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Radiation Cleanup of Vacuum Systems

(Radiation-Induced Outgassing)

Final Report

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J. N. Anno

University of Cincinnati

Cincinnati, Ohio 45221

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Abstract

A stainless steel-304 vacuum system has been designed and constructed to study radiation-induced outgassing when this material is exposed to cobalt-60 gamma radiation. The system is pumped with an ion pump and sorption roughing pump. No foreign materials have been introduced except for copper seals at the flanges. An analytical model has been developed which predicts the outgassing from SS-304 to be 8.27×10^{-12} torr-liters/(cm^2) (sec) per megarad/hr. Extrapolation of existing data for aluminum suggests a lower value of 1.0×10^{-12} torr-liters/(cm^2) (sec) per megarad/hr. Experiments determined the value for stainless steel-304 after bakeout at 300 C to be $(7.78 \pm 4.36) \times 10^{-12}$ torr-liters/(cm^2)(sec) per megarad/hr., in good agreement with the analytical model predictions. Studies on thermally-induced outgassing from SS-304 showed that after bakeout at temperature T*, thermal outgassing Δ obeys the relationship $\Delta = \Delta_o e^{-\bar{Q}/RT}$, where both the constant Δ_o and the average desorption energy $\bar{Q}$ are functions of T*. Water vapor and hydrogen are the principal residual gases in a 304 SS vacuum system, with hydrogen being dominant at low pressures after bakeout.

I. INTRODUCTION

A number of years ago Dr. J.N. Anno and his colleagues discovered that by exposing a vacuum system to a moderate exposure of gamma radiation the ultimate vacuum is improved by about two orders of magnitude[1*]. In a simple demonstration experiment (to be described later), the vacuum in a one-liter vessel connected to a getter-ion pump was improved from 10^{-7} torr to the mid 10^{-9} torr range after exposure for 22 hours to a gamma radiation field of approximately 10^{5} rad/hr. Thus radiation-induced desorption of surface atoms (radiation clean-up of surfaces) was demonstrated. There are several implications and interests in the magnitude of radiation-induced outgassing. One of these is the significance to the Energy Research and Development Administration (ERDA) in its quest for fusion power. Most of the research reported herein was sponsored by the Fusion Division of ERDA.

The long range goal of the Fusion Division of ERDA is the successful generation of power through the fusion of light nuclei. One of the prominent problems in fusion is the influence of radiation from a plasma on the first wall (plasma cladding) and related structural materials. The evaluation and resolution of these factors may well dictate the criteria which must be satisfied in order to maintain a plasma "burn" which will not be quenched by impurities[2]. The vacuum vessel that contains the plasma should be at ultra high vacuum (about 10^{-7} torr) for start up[3]. A pressure of this same magnitude must be maintained, and contamination from heavy (high atomic number) ions must be prevented since the radiation losses are proportional to the square of the atomic number of the ions in the plasma.

* References at end of report

It has been shown in two experiments by a group at the National Bureau of Standards that the outgassing effect is due primarily to electron and gamma flux and not the neutron flux[4]. These important data allow experiments to be performed with gamma radiation alone. In the present project a stainless steel-304 system was irradiated with cobalt-60 gamma rays and the attendant outgassing measured. The ultimate goal was to obtain a yield fraction Δ for SS-304 under high energy radiation:

$$\Delta = \frac{\text{gas atoms released per unit area per unit time}}{\text{energy absorbed per unit time per unit mass}}$$

$$= \frac{\text{torr-liters}/(\text{cm}^2)(\text{sec})}{\text{megarad/hr.}}$$

These data will be important in the design of vacuum pumping systems for the future fusion reactors[5].

Another possible area of interest for radiation-induced outgassing is application to industrial and scientific processes. The potential advantages of radiation clean-up over, say, direct electron bombardment or thermal bakeout are:

(1) Hard-to-reach "nooks and crannies" are outgassed simultaneously with the other surfaces.

(2) The clean-up can be done at room temperature (or any desired temperature).

(3) No internal cleaning apparatus is required: gammas are "applied" externally.

(4) The gammas and their "daughter" electrons bombard the vessel walls and interior components not just at the surface layers, but throughout the material. Possibly such action can purge the surfaces of deeper-lying gas atoms which would otherwise slowly diffuse to the surface and prevent the attainment of ultra-high vacuum.

