical properties quite different from the noble gases, a problem which will be addressed in the next section.

A number of chemical companies had been contacted and their literature and commentary reviewed in attempts to discover appropriate foaming agents. Discussions were held with staff members at government and private research installations and with industrial foam formulators in an attempt to define a combination of surfactants and thickening agents as a possible avenue toward a longer-lived foam.

This search did not develop any directly useful information, although progress was expected in the correlation of various sources of information with regard to the physical aspects of foam generation. One authority was adamant that high expansion foam cannot be modified with any success to extend its life. A second authority indicated possible success in foams in the medium range expansion ratio by use of thickening agents.

Various materials such as the fluro carbon surfactants exhibiting unusually low surface tension and good temperature insensitivity and thickness as the high molecular glycols and water soluble ethylene oxide polymer resins were all of considerable interest.

Early in FY-1970, therefore, only the confidence that a foam could be developed persisted but no concrete evidence existed.

C. Successful Development of Foaming Agents

A preliminary screening of foam materials in 1967 indicated that a combination of surfactants and materials capable of improving the elasticity and flow charactertistics of the water-based foam solution held promise. Higher molecular weight glycols and a line of water soluble ethylene oxide polymers were obtained. A number of surfactants were also identified. In addition to the water soluble ethylene oxide polymers, a number of other candidate thickening agents were identified, such as the micro methyl cellulose compounds. However, it was apparent that formulation of the foam solutions might be difficult. The thickening agents take time to get into solution and hydrolyze before the thickening action becomes apparent. This involves coordinating the time for introducing the thickening material, dispersing it in the water surfactant, and generating the foam in a sequence which will result in the cell wall retaining the water with a minimum loss. The discussion with manufacturing representatives revealed several materials which might avoid this problem, including a liquid thickener already hydrolized. Samples were procured and tested in various concentrations and under a series of various conditions.

The preliminary work in 1967 provided a sound basis for the current program. Various surfactants and materials were obtained for modifying the viscoelastic characteristics of water as well as jelling the water. The continued literature survey had served to firm up this approach as well as provide the investigators a better working knowledge of the phenomena involved and the influence of various materials on water.

This effort has from its inception been directed toward the use of a water-based foam rather than something more exotic such as a latex or plastic-based foam. A latex or plastic material could undoubtedly be found which would readily provide the desired encapsulating cell structure, but the associated problems in handling, storing and dispersing of a semipermanent fixed material would be difficult to resolve. Encapsulating a large volume of air in a fast setting plastic or rubber foam from a fixed generating station would be very difficult. Slower setting lattices or plastics would present problems similar to the ones associated with water foams - collapse of the cell structure and liberation of the encapsulated air.

Moderate success was achieved in that some foams with a half-life of three days when generated two feet deep were produced in the Douglas United Nuclear laboratories.

Realizing the task of investigating the many additives, thickness surfactants and other possible agents that could be included for their respective properties, could be a life-long quest; assistance was considered necessary in order to investigate promising avenues of approach.

The blowing of bubbles to some extent is an art practiced by few. In addition, only the most optimistic individuals could be relied on to accomplish the task with relative success. Two individuals were located - Mr. Ralph Hiltz of the Mine Safety Appliance Research Corp. and Dr. A. V. Grosse of the Germantown Laboratories, Inc. These individuals among other endeavors have made extensive studies of foam and its generation and, most important, exhibited the confidence that a relatively high expansion, long-lived foam could indeed be produced. The above two men were retained on short-term consulting contracts (three months) and three parallel avenues of investigation were begun.

In mid-December, 1969, Mr. Ralph Hiltz and his co-worker, Mr. Joseph Friel of MSA, indicated a breakthrough had been made. A visit to their laboratory showed that indeed the quest might be over. The main foam constituents were packaged and carried to the DUN laboratories where, on December 19 at 8:00 a.m., the foam was reproduced at an expansion ratio of 300 to 1, using the following formulation:

Two parts PEI-1000 (Dow Chemical)*
One part PVA (Airco VINOL 325-4% solution)*
Two parts MSA (Surfactant)
Five parts water

* Note: PEI - Polyethyleneimine
PVA - Polyvinolalcohol

Special note should be made of Figures 3 through 6, taken on the date of foam generation through January 9, 1970. Approximately a five-inch degradation 25 percent of volume in the foam can be noted over this period of time. Without a doubt, a considerable amount of degradation is due to curious people poking fingers into it.

Some properties of the foam formulation that have been noted are the following:

1. With the formulation mentioned, a two-thirds solution run-off was seen within 24 hours. The additional solution carried with the foam may prove necessary to aid its flow characteristics when initially generated.

2. The run-off can be used to generate additional foam with no immediate noted difference in properties. This was done with the first run-off in the compartment immediately to the left of the exhibited foam seen in Figures 3 through 6.

3. Within a matter of minutes, the foam will set up into a semiplastic state with the bubbles becoming quite tacky. The bubbles will not burst as a common soap bubble, but will very slowly pull apart and collapse from the point on the bubble where ruptured.

4. No degradation of the internal structure of the bubble layers can be noted. Degradation took place at a rather linear rate from the exposed top layers at about one-fifth of an inch per 24 hours.

5. A sample of the solution prepared for the initial test has at this writing after almost 250 days exhibited no segregation of ingredients. It appears to still be well mixed and usable. The formulation, therefore, appears to have good storage life and goes into solution readily.

Suspected properties if analysis of what is taking place should be correct might all be of benefit.

1. The foam appears to set up into a semiplastic state and is made up of a somewhat complex organic chain.

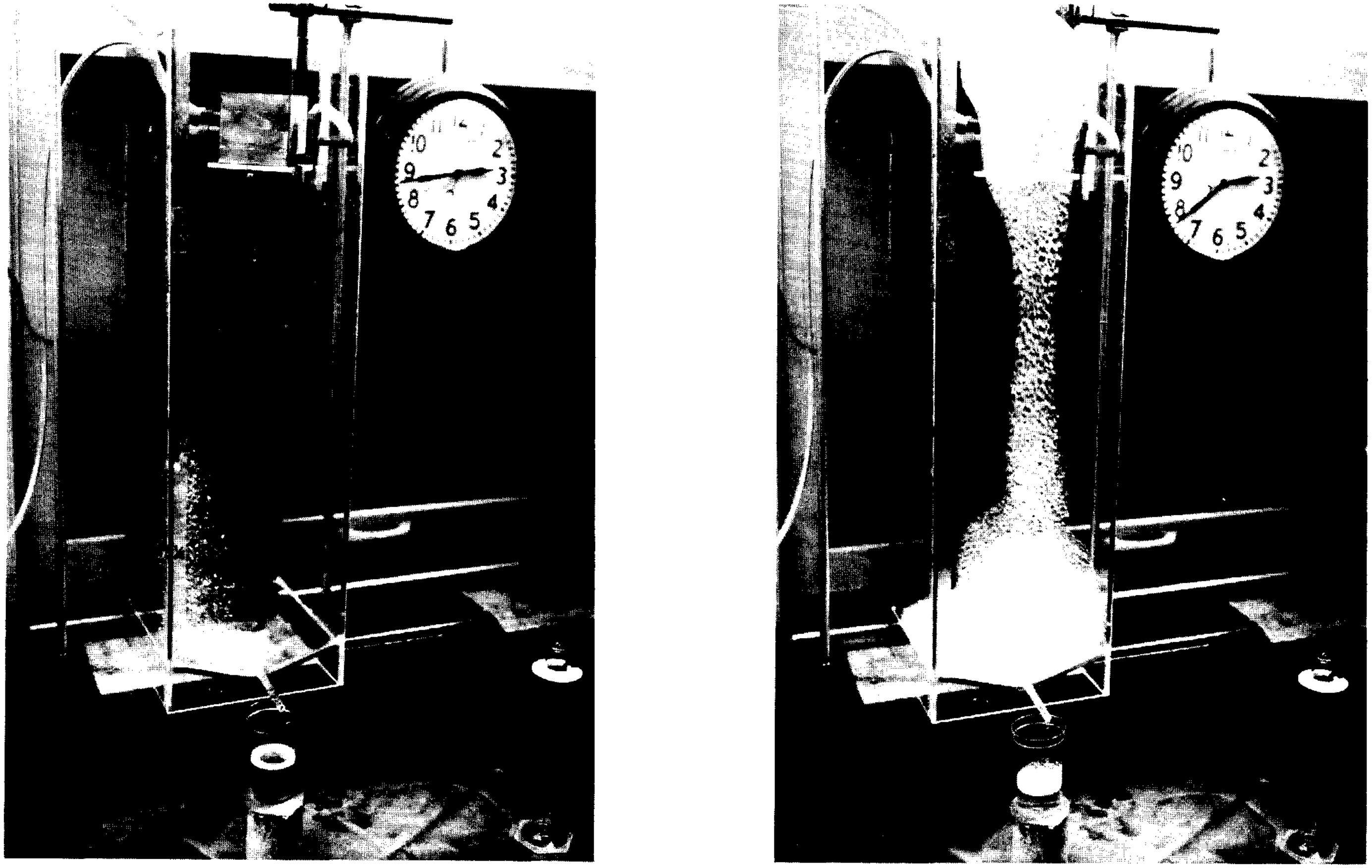


Figure 1

Figure 2

Figures 1 and 2 Exhibit a Typical Laboratory Bench Generation Set-Up With the Generator Mounted in a Plexi-Glas Container.

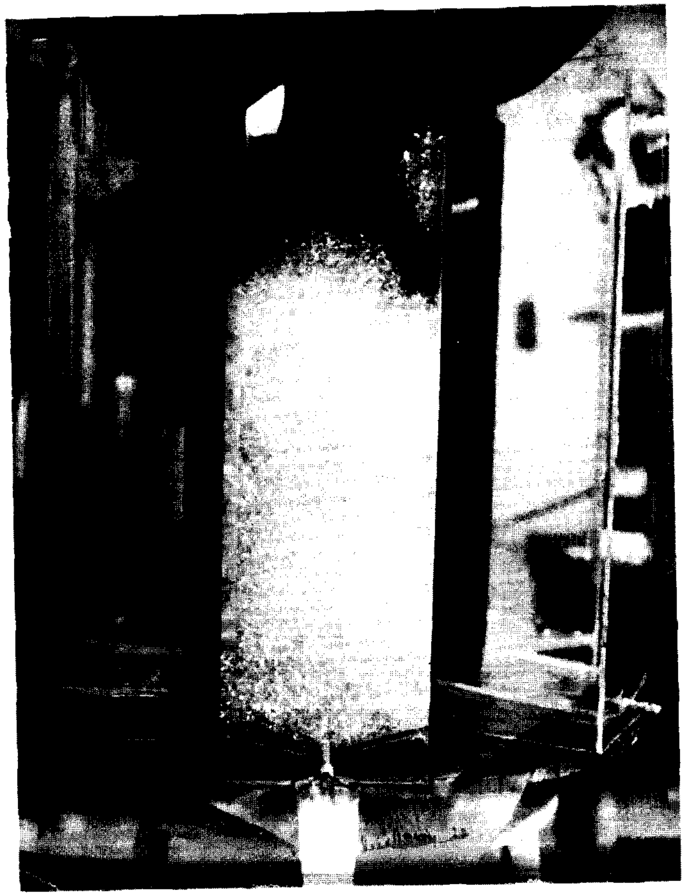


Figure 3

Formulation No. 99, Long Lived Foam as Generated on 12-19-69.

Two Parts PEI, One Part PVA, Two Parts Foam Agent and Five Parts Water.

Figure 4

Formulation No. 99, as It Appeared on 12-28-69 After 10 Days.

Formulation No. 100 Can Be Seen to the Left of No. 99. Generation was from No. 99 Run Off on 12-29-69.

Figure 5

From the Left Formulations 100 and 99 as They Appeared on 1-5-70, 17 Days After Generation.

Figure 6

From the Left Formulations 100, 99 and 104 as They Appeared on 1-19-70. No. 99 Being 30 Days Old With a 25% Volume Loss.

2. Because of the type of chemistry involved, the foam should be rather unaffected by even additional vapors such as iodine and methyl iodide. The pH of the formulation might not be affected as it is in some normal fire-fighting foams leading to premature collapse.

3. When foam breakdown does indeed take place, pollutants as methyl iodide might very well be held in a salt form.

4. Heat due to sunlight or radioactive decay should enhance the foam and may not be detrimental to it.

A continuing effort for the months of January and February 1970 were undertaken. Some additional study of variations of the formulation to additionally improve the foam characteristics as well as to tighten up the suspected semiplastic organic complex was dealt with. In the final analysis, a candidate foam formulation for larger tests and noble gas encapsulation had been at this time developed.

The continuing effort by both the Germantown Laboratories and the Mine Safety Appliance Research Corporation into February did indeed render improvement to the foam formulation and produced other formulations also in the 100-day half-life realm exhibiting the wanted properties. A more complete description of the work performed and the respective consultants' reports can be found in Reference 4.

D. Foam Generator Development

Early screening of candidate foam materials utilized a common kitchen blender. The results obtained from these tests were not reproduced by a 3,000 cfm foam generator. Consultation with industrial contacts suggested testing on a bench type generator duplicating the large-scale system. The standard foam generator exhausts air through a cloth mesh flooded with liquid supplied by spray nozzles. This type of generator appears to have several disadvantages from long-term standby considerations. An alternate foam generator, Figures 9 and 10, has been devised in which air exhausts up through a horizontal metal plate perforated by 1/16 inch holes on 3/16 inch centers. A sheet metal deflector is positioned above each hole.

The plate is flooded with liquids, and the air jetting up through the perforations is dispersed through the surrounding liquid when the air jet impinges against the deflector. Proper control of the liquid level has generated a good encapsulating foam. This type of foam generator is expected to provide high reliability after long periods of standby status, and has been relatively easy to duplicate on a small scale. The smaller generator has been constructed, as seen in Figures 7 and 8, for bench work in which all surfactant-thickening formulations have been evaluated to date.