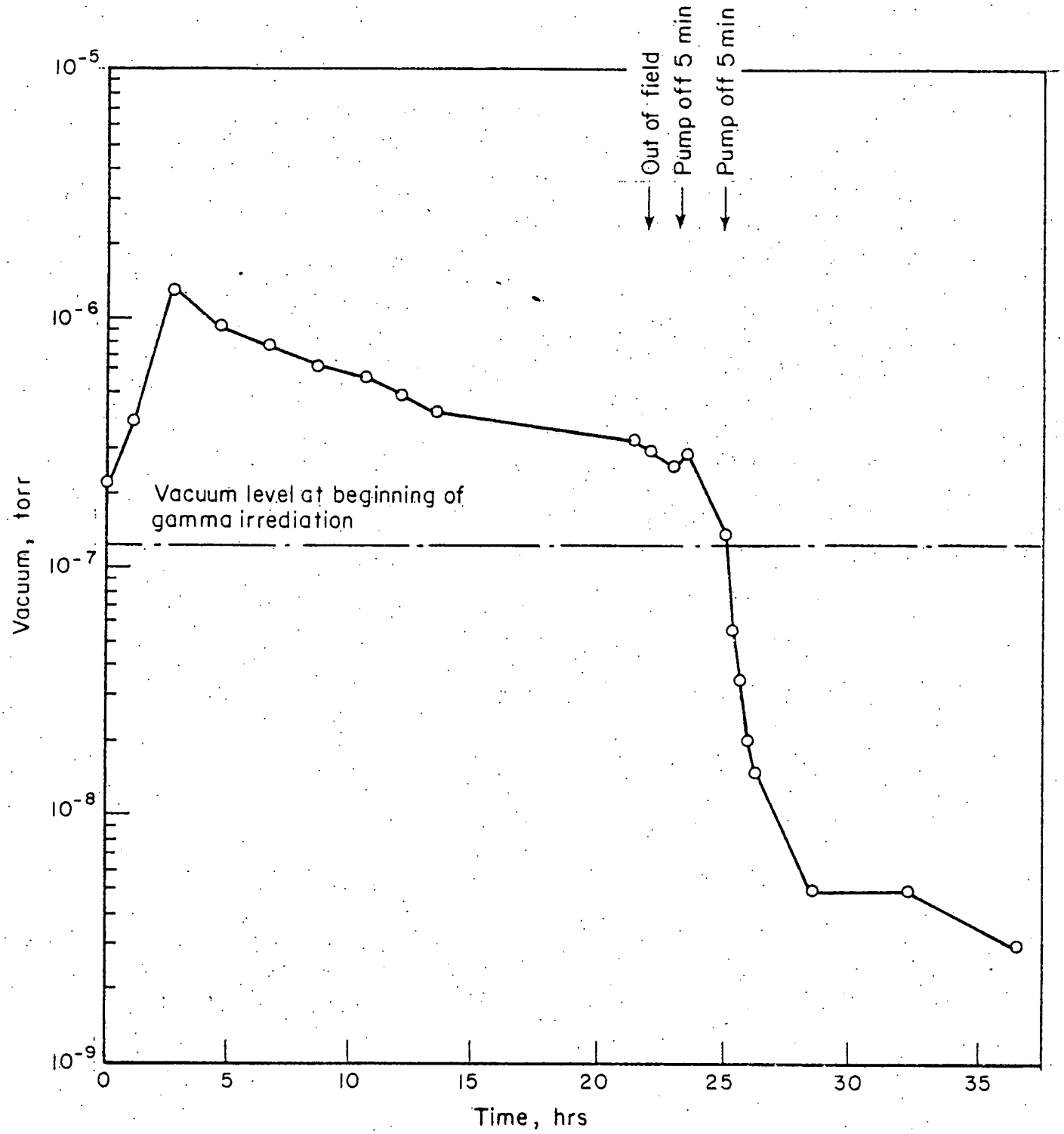
The principal disadvantages appear to be the general problems associated with the use of an intense radiation source, and possibly, a long cleaning time.

II. Technical Background

Experiments in mid-1960 indicated that a large number of electrons were released from surfaces exposed to gamma radiation[6]. Almost simultaneously it was reported that high energy electrons were quite effective in releasing gases from surfaces[7]. From these observations, it was speculated that gamma radiation might be effective in cleaning up a vacuum system. To investigate this possibility, a simple demonstration experiment was performed. A small stainless steel chamber (one liter) was close coupled to a compact getter-ion pump (11 liter/sec.). A Philips-type cold-cathode gage was attached to the chamber. The entire unit was enclosed in a watertight aluminum box. The chamber was evacuated (without bakeout) to 1.2×10^{-7} torr. It was installed in the box which was positioned next to the core of a nuclear reactor immediately after shutdown of the reactor, thereby exposing it to the residual gamma radiation in the absence of neutrons. The gamma field was about 10^5 rad/hr. The vacuum level in the chamber increased by about a decade during the first two hours and then slowly dropped. After 22 hours of exposure, the system was removed from the radiation field. The vacuum level decreased rapidly for about 5 hours and finally appeared to level out in the mid-10^{-9} torr range. This behavior is shown graphically in Figure 1. The temperature of the chamber was 92 F, and remained essentially constant throughout the experiment.

Almost simultaneously with the above-described work, Muehlhause, et. al. (National Bureau of Standards)[8] measured the outgassing from aluminum surfaces exposed to cobalt-60 gamma radiation to be 1.9×10^{-13} torr-liters/(cm^2)(sec) per megarad/hr.

Figure 1
Vacuum Levels in a Gamma Field of 10^5 R/hr



III. Analytical Model of Radiation-Induced Outgassing

In developing an analytical model for radiation-induced outgassing, it is assumed that the electrons produced in the material by the various gamma ray interactions (Compton effect, pair production and photoelectric effect) desorb atoms from the surface. Specifically, the model considers the following events:

(1) Gamma rays produce electrons of average energy $\bar{E}$ within the material. An isotropic distribution of electrons is assumed.

(2) The electrons born within a mean range r of the surface travel an average distance $\bar{r}$ to the surface losing energy in the process.

(3) The electrons with reduced energy $\bar{E}_p$ reach the surface and produce secondary electrons of average energy $\bar{E}_s$.

(4) Both the primary and secondary electrons cause electron stimulated desorption of gas molecules from the surface.

From the measured gamma dose rate in the test chamber, the average flux of gamma $\bar{\phi}_\gamma$ can be calculated. The number of electrons produced per cm^3 of material is then

$$N = \Sigma \bar{\phi}_\gamma \nu \qquad (1)$$

where Σ is the macroscopic cross section for electron production and ν is the average number of electrons produced per interaction. Of the electrons produced within a mean range r of the surface, one fourth escape from the surface. The flux of primary electrons at the surface is thus

$$\phi_{ep} = \frac{rN}{4} = \frac{r\Sigma \bar{\phi}_\gamma}{4} \qquad (2)$$

These produce Δ_s secondary electrons per primary electron. The primary electrons desorb the gas atoms with a yield Δ (atoms/electron) and the secondary electrons desorb the gas atoms with a yield Δ'. Thus the number of gas atoms desorbed per unit area per unit time is

$$n = \frac{r\Sigma\bar{\phi}_\gamma \nu}{4} \quad (\Delta + \Delta_s \Delta') \tag{3}$$

The average distance the electrons produced with energy $\bar{E}$ (within range r from the surface) travel is $\bar{r} = 0.795$ r. The resulting attenuation in energy can be determined from range-energy curves for electrons. There are abundant data on low energy electron stimulated desorption[9,10], but little data are available for electrons of the primary energy range of interest here. A rather wide range is found in the yield depending on the condition of the surface. All available data show that the yield from the surface decreases as a function of irradiation time. Table 1 summarizes some of the available data[7,11,12].