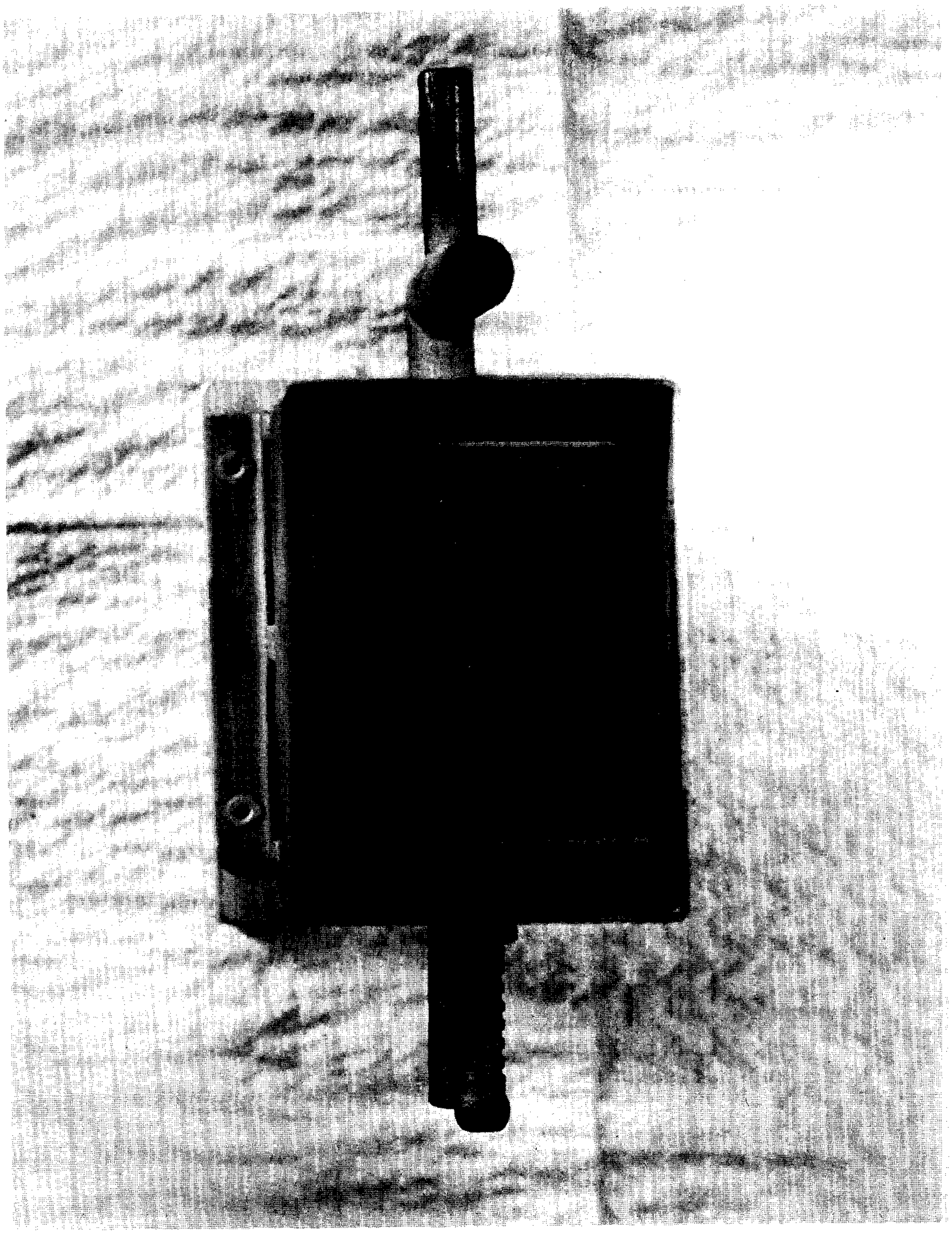


Figure 7. Top view of the small bench top generator housed within its flood tank

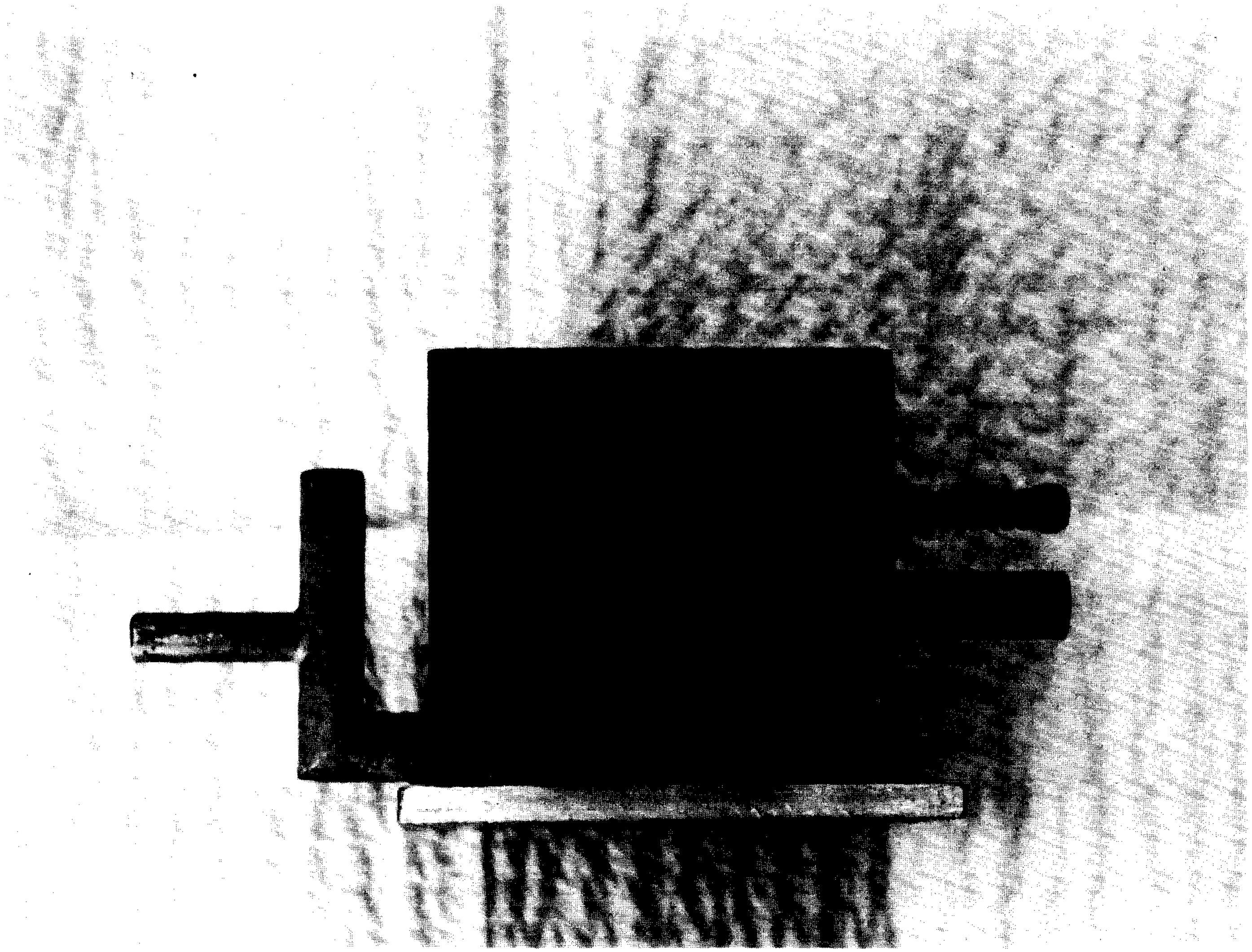


Figure 8

Side View of Small Generator Seen in Figure 6.
(Generator as Seen Here is Close to Its True Size.)

The small plate used in the bench top work has proved to be quite successful and easy to use. Besides being a foam maker, it is a unique gas scrubber. It will produce foam from solutions otherwise much too viscous to be utilized in most common fire-fighting generators and is being evaluated currently for other applications.

Testing of the impingement baffle plate concept for use as a foam generator progressed then in two stages. The small plate approximately two inches square is currently being utilized for bench work. At a velocity of 500 fpm, the 1/16 inch diameter perforation on a 3/16 inch center will generate approximately 1 cfm foam, which will allow handling of a reasonable volume of foam in the laboratory. This amount of foam requires about 50-100 cc surfactant solution per minute at 300-600 expansion ratios. The next phase of testing evaluated foam generation using prototype plates, seen in Figures 9 and 10. These plates allowed the generation of 50 to 100 cfm of foam and allowed the evaluation of tracer gases and studies of foam permeation rates and other parameters. The experience gained with this size generator should allow sizing up to an adequate 1,000 cfm pilot plant and eventually to a full-scale generator capable of encapsulating the 50,000 cfm air exhausting from a production reactor confiner.

A full capacity foam generator would comprise the general specifications outlined in the following table:

TABLE I

FOAM GENERATOR PLATE CAPACITIES

Plate Dia. of Hole (in.)	Perforation Center (inches)	50,000 cfm at 500 fpm		50,000 cfm at 1,000 fpm	
		Plate Area (ft^2)	Plate Dia. (ft)	Plate Area (ft^2)	Plate Dia. (ft)
3/16	3/8	410	22.8	205	16.0
1/8	3/8	950	34.8	475	24.4
1/16	3/16	1,350	41.0	675	29.0

Note that the air volume is based on 50,000 cubic feet per minute and the air velocities on 500 and 1,000 feet per minute. These velocities are in the range of normal foam generators. Five hundred feet per minute is generally accepted as a maximum for the sprayed-net, cone-type foam generator. The flooded impingement plate is expected to reach much higher air velocities without breakthrough and foam generation at various air velocities in excess of 500 feet per minute would be evaluated in order to minimize the necessary plate size.

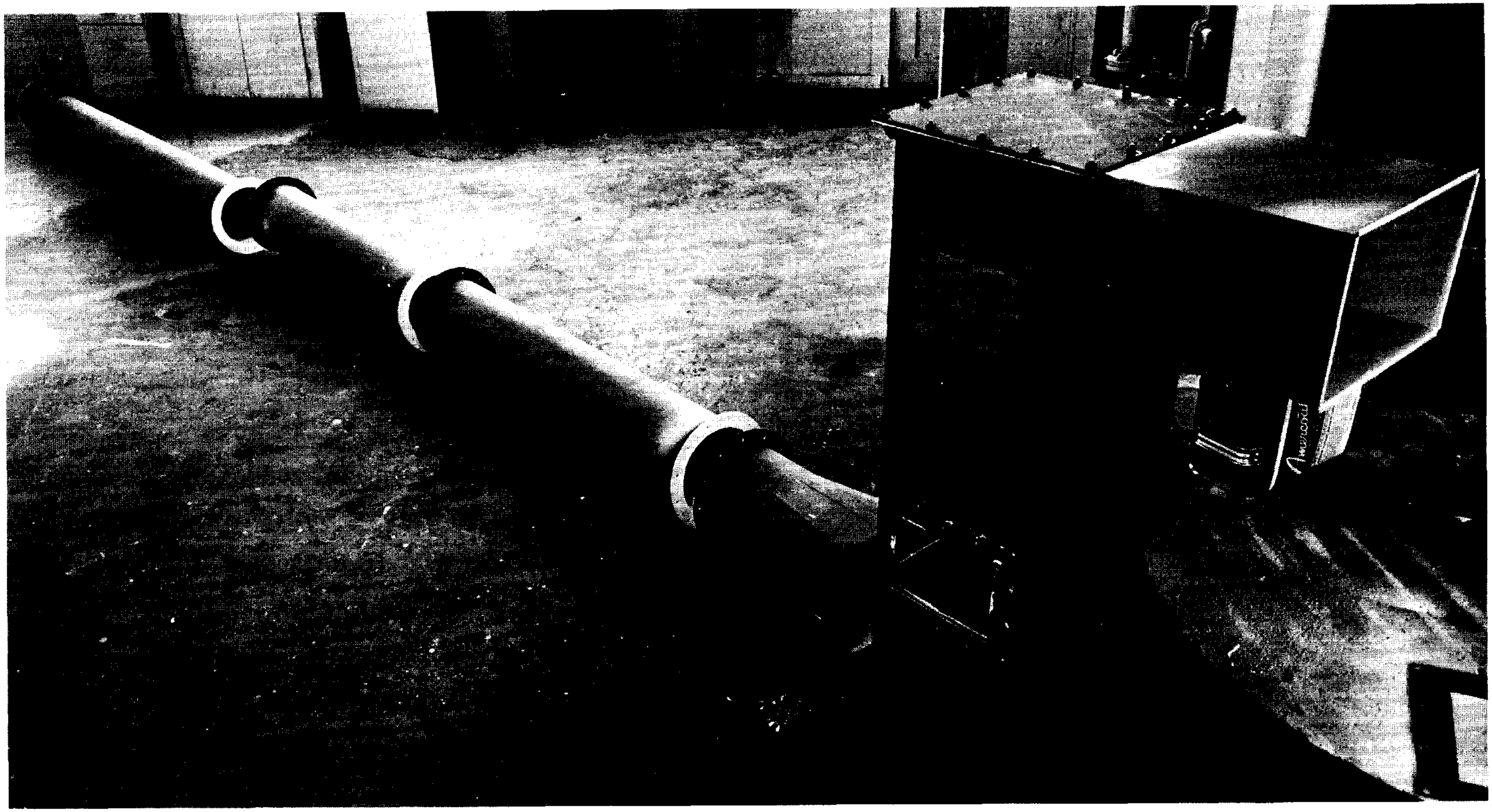


Figure 9. Fan duct being assembled

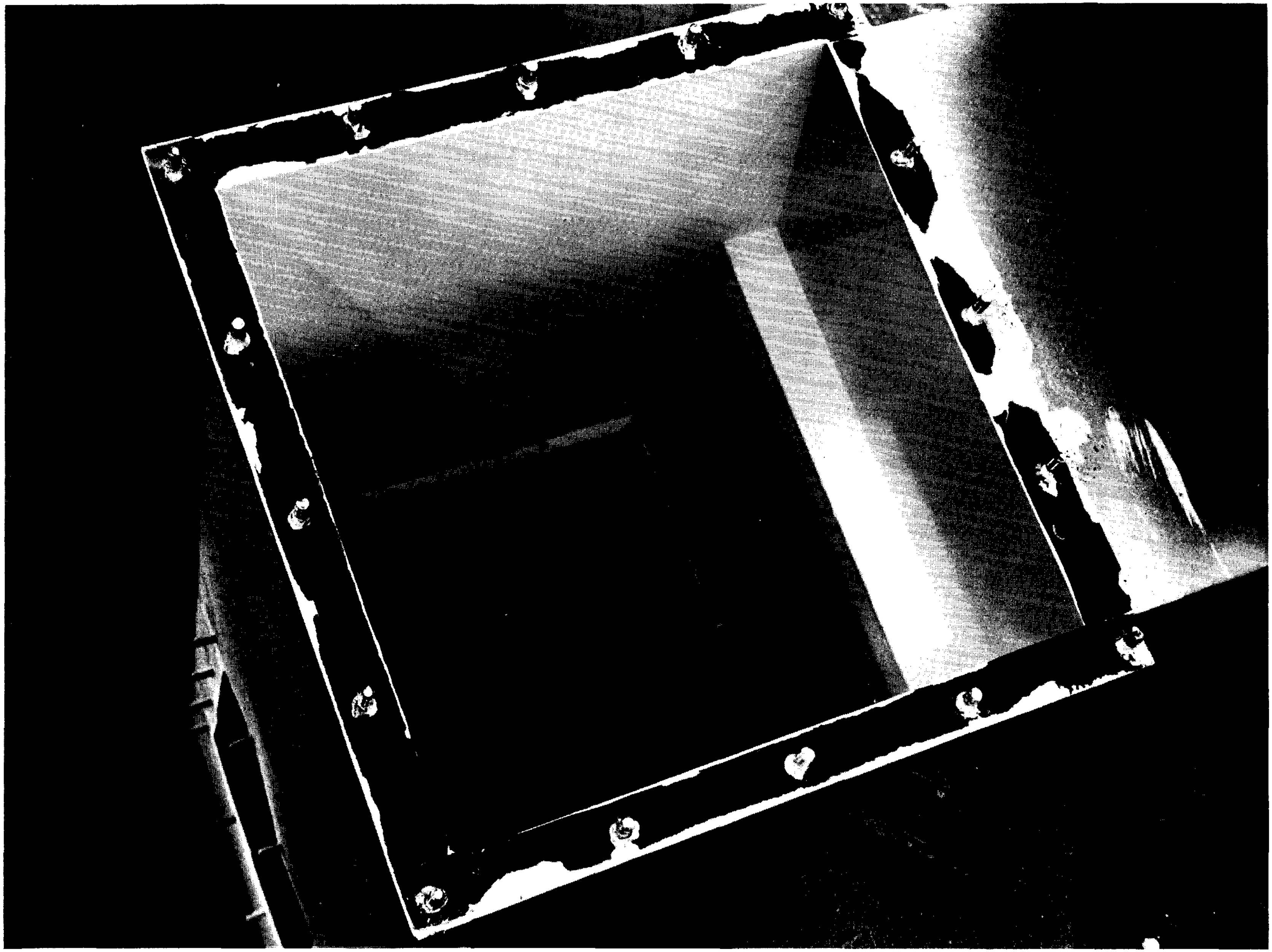


Figure 10. Deflector plate generator being assembled

The fan system seen in Figures 9 and 10, which accommodates the one square foot generation plate, was installed in the 190-H tank room. Foam was produced utilizing the technique developed in the bench top work with the candidate formulation described. The foam was generated into a large plastic bag as described in the next section. Several locations of the generator were tried, the most successful being at the 20-foot level on a scaffold as seen in Figure 19. The least successful location was that seen in Figure 11 at the floor level. Problem areas in the use of this type of generator were encountered on the large bag tests but are not considered unsoluble and will be discussed later.