IV. Predictions of Experimental Results

The previously described analytical model was applied to both aluminum and SS-304. The results of the calculations are summarized in Table 2 and compared with available experimental results. The first comparison is of the predicted electron flux at the surface. The value for SS-304 of 2.19 $\times 10^{-16}$ amps/cm^2 per R/hr is in good agreement with data on gamma-induced currents in a nuclear reactor environment[6]. However, the value predicted for aluminum is a factor of 6.6 higher than the value measured for reactor gamma radiation. The second comparison is that of the predictions of gamma-induced outgassing for aluminum with the experimental result from the National Bureau of Standards[8]. For this comparison, questionable values of $\Delta = \Delta' = 0.1$ were used, with $\Delta_s = 1.0$. The predicted result of 9.35 x 10^{-12} torr-liters/(cm^2)(sec) per megarad/hr is almost a factor of 50 larger than the measured value. The predicted result for SS-304 is thus to be suspected as being too large. If one adjusts the NBS value for aluminum by the ratio of the measured electron currents in a reactor environment[6], the outgassing prediction for SS-304 decreases from 8.27 x 10^{-12} to 1.0 x 10^{-12} torr-liters/(cm^2)(sec) per megarad/hr. Thus the two predictions of the experimental

TABLE 1

Surface Atom Desorption

Electron Energy	atoms/electron	Surface Condition	Reference	Remarks
.1 kev	1	dirty	Clausing (7)	Surface was a copper material with diffusion oil contamination. Clean represents a bake out for 20 hrs at 100-145
	5×10^{-2}	clean	"	
1 kev	2	dirty	"	
	6×10^{-2}	clean	"	
10 kev	2.5	dirty	"	
	8×10^{-2}	clean	"	
Photon Energy	**p atoms/photon**			
30 kev	7.5×10^{-4}	non-discharge Cleaned	Brumbach and Kaminsky (11)	Surface was SS-304 but yield is for CO_2 only.
40 kev	6×10^{-4}	"	"	
50 kev	2×10^{-4}	"	"	
50 kev	6×10^{-5}	discharge, clean	"	
0.8 Mev (reactor radiation)	4×10^{-3}	unbaked, initial value	Dobrozemsky (12)	Surface was SS, aluminum and mu metal
0.8 Mev (reactor radiation)	4×10^{-4}		"	After 3.5×10^{5} MRad.

TABLE 2

Comparison of Results from Analytical Model

(Gamma energy = 1.25 Mev)

	Aluminum	SS-304
Average electron energy	.6 Mev	.6 Mev
Maximum range of electron	.76 mm	.25 mm
μ, macroscopic cross-section	.148 cm^{-1}	.398 cm^{-1}
$\mu\phi$, electrons/cm^3	$8.13 \times 10^{9}/cm^3$	$2.18 \times 10^{10}/cm^3$
Average range of electrons in material	.60 mm	.198 mm
Average energy of electrons at surface of material	.19 Mev	.18 Mev
I_p, predicted electron flux at surface	2.50×10^{-16} $\frac{\text{amps}}{cm^2}$ R/hr	2.19×10^{-16} $\frac{\text{amps}}{cm^2}$ R/hr
I_p, experimental electron flux for a reactor spectrum of gamma radiation[6]	$.38 \times 10^{-16}$ $\frac{\text{amps}}{cm^2}$ R/hr	$1\text{-}2 \times 10^{-16}$ $\frac{\text{amps}}{cm^2}$ R/hr
Gamma induced outgassing (Model Predictions)	9.35×10^{-12} $\frac{\text{torr-liters}}{cm^2\ \text{sec}}$ M Rad/hr	8.27×10^{-12} $\frac{\text{torr-liters}}{cm^2\ \text{sec}}$ M Rad/hr
Gamma induced outgassing (experimental)[8]	1.94×10^{-13} $\frac{\text{torr-liters}}{cm^2\ \text{sec}}$ M Rad/hr	Univ. of Cincinnati Experiment ERDA-E(11-1)-4093

results for SS-304 are:

$$1.0 \times 10^{-12} \frac{\text{torr-liters}/(\text{cm}^2)(\text{sec})}{\text{Megarad/hr}}$$ (extrapolation of NBS value)

and

$$8.27 \times 10^{-12}$$ " (model prediction)

V. Outgassing in a Vacuum System

There are three fundamental processes which are involved in the "outgassing" of a vacuum system:

1) adsorption

2) desorption

3) diffusion.

Each of these processes depend on quantities such as: pressure, temperature, fractional surface coverage, multilayer coverage, species of gas, visible surface area versus true surface area (which includes scratches, pores, etc.), composition of adsorbing surface, site of adsorption on the surface, diffusion constants, activation energy (chemisorption), and so on. Obviously the entire process of "outgassing" is a complicated interaction of these processes depending on the particular parameters involved.

It would be convenient to have a formula which would give the outgassing rate and its time evolution in terms of all of the involved parameters. Dayton[13] has given this problem an elaborate mathematical treatment. However, in order to use his mathematical model, one must know all of the required parameters, most of which are not readily available (or which must be measured in a vacuum system).

In an equilibrium situation (where no leaks and no pumping is involved) the number of molecules leaving the surface per unit time will equal the number striking and sticking on the surface per unit time.

Simply put: Adsorption = desorption

In true equilibrium, the number of gas molecules per cm^3 of the jth species (n_j) in the vacuum will be constant. Of course, if diffusion of a gas through the wall of the chamber is occurring and no pumping is involved, the density of the diffusing gas, n_j, will be increasing. For an all metal system, hydrogen seems to be the most important species involved in the diffusion process.

In the typical vacuum system, the rate of change of the density of the jth species can be written as:

$$\frac{d\, n_j}{dt} = (\text{desorption} + \text{diffusion} + \text{leaking} - \text{adsorption} - \text{pumping})_j \qquad (4)$$

Anything influencing one of the terms in the expression can cause a change in the density and consequently a resulting change in the pressure.

If one assumes that the "leak term" is much smaller than any of the others, then it can be neglected in the calculation of the outgassing. Thus, when a quasi-equilibrium pressure is reached, $dn_j/dt = 0$. If all species are in equilibrium, then

$$\text{desorption} + \text{diffusion} = \text{adsorption} + \text{pumping} \qquad (5)$$

Now if pumping is removed by valving off the pump from the system, the equilibrium is disturbed and

$$\text{desorption} + \text{diffusion} - \text{adsorption} = dn/dt = \text{"outgassing rate"}$$

This is the quantity which is usually measured in a vacuum system. Note that the outgassing rate depends on these three processes and on all of the parameters involved with each process.

From thermodynamical considerations, Frenkel[14] derived a relation between the "sticking time" and the heat of adsorption of a gas on a surface,

$$\tau = \tau_o \exp\,(Q/RT) \qquad (6)$$

where $\tau_o \cong 10^{-13}$ seconds, Q is the adsorption energy (usually measured in kcal/mole), R is the gas constant and T is the Kelvin Temperature.

Here the "sticking time" means the residence time on the surface. This length of time depends upon the structure of the surface material, including the particular site on the surface and upon the heat of adsorption of the particular molecule which is "sticking". The heat of adsorption depends on the molecular statistics of the particular gas-surface interactions.

One would expect that the heat of adsorption would be the same order of magnitude as the latent heat of vaporization. If the surface were covered with many layers of the same type molecule, one would expect the heat of adsorption to be exactly equal to the latent heat of vaporization. Table 3 from Robinson[15] provides a comparison between the heat of adsorption and the latent heat of vaporization for various substances. The value for water (H_2O) is of particular interest since this is the primary adsorbed gas in a SS-304 system when starting from ambient temperature and pressure.

Table 3

Gas	Heat of adsorption (cal/mole)	Latent heat of vaporization (cal/mole)	Sticking time (sec)
He	100		
H_2	2,000	220	
O_2	5,000	1,600	
N_2	5,000	1,340	
CO	6,000	9,000	
CH_4	5,000	2,180	
C_2H_4	8,000	3,500	
C_2H_2	9,000	1,740	3.10^{-3}
NH_3	9,000	5,560	
H_2O	14,000	10,570	

As a crude model for thermal outgassing, based upon Equation (6), one might assume that the outgassing rate Δ is related to temperature as

$$\Delta = \Delta_o e^{-\bar{Q}/RT} \tag{7}$$

where $\bar{Q}$ is an average heat of adsorption for all species present. Both Δ_o and $\bar{Q}$ would, in general, be expected to be a function of the bakeout temperature, T*.

Radiation-induced outgassing would be expected to depend primarily on $\bar{Q}$, the average energy which must be imparted to the surface atoms by the gamma-produced electrons to desorb them. A dependency on $\bar{Q}$ therefore implies a dependency on the bakeout temperature prior to exposure of the surfaces to the radiation field. Stated another way, the parameter Δ and Δ' in the model previously presented are probably functions of the bakeout temperature.