E. Experimental Setup

The large-scale foam tests were initially set up as shown in Figure 11 and 12 with the generator located at the floor level. The experimental facility was located within one of the 7,000,000 gallon water tanks in the 190-H tank room. The large plastic bag measured 20 feet square and 30 feet high. The large bag enabled tests to be conducted utilizing 5,000 to 10,000 cubic feet of foam.

Location of the facility on the inside of the tank was chosen so that any escaping tracers would be confined to the tank interior and vented through the top of the tank to the atmosphere. In addition, it was thought necessary at the time to locate the facility in a location with a minimum of light so that the special G.M. detectors mounted on and in the bag would respond properly. A typical Noble Gas Detection Probe can be seen in Figure 14. Some 25 probes were mounted in and on the bag in three levels from the floor. Level one was comprised of seven detectors on the bag sides and one in the middle of the bag four feet off the floor, levels two and three in the same arrangement were located upwards with an eight-foot distance between detection levels. An additional detector was located in the middle of the bag at the top.

The monitoring instrumentation used was that utilized in the noble gas atmospheric and meteorological experiments conducted at Hanford by Battelle Northwest Laboratories.(5) The monitoring instruments mounted on the bag at various strata and bag positions fed their information back into an automatic data collection system capable of monitoring in excess of 24 hours duration. Data were retained for readout on a magnetic tape system, which has proven quite reliable. In excess of six days' worth of information could be collected by the tape system before a change in tapes was necessary. An example of the type of magnetic tape data readout can be seen in Figure 15. The monitoring instrumentation seen in Figure 16 was located some 100 feet away from the tank in its own temperature-controlled room.

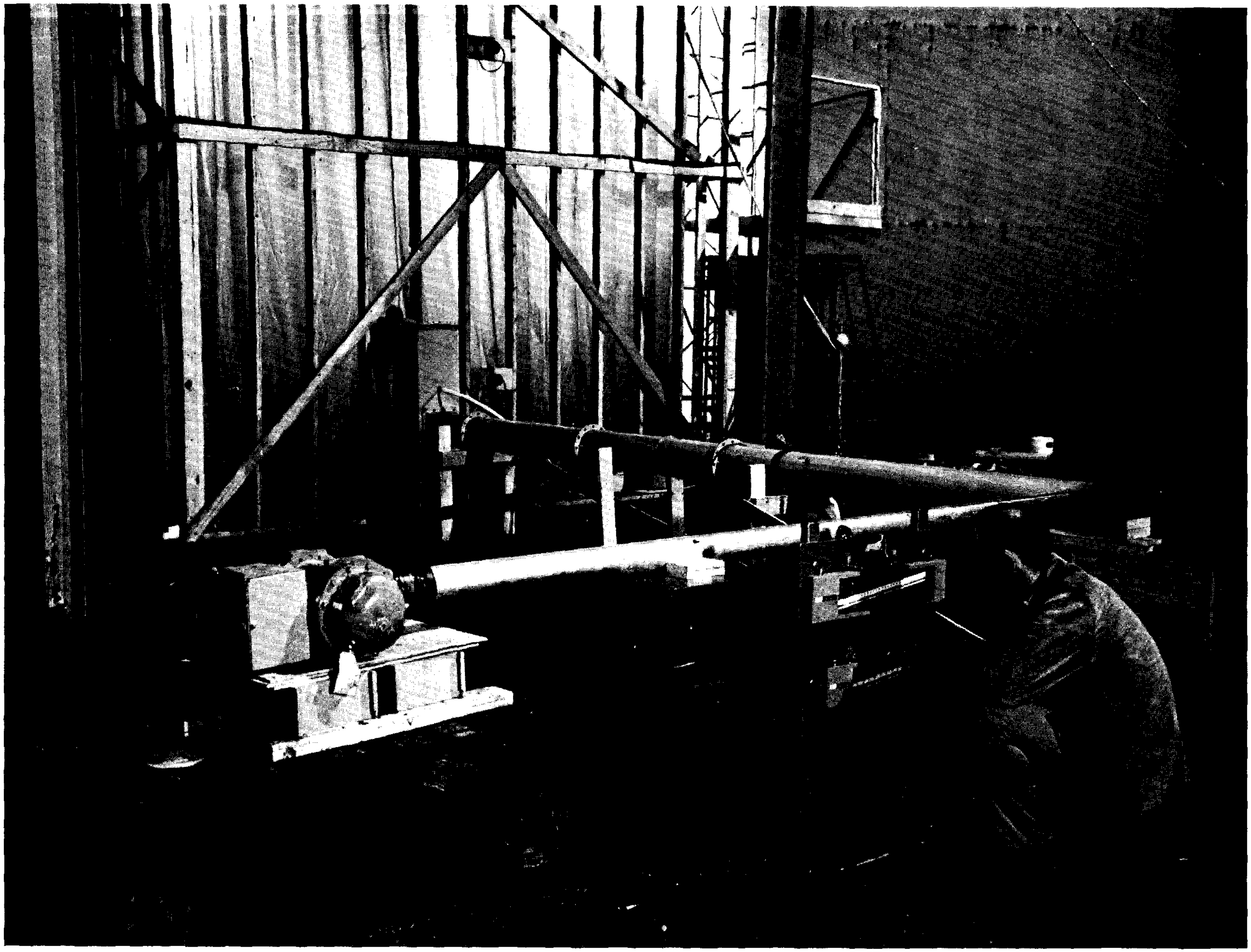


Figure 11. Original experimental set-up with the generator plate completely enclosed and located outside of the plastic bag on the floor level

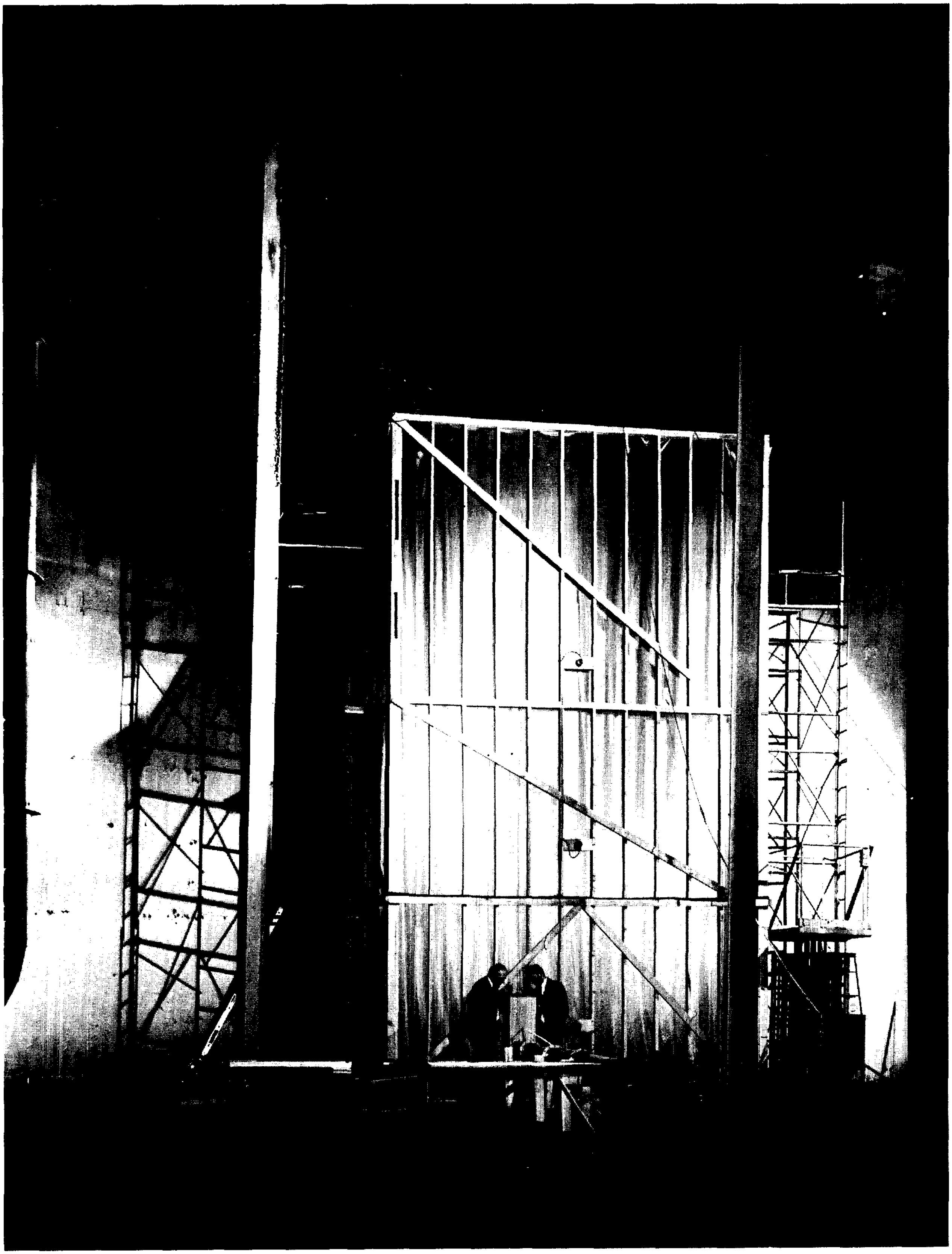


Figure 12. Overall view of the original experimental set-up located on the inside of a 190-H, water tank

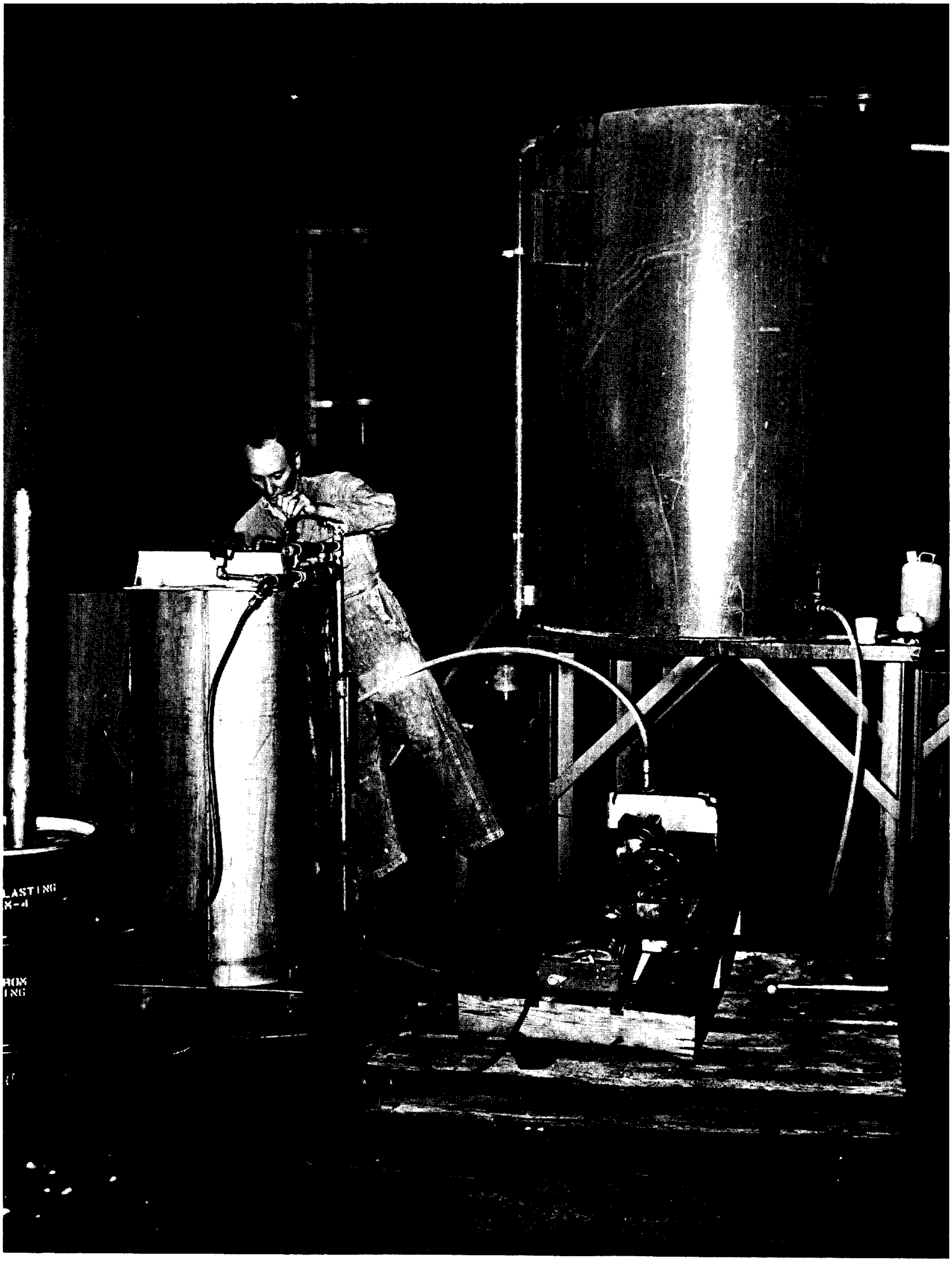


Figure 13. 190-H tank room view, where the chemical mixing vats and pumps were located