Δ can be easily determined from the rate-of-rise technique, knowing the quantity of surface area A which is outgassing. The differential equation of continuity for a quantity of gas in a volume V at pressure P which is being pumped at a speed S is given by

$$\frac{d}{dt}(PV) = Q - SP(t) \tag{8}$$

where Q is the outgassing source term (torr-liters/sec.), assuming no leaks. When the ultimate pressure is reached, one can valve-off the pump (S =0) and measure the slope of the pressure rise with time, thereby determining Q. Δ is then simply Q/A. To determine the radiation induced outgassing, one determines Q in the absence of the radiation source and Q' in the presence of the radiation source, so that the radiation-induced outgassing is

$$\Delta = \frac{Q' - Q}{A_R} \tag{9}$$

where A_R is the surface area exposed to the radiation.

VI. Design and Construction of the Experimental Apparatus (Vacuum System)

In the design of the vacuum system, several criteria were deemed to be of high importance:

(1) The system should be constructed entirely of SS-304, even in the regions not exposed to gamma radiation.

(2) The system should have accurate means of determining the outgassing rate, not only in total, but by gas species.

(3) The system should be "clean" with respect to the possible introduction of foreign species.

(4) The surface area exposed to the gamma radiation should be as large as possible compared to the surface area of the remainder of the system.

(5) The entire system should be capable of thermal bakeout to 300 C, with control of the bakeout temperature.

(6) The system must be capable of being inserted under high vacuum conditions into the cobalt-60 source located in a water pool.

With these principal criteria, the system that resulted is sketched in Figures 2 and 3. The components are detailed by manufacturer in Table 4. This system meets the previously-stated criteria as follows:

(1) All piping, valves, tees, etc., are constructed of SS-304. The only foreign metal introduced is high purity copper used for the gaskets at the flanges in the system. Copper is required because it "flows" to make the high-vacuum seal, whereas stainless steel does not.

(2) As shown in Figure 3, a mass spectrometer is included in the system. By using a quadrupole mass spectrometer, not only can the gas species be identified, but changes, if any occur, can be monitored. It will

TABLE 4

Vacuum System for Study of Radiation-Induced Outgassing

	Component	Manufacturer	Part Number
1.	Nude ion gauges (3)	Granville-Phillips	274-022
2.	UHV ion gauge controller (2)	" "	271
3.	Variable leak valve	" "	203
4.	UHV tee valve (1-1/2")	Ion Equipment Corp.	BVV-153T
5.	Ion pump	" " "	IP-020
6.	Ion pump controller	" " "	PS-150
7.	UHV right angle valve (1-1/2")	" " "	BVV-152
8.	Sorption pump	" " "	SP-11
9.	Dewar	" " "	SPD-11
10.	Mass spectrometer	Spectrum Scientific	SM-80
11.	Thermocouple gauge	Comptech Inc.	TVT-1504
12.	Thermocouple control	" "	300-00
13.	Thermal bakeout jacket	Briscoe Company	- - -

Figure 2
Side View of Vacuum System

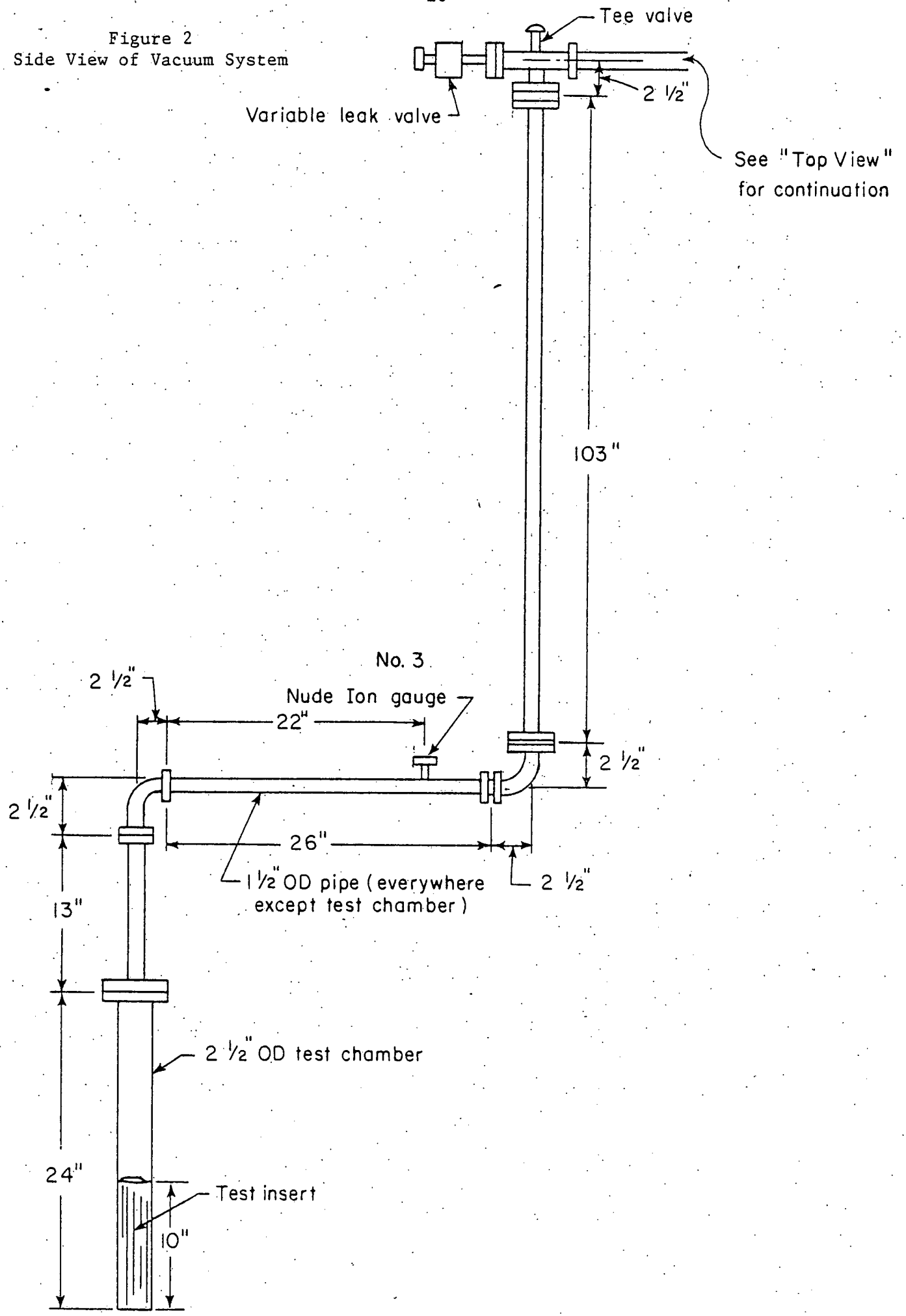
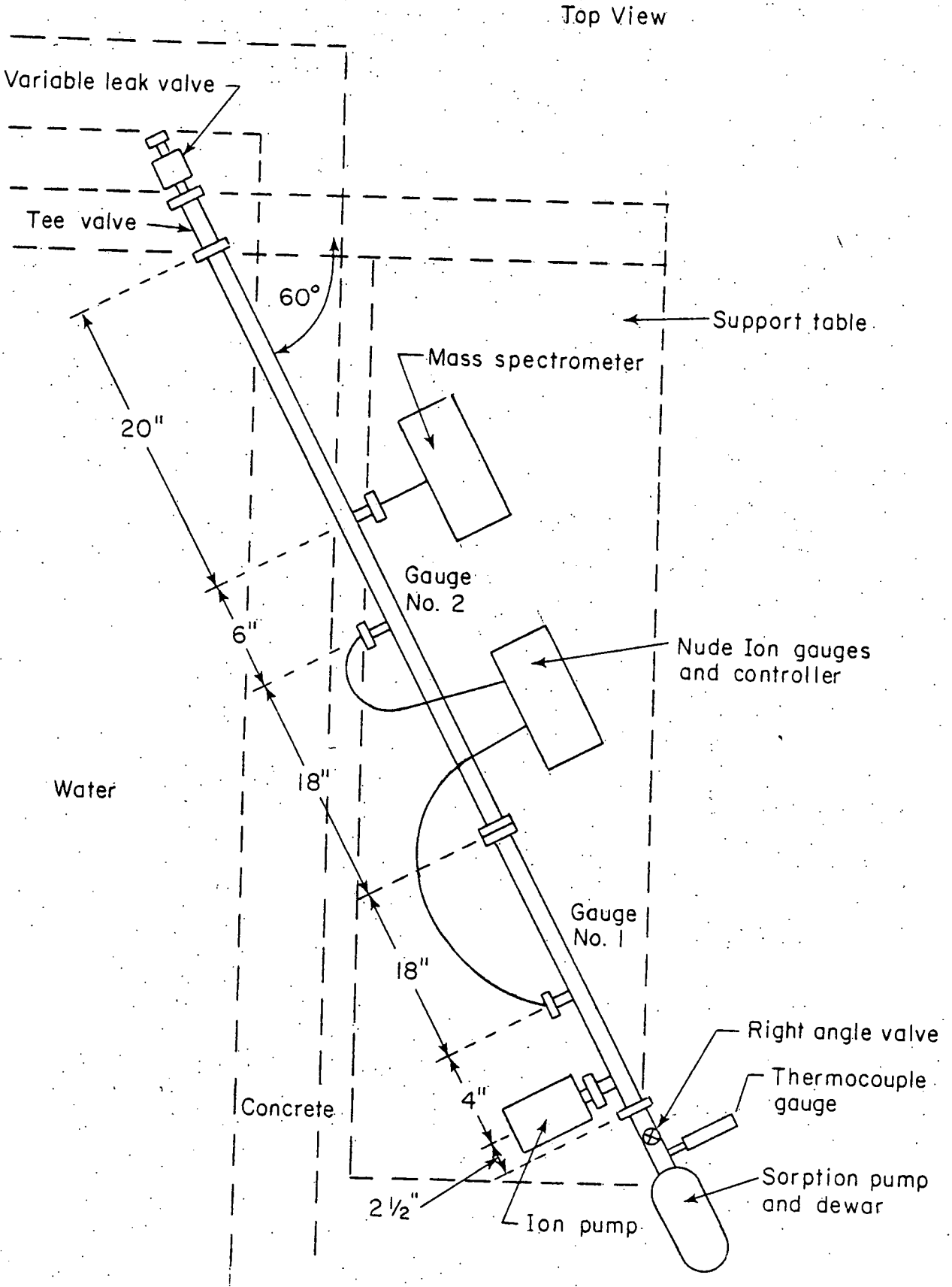