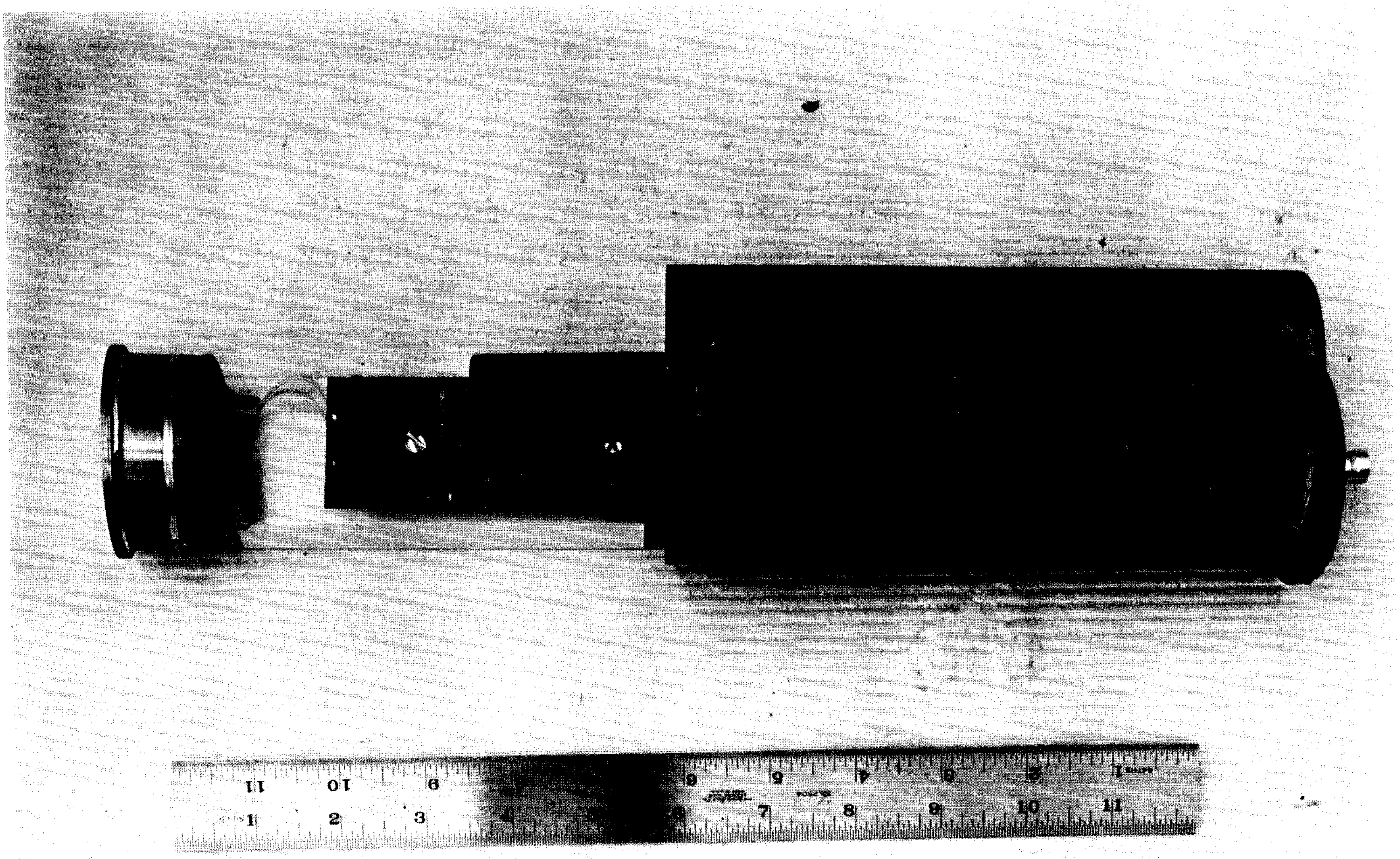


Figure 14. Typical noble gas detection probe for noble gas foam diffusion studies

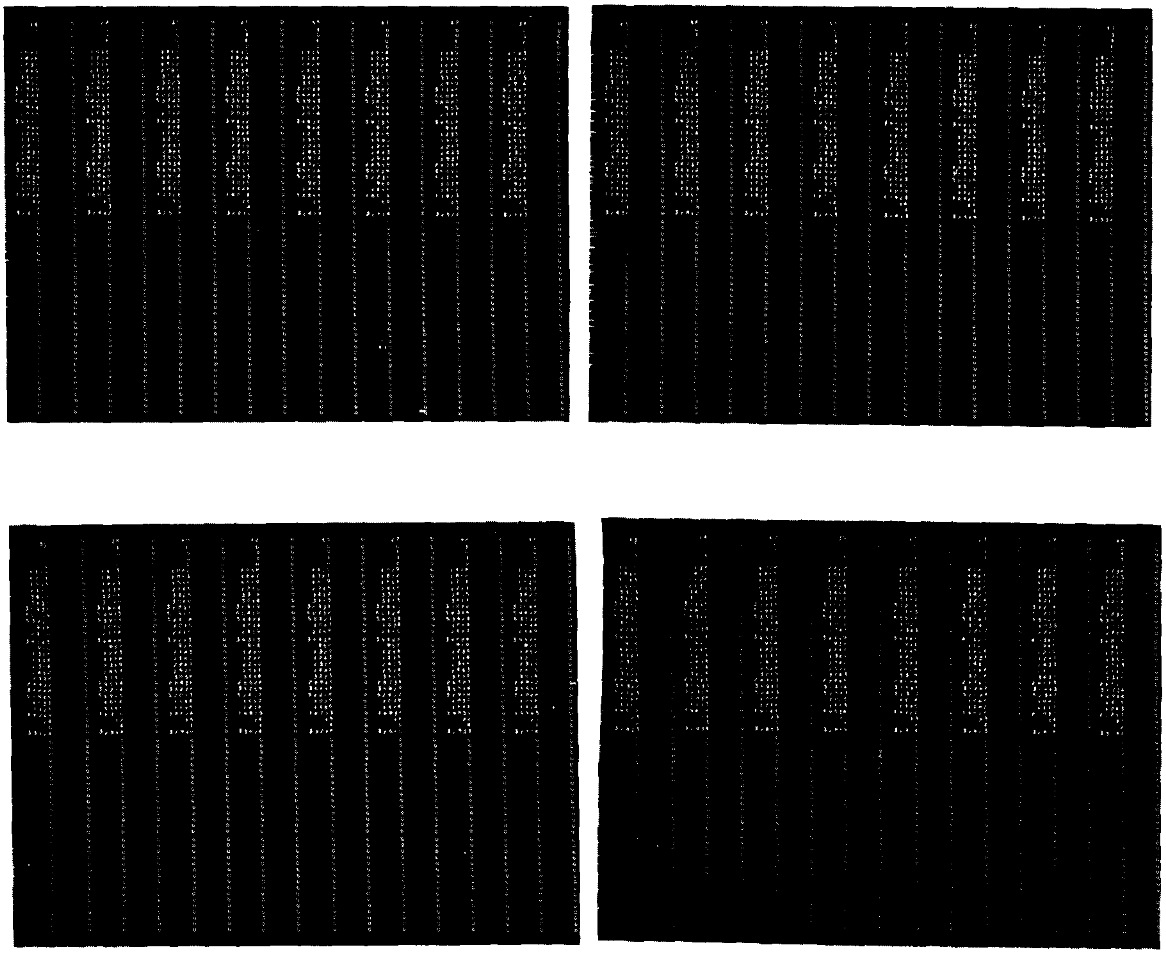


Figure 15. Magnetic Tape Readout. Seen above is a typical magnetic tape display each column representing about 1/2 hrs. worth of information collected by the 25 detectors. In excess of 150,000 pieces of information as seen above were collected for the two weeks.

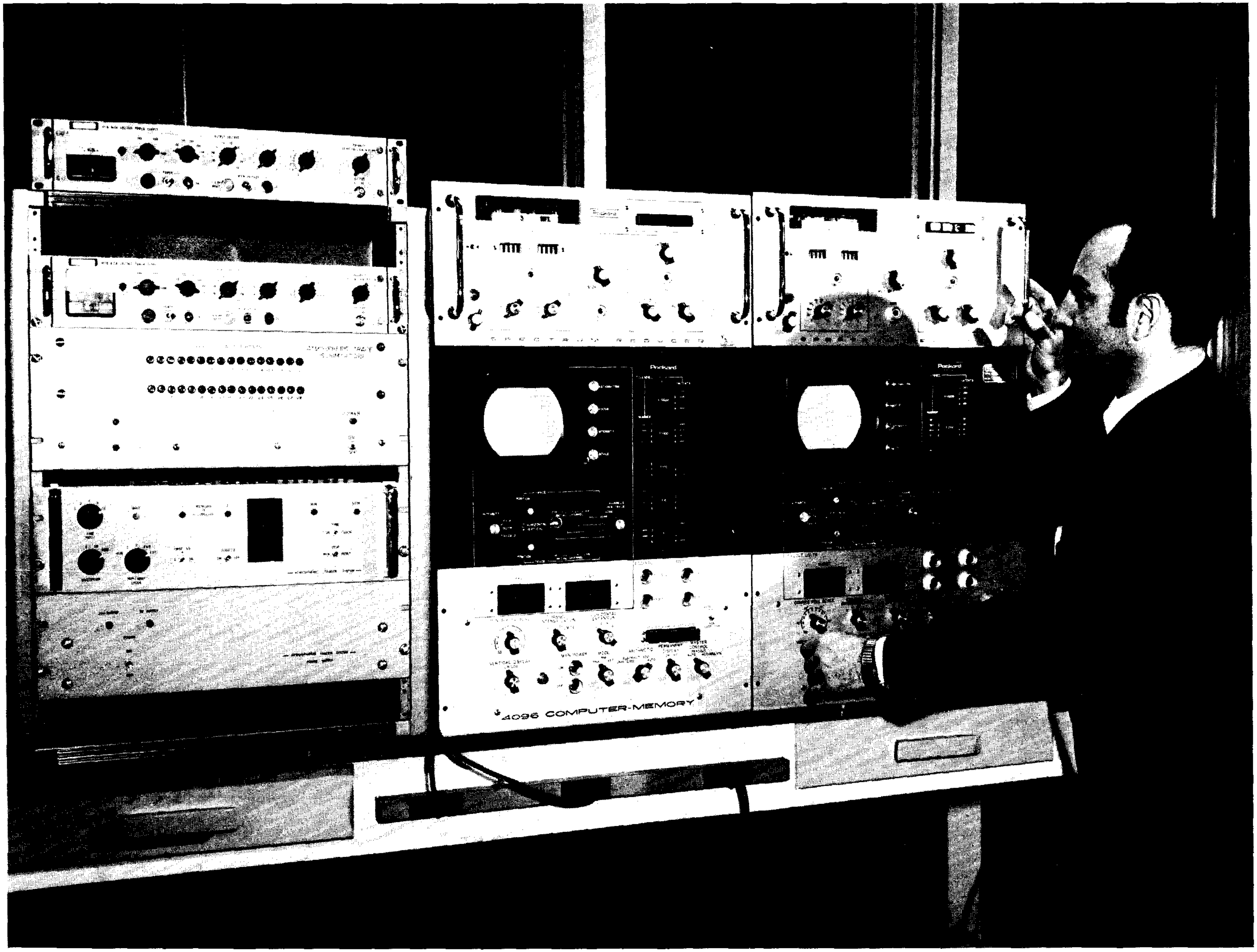


Figure 16. Data Collection System. The 25 detectors monitoring continuously 24 hrs/day fed their information into the analyzer and memory system shown above, which was then read out to the magnetic tape deck seen above the analyzers. Six days of information could be stored by the system without a change in tapes.

NOBLE GAS DECAY
VS
TIME

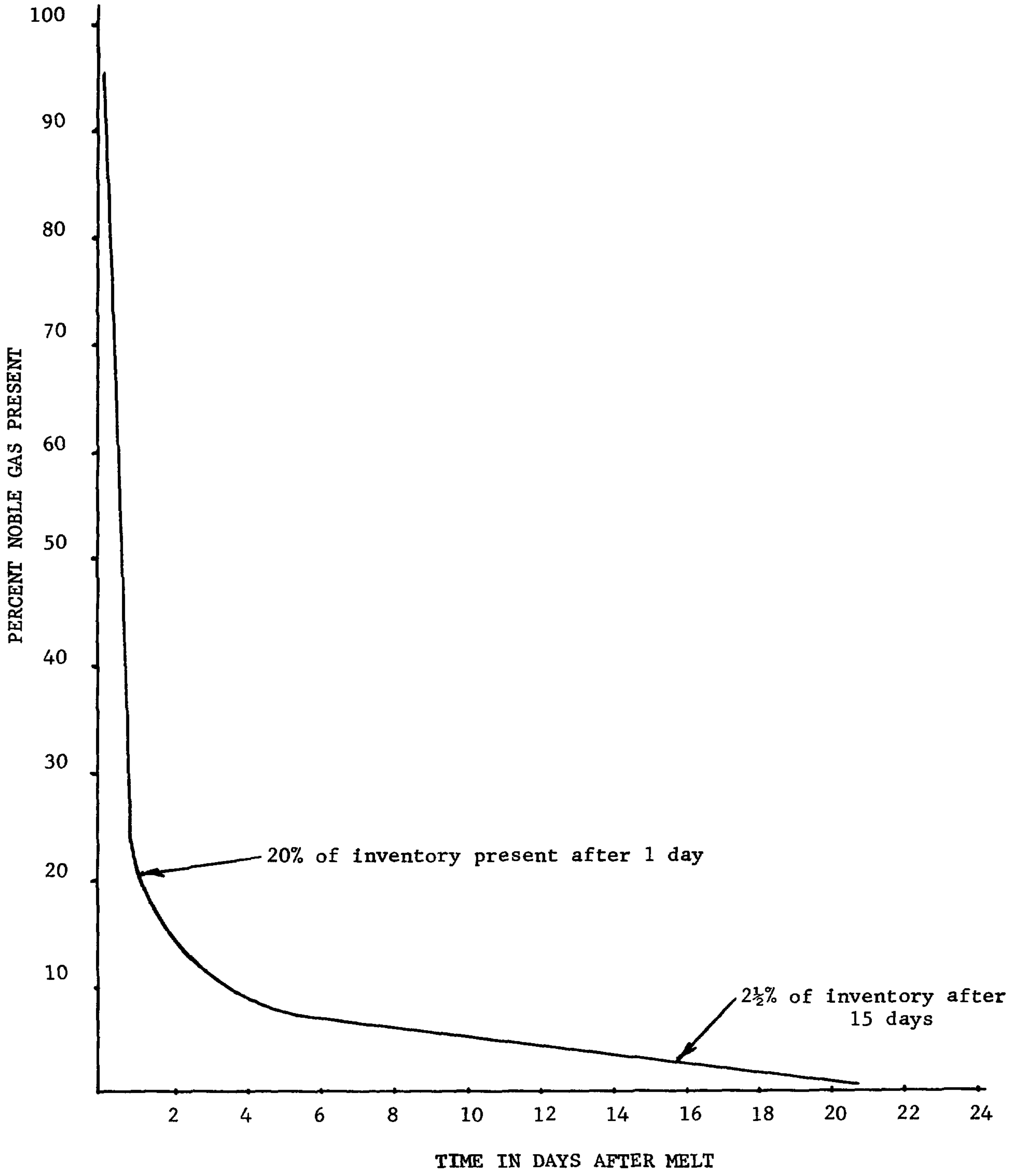


Figure 17

Figure 18. Generator at the 20 foot level. Note the foam in the bag and the detector.

Figure 19. Generator installed at the 30 foot level; the generator plate housing was cut away to allow free foam flow.

The tank and plastic bag have been instrumented as described for monitoring the foam depth and radiation levels of noble gas tracers at various strata to study the diffusion of noble gas through the foam and gas layer above. The plastic bag concept also allowed some study of bubble cell structure with depth and was reinforced on the bottom to facilitate run-off collection and reuse of the reclaimed solution.

The foam solutions were mixed in 500-gallon batches outside of the tank proper and pumped to the generator inside of the tank. An idea of location and tank size can be obtained from Figure 13.

F. Noble Gas Release from Molten Fuel

Conservative practice in safety analyses is to assume that all of the noble gas fission product inventory is released from molten fuel. To establish boundaries on the range of noble gas concentrations to be considered in the confinement experiments, the noble gas content of the N-Reactor core was calculated. The N Reactor operates at a power level of 4,000 Mw thermal, and hence carries a somewhat higher noble gas inventory than current generation light-water reactor cores. On the other hand, the N-Reactor dual-purpose metallic uranium fuel is carried to only limited burnup levels, and hence contains a limited amount of the stable noble gas isotopes. A hypothetical fuel residence time was used in the contained calculations.

The radioactive noble gas inventory of the reactor is shown in Table II, as a function of time after shutdown. As is apparent from the Table II, a holdup time of almost five days is required to effect a reduction in radioactivity of a factor of ten. Of course, the advantages of extended and controlled release times go beyond simple decay since control of the release timing would introduce the possibility of utilizing advantageous meteorological conditions and even temporary evacuations to minimize dosages during the release.

While the radioactive inventory steadily decreases with time after shutdown, the total inventory of noble gases remains essentially constant since the vast majority of the isotopes are stable. In the example case, the total inventory of noble gases is about 35,000 liters at standard temperature and pressure, or about 1,250 cubic feet (about one cubic foot is initially radioactive). If this volume is released into the N-Reactor confinement space (800,000 ft^3), a concentration of 0.16 volume percent of noble gases would result. In the actual case, the confiner is open to atmosphere through a filter system and stack. The process of venting and "breathing" as steam is released and condensed by the fog sprays would result in considerably more dilution. In the limiting possible case of continued forced ventilation of the confiner with a 100,000 cfm air flow and assuming a two-hour release of the noble gases, their concentration could be as low as 100 ppm, or less for smaller fractional releases other than a full melt.

TABLE II

NOBLE GAS ACTIVITY VERSUS TIME

Time	Noble Gas Activity (Curies)
0	1.8×10^9
1.5 hrs	4.0×10^8
5.0 hrs	3.6×10^8
10.0 hrs	3.4×10^8
5 days	1.4×10^8
10 days	7.3×10^7
15 days	3.8×10^7
45 days	8.9×10^5

Obviously, the higher concentrations of noble gases could only be achieved at lower flow rates or by higher rates of release from the core. For the purposes of these experiments, 100 ppm of krypton gas was chosen.

TABLE III

NOBLE GAS CONCENTRATION VERSUS FLOW RATE FROM 105-N

Concentration (ppm)	Volumetric Flow Range (cfm)
5,000	1,000-10,000
1,000	1,000-10,000
100	10,000-100,000
10	10,000-100,000

This range of variables will simulate the range of conditions which might be equivalent to, on the other hand, release of the noble gases into a stagnant containment vessel equipped with a flow air cleanup loop and, on the other hand, release of approximately ten percent of the noble gas inventory of the core into a forced ventilation system. The latter situation represents one which, while not negligible, would not result in doses at the Hanford site boundary over a two-hour period in excess of Federal Regulation Guidelines.

An additional insight into the noble gas problem can be gained from reviewing Figure 17, Noble Gas Decay Versus Time Curve and Tables IV and V. Of interest are the quantities left after

TABLE IV

KRYPTON ISOTOPES

		% Isotope Contribution to Total Krypton Present		
Isotope	Half-Life	At Melt	After 1.5 Hours	After 5 Days
Kr-83m	144 min.	1.77	12.69	0.0
Kr-85m	4.36 hr.	2.81	17.28	0.0
Kr-85	10.27 yr.	0.05	0.46	100.0
Kr-87	78 min.	6.00	20.78	0.0
Kr-88	2.77 hr.	9.17	48.78	0.0
Kr-89	3.18 min.	11.09	0.01	0.0
Kr-90 to 97 Inclusive		69.11	0.00	0.0
% Curies of Original Kr Present		100	12.99	0.05
% Curies of Total Noble Gas Inventory at Time Indicated		32.35	18.66	0.24

TABLE V

XENON ISOTOPES

Isotope	Half-Life	% Isotope Contribution to Total Xenon Present			
		At Melt	After 1.5 Hr.	After 5 Days	After 15 Days
Xe-131m	12 days	0.08	0.32	9.68	1.81
Xe-133m	2.3 days	0.61	2.21	1.47	0.27
Xe-133	5.27 days	18.96	70.05	97.80	97.92
Xe-135m	15.6 min.	5.61	17.06	0.00	0.00
Xe-135	9.13 hr.	0.80	9.76	0.05	0.00
Xe-137	3.9 min.	18.71	0.00	0.00	0.00
Xe-138	17 min.	16.65	0.72	0.00	0.00
Xe-139 to 144 Inclusive		38.58	0.00	0.00	0.00
% Curies of Original Xe Present		100.00	27.07	11.74	3.19
% Curies of Total Noble Gas Inventory at Time Indicated		67.65	81.33	99.76	100.00*

*The 100 percent value is based on the premise that any ^{85}Kr available will have at this point in time been dispersed to the atmosphere.

only 15 days' duration; as can be noted, almost 99.75 percent is Xenon-133 and 0.25 percent is Krypton-85, a good portion of all other isotopes having decayed off to negligible inventory. In terms of the original inventory available, only about 2.5 percent would be present at this point in time. As indicated by Table II, however, this can still be an appreciable amount of activity.

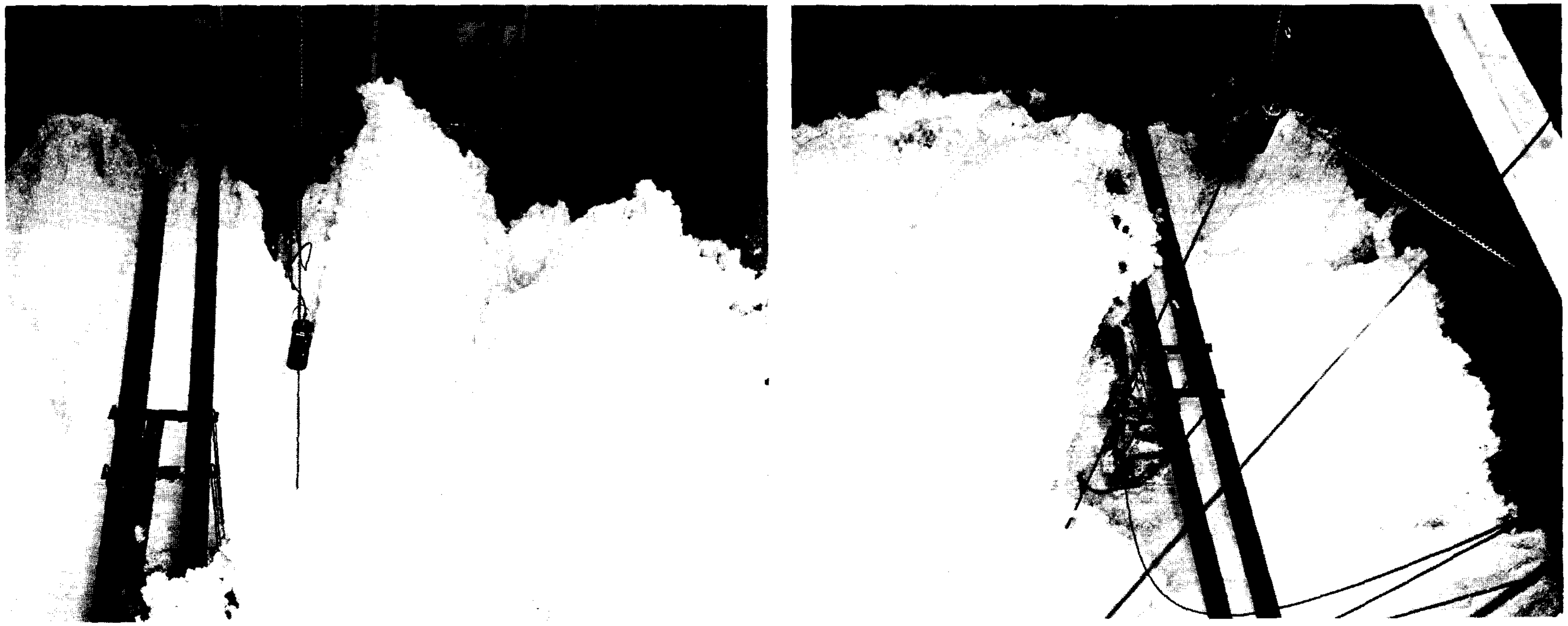
III. KRYPTON DIFFUSION TESTS

In the last quarter of FY-1970, two relatively large-scale diffusion tests were carried out. The durations of the tests were for 15 and 42 days, respectively.

A. Test One

In the initial test, a ten-foot column of clean, unentrained foam was generated and allowed to stand for 24 hours. On the next day, an additional ten-foot column of foam was generated into the large plastic bag this time containing 100 ppm of krypton gas with Krypton-85 tracer in the exhaust air stream.

The generator location was at the 20-foot level as seen in Figure 18 on the scaffolding with the generating plate exposed in the middle of the large plastic bag. An exposed working generator can be seen in Figure 19. As may be noted in the Figure 19, the foam was free to fall from the generating location in the middle of the bag. The effect seen was that a three-foot diameter hole was broken through the old foam. The new foam, being much heavier due to its moisture content and having good flow characteristics, flowed beneath the old foam layer, lifting it and providing a clean unentrained cap of foam. Figures 20 and 21 are views taken from the top of the bag looking into the foam, giving some ideas as to what the foam looked like one day after generation. Figure 22 is an overall view of the plastic bag with the foam piled to the 20-foot level. The air flow rate for the initial test was at about 25 cfm. The expansion ratio was at 150:1 based on the cubic feet of bubbles produced when compared to the cubic feet of foam solution used. Bubble size averaged between 3/4 to one inch in diameter. The average migration rate of the krypton through the bubble layers has been calculated out at one foot per day per 1.0 percent of the krypton material. Shown in Figure 23 is a composite or family of curves for the three tiers of detectors, plotting time after generation versus count rate. It was noted that, through the fifteen-day period, krypton diffusion was selectively upwards and that about six inches had decayed from the top layers of the foam material.



Figures 20 and 21. Foam as it looked one day after generation, Test One. Note the generator in the middle of the bag, top ros of detectors and the detector number 25 at the top of the plastic bag.

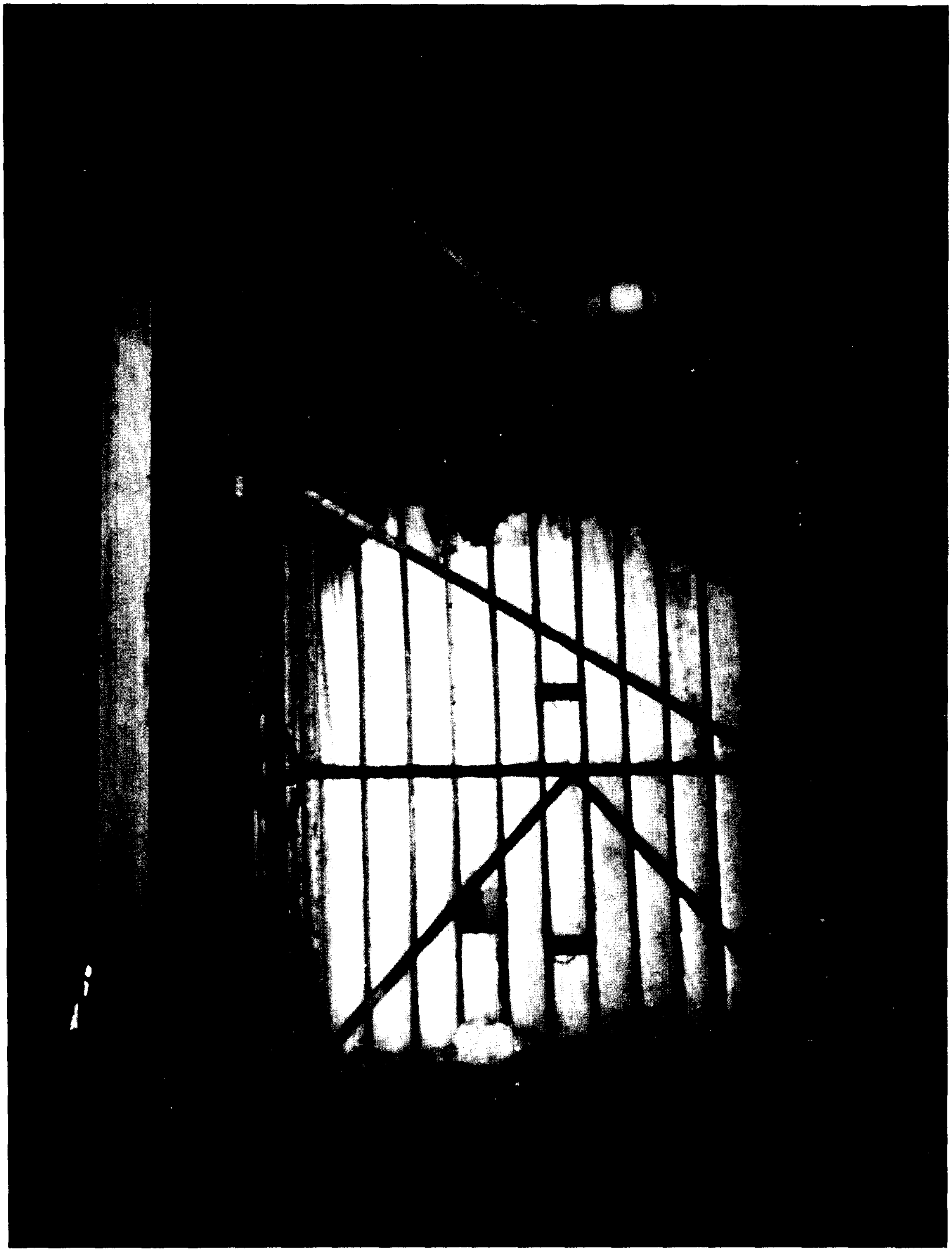
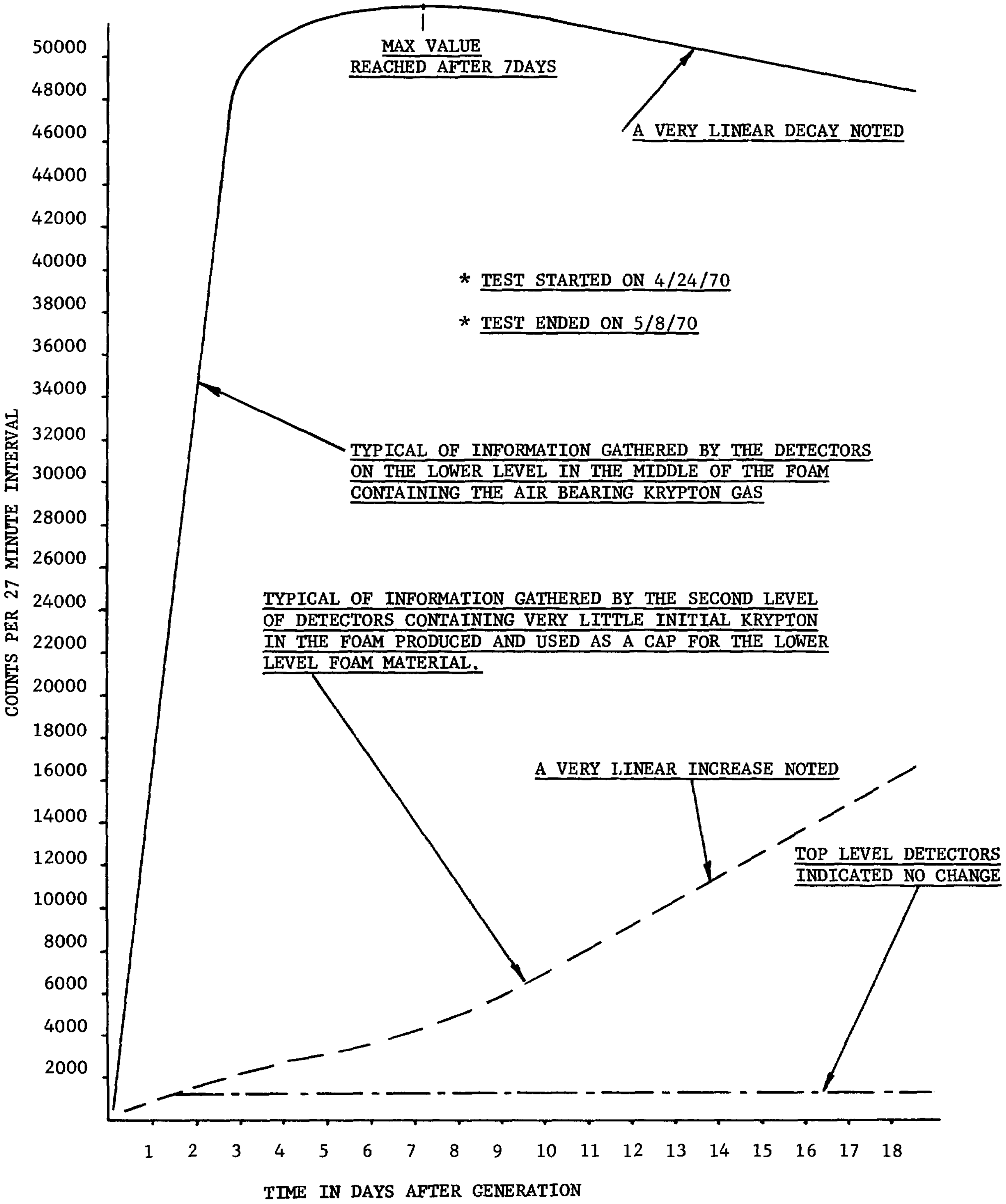


Figure 22. Foam Test One. Seen above is a bag full of foam material piled to about the 20 foot level. The detector locations: top row - no foam; middle row - no Kr in foam; and bottom row - Kr entrained foam product can be seen readily between the horizontal 2 x 4's.

COMPOSITE CURVES FOR TEST NO. ONE; COUNTS VS TIME



MAX VALUE REACHED AFTER 7DAYS

A VERY LINEAR DECAY NOTED

* TEST STARTED ON 4/24/70

* TEST ENDED ON 5/8/70

TYPICAL OF INFORMATION GATHERED BY THE DETECTORS ON THE LOWER LEVEL IN THE MIDDLE OF THE FOAM CONTAINING THE AIR BEARING KRYPTON GAS

TYPICAL OF INFORMATION GATHERED BY THE SECOND LEVEL OF DETECTORS CONTAINING VERY LITTLE INITIAL KRYPTON IN THE FOAM PRODUCED AND USED AS A CAP FOR THE LOWER LEVEL FOAM MATERIAL.

A VERY LINEAR INCREASE NOTED

TOP LEVEL DETECTORS INDICATED NO CHANGE

Figure 23

B. Test Two

Several physical parameters were changed in the second test run; first, a plastic cap was provided for the bag which on test one had been left open to the tank atmosphere and, next, the generator was pulled to the edge of the bag at the 20-foot level and a plastic trough was hung for the purpose of conveying the foam to the bottom of the bag rather than allowing it to fall or drop. The air flow rate was reduced to 10 cfm and the expansion ratio was noted to be about 65:1. The bubble size was reduced, being in the realm of one-half inch diameter. About 100 ppm of the krypton gas was used. The second test was performed by again generating a ten-foot column of clean foam and without stopping this time an additional ten-foot column with air-entrained krypton gas. The effect was similar to test one. The foam generated initially continued to float on the top as the newly-generated heavier product was noted to tunnel beneath. As the test progressed for 42 days, breakdown of the foam again from the top layers was noted. About two feet had decayed from the top layer after 42 days. Krypton migration through the foam layers was noted once more as selectively upwards but at a much reduced rate. The value calculated for the migration was 0.5 foot per day per 0.3 percent of the krypton material. Figure 24 portrays the composite curves plotted for this test run.

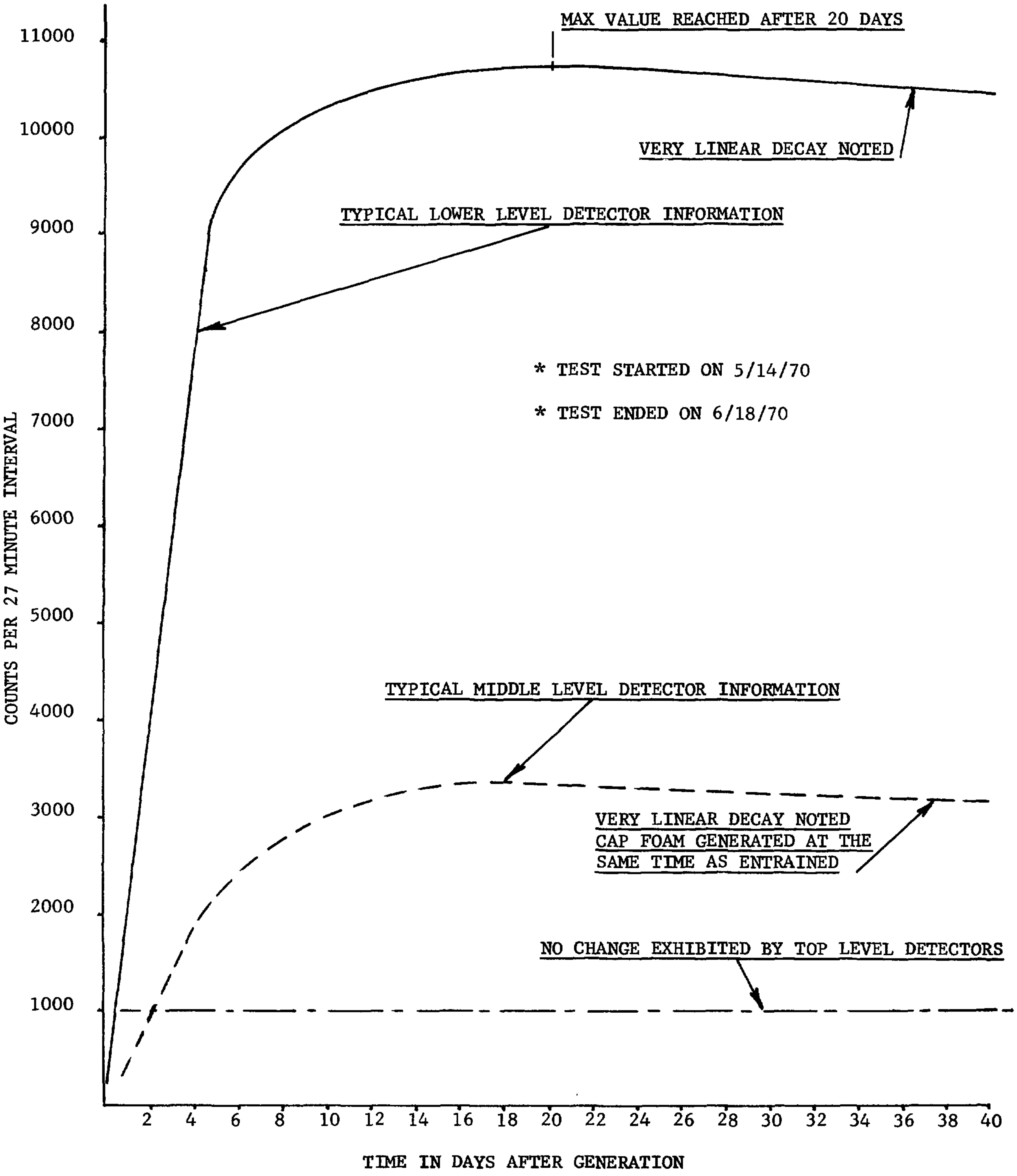
IV. SUMMARY

The high-expansion foam encapsulation concept of entrapping the air bearing the noble fission gases is dependent upon the development of highly reliable foam generation techniques, and on the development of a foam formulation which possesses the structural integrity and life necessary to achieve a substantial holdup time, thus permitting radioactive decay of the entrapped gases before their release.

A. Foam Development

The testing of additives to the foaming agents was carried out on a small 1 to 2 cfm bench top facility seen in Figures 1 and 2. In excess of 250 tests have been performed in the quest for additives which would improve the structural integrity and life of the foam. Besides the polyethyleneimine base product described earlier, other candidates with half-lives of 100 days and more are now also available. Some of these products are described in the References 1, 2, and 3.

COMPOSITE CURVES FOR TEST NO. TWO; COUNTS VS TIME



* TEST STARTED ON 5/14/70

* TEST ENDED ON 6/18/70

Figure 24

The formulation developed by the Mine Safety Appliance Research Corporation and generated on December 19, 1969 to a depth of 20 inches degraded only five inches by January 13, 1970, a span of over 25 days.

Because of the amount of time available, some superior chemical and physical properties exhibited and its relatively low cost, the initial polyethyleneimine candidate has been the one worked with most extensively.

B. Generator Development and Krypton Diffusion Study

The technique of blowing a high-expansion foam, 300 to 1 expansion ratio, with the use of the diffusion plate was proven quite successful in the early stages using the small 1 to 2 cfm generator. A scaled-up system from the bench top prototype was necessary and successfully utilized for the 15 and 42 day diffusion tests, but not without indicating that problem areas of generator reliability could exist. The small bench top generation tests were never time extended. The facility was only used to generate formulation candidates and generation never lasted more than one or two minutes. The larger plate, however, was required to generate reliably for several hours and did promote problems. The most severe was back pressurization when the system was installed at the floor level and expected to either push or lift previously generated foam. It was learned that the generator in order to function smoothly must be exposed so that the foam as generated can escape readily. In addition, plate flooding depth must be controlled to a rather accurate degree with air flow rate or again back pressurization will occur or worse bypass areas might develop. The use of the larger plate in the diffusion tests did allow items as the above to be identified and all are considered soluble given ample time and effort.

The diffusion tests were performed with the sole purpose in mind of determining if the krypton could be held within the bubble layers. If the candidate could not hold the noble gases for an ample period of time, additional exhausting tests on foam properties might not be worthwhile. The two diffusion tests carried out for periods of 15 and 42 days respectively have indicated that, once encapsulated, the noble gas indeed can be held. Migration rates were determined as one foot per day per one percent of the krypton material for test one and one-half foot per day per 0.3 percent of the krypton material for test two. The migration rate, therefore, along with the long half-life of the candidate formulation indicates that the feasibility of substantial noble gas holdup allowing for decay of the short-lived isotopes before release to the environs is within the scope of reality.

C. Future Plans

Program developments as the inability of other laboratories to supply promised foam formulations for testing forced project goal reorientation to include a foam formulation development program. Since progress in an endeavor, such as foam development, is not easily predictable and may have conceivably taken five years had alternate routes of study been attempted, funding for FY-1971 and beyond was difficult to project. No funding is, therefore, available for FY-1971.

A realignment of the project goals and program continuation in FY-1972 and beyond is anticipated. Testing of the formulation with xenon gas, testing under conditions of steam and heat, testing of irradiation properties, studying the effects of other pollutants as iodine and methyliodide, the solution of plate generating problems and the fabrication on and operation of a 1,000 cfm system allowing the engineering and operating techniques developed to be used in designing a full reactor abatement system are some of the problems which remain to be investigated and worked out.

D. Other Uses

There are industrial processes, which produce items similar to methyliodide, which are difficult to remove and and may even require quite a long residence time to be removed. Systems might be designed using foams that may allow proper residence time of gases within a bubble to effect removal, while at the same time acting as a particulate scrubber. Most formulations to date have been found to be soluble and reusable and might even lend themselves to some product reclamation.

Specific fire-fighting problems might take advantage of the plate method of generation as well as the formulations developed.

Other uses which have been noted but not exploited at this time are: (1) foam scrubbing and filling of reactor containment vessels providing another barrier prohibiting radioactive escapage, (2) dust suppression by laying a thin coat of foam and film on a moving conveyer belt such as may be found in a mining operation, and (3) utilization of the foam for frost protection in early spring and late fall to provide growing season extension of certain food plants.

V. ACKNOWLEDGMENTS

The authors wish to express their graditude and acknowledge the assistance given by all, but especially that of the Associate Investigators Messrs. E. L. Etheridge and H. F. Jensen whose experimental design and laboratory effort were responsible for conversion of an idea into an experimental reality. Messrs. R. H. Hiltz and J. V. Friel of MSAR, and Dr. A. V. Grosse of the Germantown Laboratory whose optimism and fine laboratory work have provided the foam making products so vital to this study.

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DISCUSSION

MERZ: Do you have any information on the temperature and radiation stability of the foam?

MECCA: We were going to investigate further the temperature stability of the material and the radiation stability with additional experimentation. We have irradiated to around 10^6 r and it seems to hold up very well. Like any other normal plastic type of material it does darken a little. We feel the temperature should also enhance its setting up a little quicker.

SMITH: How do you think this foam will be to clean up? Is it going to be a very expensive and messy job? What kind of operation will clean-up be?

MECCA: At the moment, even after 42 days, we went into our polyethylene bags and we were able to break the foam down with water hoses. It is soluble. One of the pluses on the side of this particular foam which is a polyethyleneimine and polyvinolalchol base is that the run off appears to be reusable and we don't anticipate any problem at the moment.

OWEN: Jim, I would like to point out one other advantage of the foam at this time and that is the fact that when the foam and fission products mix intimately to begin with decontamination surfaces will be greatly enhanced. All fission products that I have seen in the past where you had to decontaminate after it had set on the surface for awhile was nearly impossible but if you can catch them initially they will stay with the material instead of adhering to the surface.

ABBOTT: What's the price per cubic foot and secondly what's the temperature effect on the foam?

MECCA: Price per cubic foot depends on how much you are going to generate. We were after a 100 day half life type of product and I would say 300 or 500 gallons of this mix via the formula stated costs us around $1,000 or somewhere in that neck of the woods. Expansion ratios can be as high as 300 to 1 and this is on a cubic foot basis so you can do a quick calculation. If you were to use reduced concentrations of the product to produce foam of shorter half-life you can reduce the cost. In long life foams it appears that one of the keys is retaining the water in the bubble wall. The longer you can retain the water in the bubble wall the longer your foam will last and have some sort of structural integrity. If you don't want a long half life I would imagine reductions of the mix proportions would reduce cost. Temperature on this particular product we're generating appears to have an enhancing affect, and allows it to set up quicker. I can see where, though, if it was a too diluted solution you could begin to evaporate your water. Some place in the middle is a happy medium. It appears to be reasonably priced for the type of situation and usage we are looking at.

ABBOTT: At what temperature does it break down and is destroyed, this type of effect?

MECCA: I really couldn't answer you on that one. We have not carried this project to that extent. We have done some small generations with steam and we are able to generate at about a 1000°C but we have not went beyond that particular point in temperature.

EVALUATION OF ACTIVATED CARBON SUPPORTED ISOTOPE EXCHANGE TECHNIQUES FOR CONTAINMENT ATMOSPHERE PURIFICATION

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INTRODUCTION

Isotope exchange in nuclear safety applications bowed in by the discovery at ORNL that MSA 85851, an iodine impregnated carbon developed for mercury vapor and H_2S - SO_2 removal was significantly more efficient in $CH_3{}^{131}I$ decontamination than other carbons. (1) At the same time, UKAEA scientists found that KI impregnated carbons had $CH_3{}^{131}I$ attenuation in excess of untreated carbons. (2) After these two discoveries, a number of papers appeared evaluating the $CH_3{}^{131}I$ - ${}^{127}I_2$ exchange properties of impregnated activated carbons (3)(4)(5)(6). The first utilization of impregnated carbon for combined iodine, $CH_3{}^{131}I$ removal was in HFIR at Oak Ridge and the first power reactor utilization for the Connecticut Yankee reactor (5).

These developments were achieved independently from the previously investigated isotope exchange reactions on unsupported surfaces, reports of which are available for almost every isotope. (7)(8)(9)(21)

The fact that isotope exchange proceeds faster on extended porous supports is a logical extension of the prior work and the application of surface chemistry.

Early work showing that isotope exchange between $Ag^{131}I$ and ${}^{127}I_2$ is dependent on the surface of the $Ag^{131}I$ can almost be called a precursor of later development work in supported isotope exchange materials.

$CH_3{}^{131}I$ ISOTOPE EXCHANGE WITH SUPPORTED ${}^{127}I$ FORMS

While considerable data was developed for the isotope exchange reactions under unsupported homogenous and heterogeneous conditions, only meager information is available for the industrially used carrier based systems.

In general, the exchange reactions between iodine and methyl iodide (alkyl iodides) are heterogeneous in the gas phase. In liquid phase, the exchange rates are near identical for both abstraction and substitution (9). While the frequency factor for CH_3I - I_2 exchange was found to be approx. 2.5×10^{11} l. mol^{-1} sec^{-1} (10) which value being greater than the collision frequency, suggests a loose transition state.

In addition to the $Ag^{131}I$ - ${}^{127}I_2$ exchange surface dependency, Maksimov (11) found that in an H_2O - CCl_4 - I_2 - KI system the exchange when $Na^{131}I$ was introduced was dependent on the surface resistance to mass transfer at the interface.

The isotope exchange evaluation between CH_3I and liquid phase -I and I_2 indicated that better exchange occurs with -I than with I_2 (12)(13).

It is also known that thermal I atom exchange does not account for the rate and the postulated exchange formation is enhanced by the radiolitic decomposition of the $CH_3{}^{131}I$ by radiation emitting from the ^{131}I atom in reaching nuclear stability. (14)

The summary reaction is

$$CH_3{}^{131}I + {}^{127}I \rightleftarrows CH_3{}^{127}I + {}^{131}I$$

It is important to realize that the exchange process is reversable and the equilibrium distribution coefficients approximate the values expected from the relative ratio of the ^{127}I and ^{131}I isotopic species of iodine.

In the case of supported reaction, the ^{127}I on the left side and the ^{131}I on the right side of the equation are on the surface of the carrier.

The isotope exchange rate becomes further complicated by the introduction of the porous substrate. Thus assuming that the exchange mechanism is dissociative and involve adsorbed radicals of the type CH_3^- then the following species take place in the reaction:

1. physically adsorbed methyl iodide
2. chemisorbed methyl radicals
3. chemisorbed ^{131}I atoms
4. chemisorbed ^{127}I atoms (bulk physically adsorbed on substrate surface in some cases.)

Taking the simplest case when the ^{127}I species is introduced with the $CH_3{}^{131}I$:

Step I. The surface concentration of each of the four kinds of species will increase and reach equilibrium values.

Step II. The exchange reaction will commence and lead toward isotopic equilibrium between the species in the system.

Step II can not be completed until all of the CH_3I is adsorbed and desorbed. The only factor which reduces the rate of isotope exchange from the initial value is the approach of the ^{131}I concentration on the surface toward the ^{127}I concentration on the surface. Thus as long as an excess of ^{127}I species is on the surface, the rate determining step is the adsorption and desorption of methyl iodide. Because the relative properties of $CH_3{}^{127}I$ and $CH_3{}^{131}I$ are near identical, no difference between the adsorption and desorption rates can be expected. Thus both processes occur at the same rate and the convenient term of "adsorption/desorption" can be used.

The activated carbons used as carriers for isotope exchange reaction will retain large quantities of ^{127}I and ^{131}I, thus the preloading of the surface with $^{127}I_2$ or $K^{127}I$ is very convenient.

In most industrial applications, additional rate controlling effects are introduced by the presence of adsorbed water on the carbon surface, which alters the rate of CH_3I adsorption/desorption. This effect was investigated by Ackerman and Grens (15).

At very high moisture loadings, where capillary condensation may be present in the pores of an impregnated carbon carrier, the relative solubility of the impregnant and the CH_3I in the solution also becomes a significant factor.

In evaluating the available data on the basis of various particle size identical impregnations (2)(16)(17), it is evident that the rate controlling process does not satisfy the Satterfield-Sherwood equation which can not be used to evaluate the process.

The values of Ref (2) are plotted on Figure No. 1 to show the significance of efficiency dependence on particle size.

For complete evaluation of the kinetics of the isotope exchange, similar techniques as used in ion-exchange kinetics evaluation can be used (18).

POISONING AND LOSS OF IMPREGNANT EFFECTS

Both homogeneous liquid phase and the Collins (2) results indicate good performance of KI impregnated carbons, however, KI impregnated carbons loose impregnant when steam is condensed in the carbon and/or the water coolant sprays are operating, and on some carriers indicate a higher loss of exchanged ^{131}I upon heating. For this reason, commercially used carbons are impregnated by both KI and I_2. As it was indicated by both Collins (2) and Ackley (19), both KI and KI_3 impregnated carbons loose exchange efficiency with weathering. It is highly probable that this poisoning effect is caused by the adsorption of organic compounds on the impregnant surface. Considering that at very high humidities the exchange takes place in an adsorbed water layer on the surface the results of a study on AlI_3 - C_2H_5I exchange in C_2H_5I as influenced by trace addition of organic compounds is significant (20).

The fact that TEDA impregnated carbons do not weather nearly as much as KI or KI_3 impregnated carbons, also indicates the likelihood of organic adsorption on top of the I impregnant on the surface as a poisoning effect.

The effect of weathering on carbons impregnated in various manners is currently under investigation at DUN. The completion of this study will shed more light on the poisoning process involved.

Figure 1

Particle Size Dependency of KI Impregnated Carbon

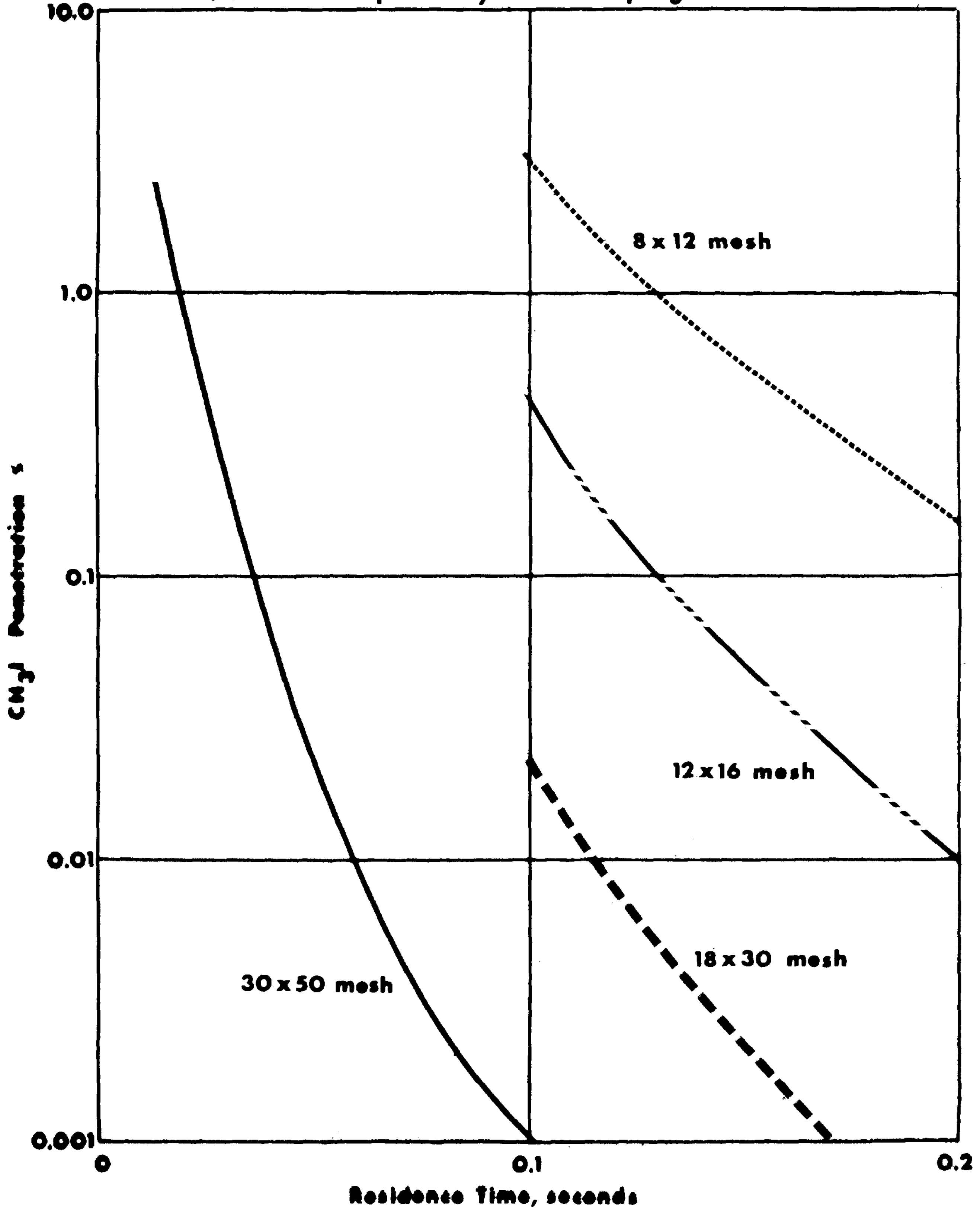


Figure 2

HTO Decontamination by Carbon

RH: 10 %

Mesh: 12 x 30

Residence time: 0.012 sec.

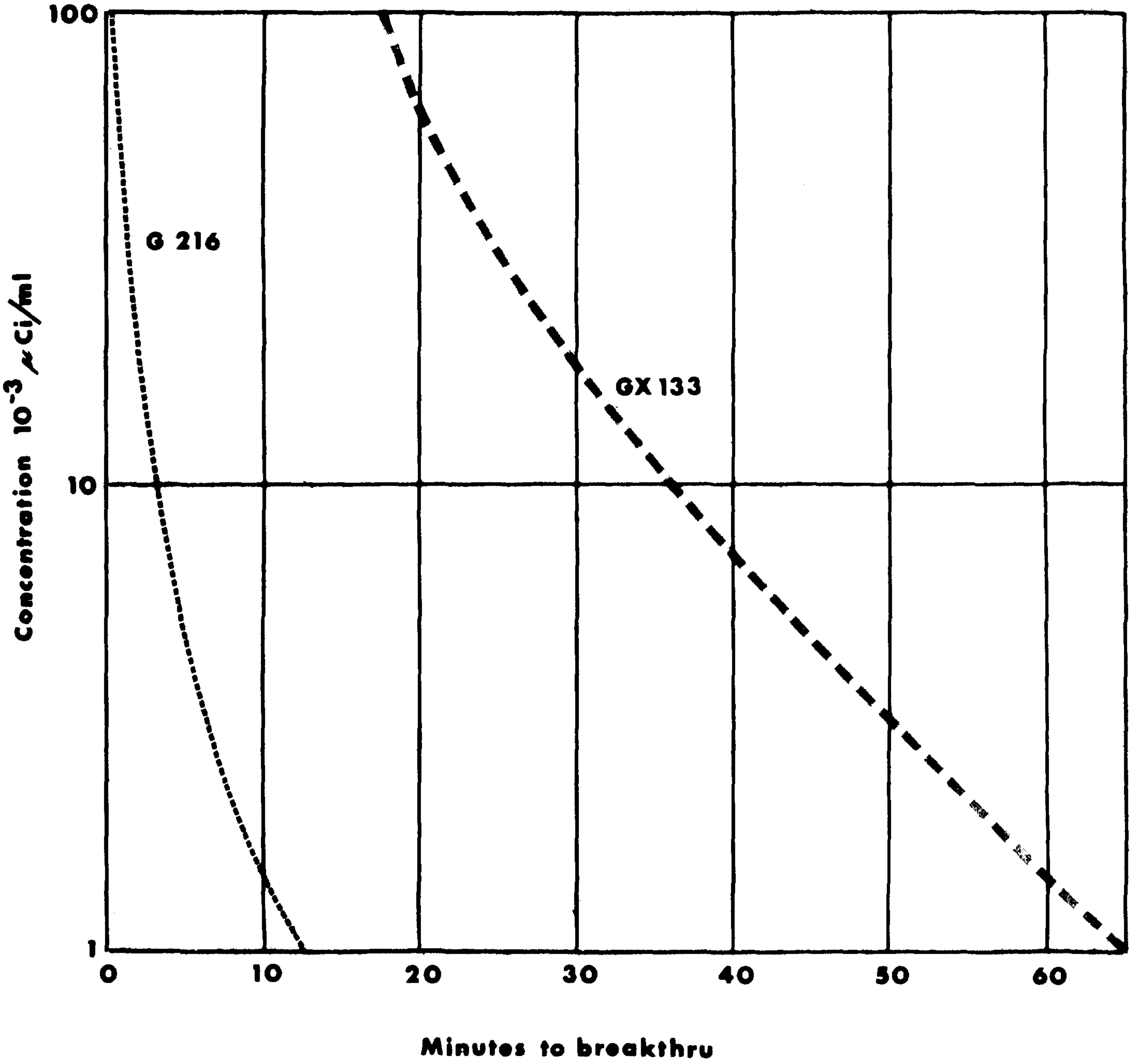


Figure 3

HTO Decontamination by GX 133

Mesh: 12 x 30
Residence time: 0.012 sec.

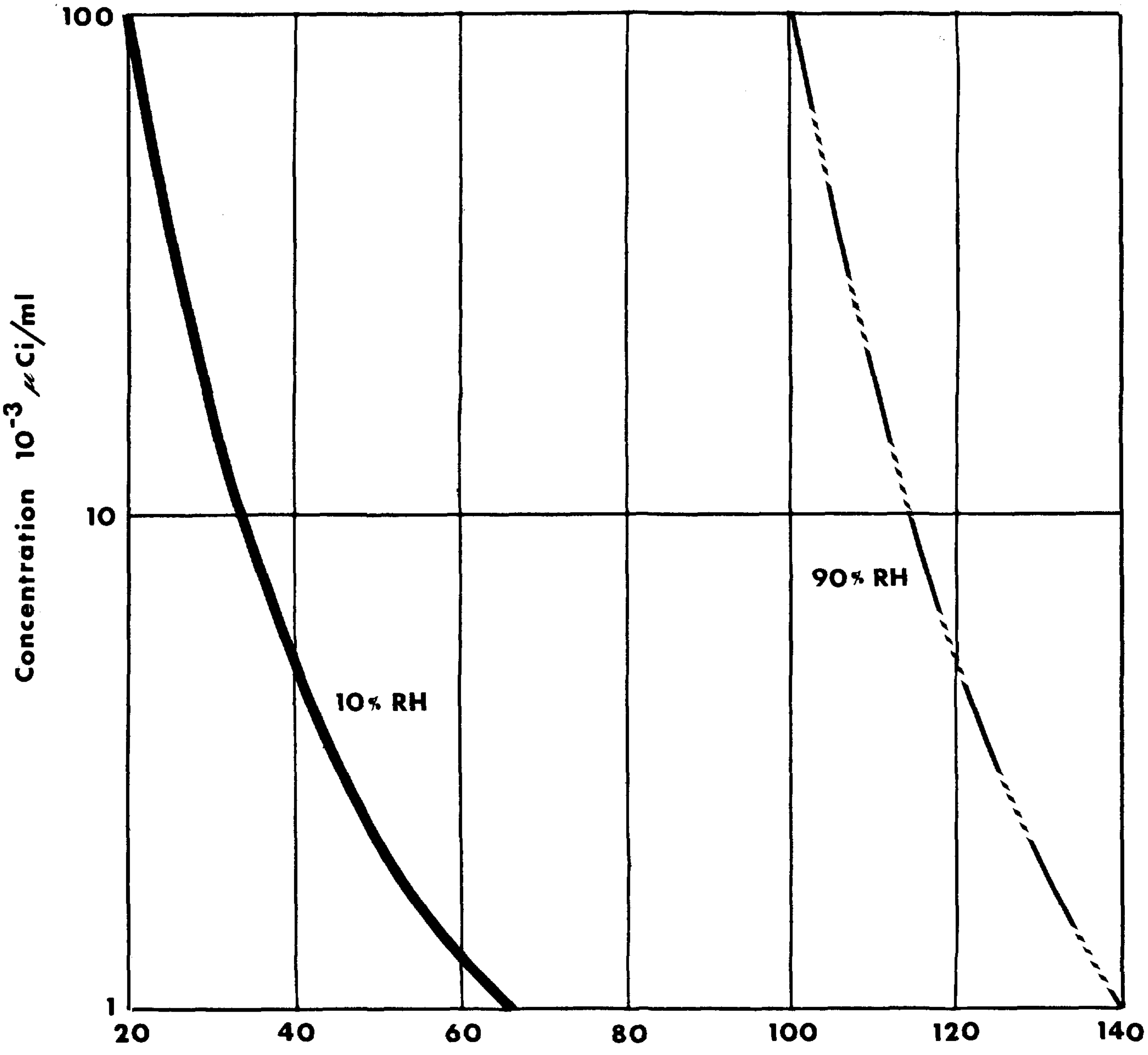


Figure 4

HTO Decontamination by GX 133

Residence time: 0.024 sec.
RH: 90%

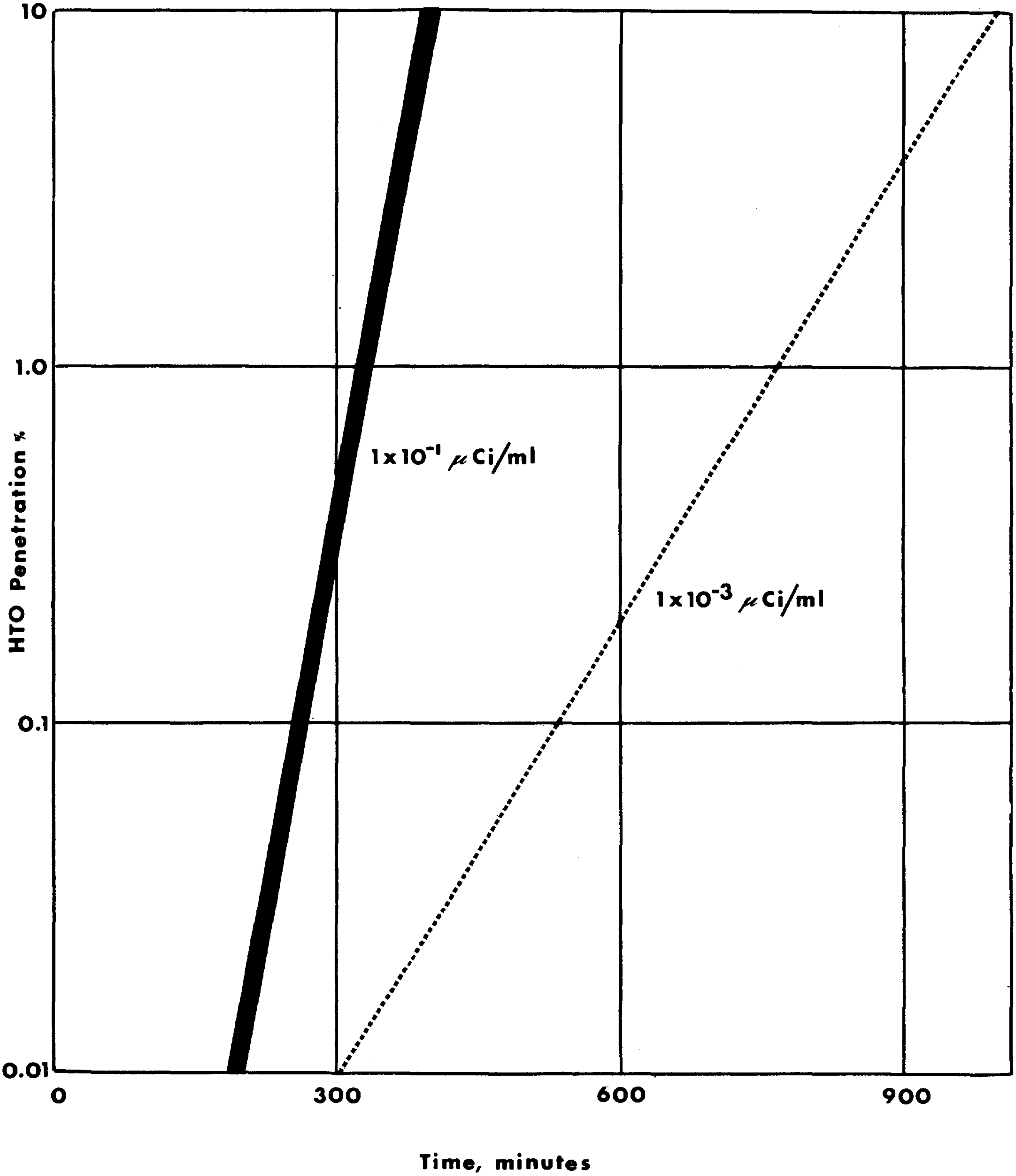
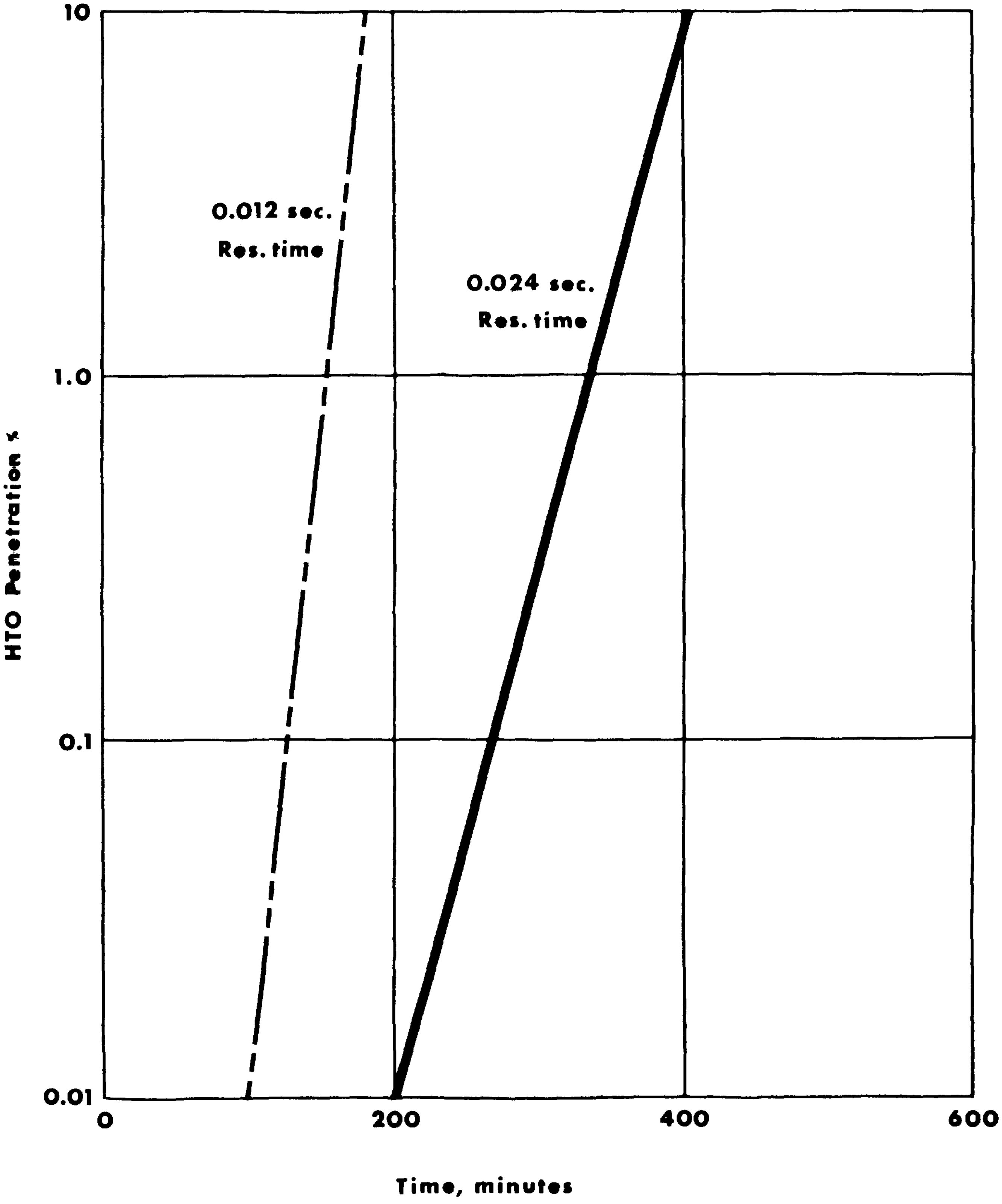


Figure 5

HTO Decontamination by GX 133

Concentration: 1 x 10^{-1} μCi/ml

RH: 90 %



However, most of the weathering effects were evaluated under ambient temperature conditions, while it is very likely that in steam-air, loss of coolant atmospheres the initial steam wave will strip the poisoning compounds from the carbon and "in situ regenerate" the impregnated carbon. These and other similar factors show the importance of testing under actual use conditions.

OTHER SUPPORTED ISOTOPE EXCHANGE PROCESSES

Extending the isotope exchange process to other than $CH_3{}^{131}I$ removal is a logical further step.

Evaluation of HTO removal by adsorption led to the testing of several unimpregnated carbons. Unimpregnated carbons were used first because the exchange was postulated to take place with simultaneous introduction of H_2O.

Unimpregnated carbons did not look promising for the isotope exchange reaction, however, a specially treated carbon, GX 133, showed significant improvement in HTO removal indicating catalyzed isotope exchange.

The evaluation of HTO concentration, relative humidity and mass transfer zone shapes are shown on Figures 2, 3, 4, and 5.

The investigation of the HTO - H_2O exchange is being continued. The currently available data indicates reasonably good retention of HTO on the carbon surface. The process is assumed to be similar to the one described for $CH_3{}^{131}I$ - ${}^{127}I_2$ exchange when simultaneous introduction of ${}^{127}I_2$ takes place.

Two carbons, GX 136 impregnated with Na_4XeO_6 and GX 121 impregnated with XeF_2, were also evaluated for ${}^{131}Xe$ - ${}^{133}Xe$ exchange. The initial results indicate that isotope exchange does take place on a supported surface, however, the stability of these impregnated carbons has to be further evaluated before commercial applications.

CONCLUSIONS

The extension of the supported isotope exchange processes from liquid or gas phase isotope exchange processes is feasible.

The evaluation of the kinetics of the supported isotope exchange processes requires further careful study.

A new carbon based catalyst GX 133 was evaluated for HTO - H_2O isotope exchange.

Carbon and other adsorbent supported stable xenon compounds are capable of isotope exchange with ${}^{133}Xe$.

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