Figure 3
Top View of Vacuum System



be important to note the possible generation of gaseous species from inside the metal - species trapped during the formation of the metal[16]. If any high atomic number atoms are evolved, this could quench the fusion reaction in a fusion reactor. The gas evolution rate can be determined in several ways. First, as seen in Figure 3, two nude ion gauges are separated by 36 inches. By measuring the pressure difference between these gauges, from the calculated conductance, the gas flow can be determined. Second, it will be noted that there is a flanged joint between the two gauges. This permits the insertaion of an orifice of accurately known conductance into the system. The flow can then be determined by the pressure reading. Third, the lower portion of the system, which contains the test section, can be isolated and the outgassing determined from the rate-of-rise of the pressure on this portion of the system.

(3) Use of an ion pump with a sorption roughing pump eliminates possible oil or mercury contamination from forepumps and "standard" diffusion pumps.

(4) As seen from Figure 2, the bottom 10 inches of the system, which is the region exposed to the intense gamma radiation, contains a test insert. It consists of 95 pieces of 1/8-in. SS-304 seamless tubing, each 10-in. long, held in a square array by SS-304 wire mesh. No foreign materials, such as would be contained in a weld, are introduced into the system. Further, the tubes are bevelled at the bottom and so as to approximate point contact with the test chamber, to avoid "infinite leaks" that result from close-tolerance area contact. The test insert and walls of the test chamber have a total surface area

of 4595 cm^2 which is exposed to the intense gamma radiation. The remainder of the entire vacuum system has a surface area of 7500 cm^2. The S/V (surface-to-volume)ratio of the test insert is 39, and of the entire system including the insert, is 1.6.

(5) All flanges and valves are bakeable. A custom-tailored bakeout jacket was constructed with Variac control of the heaters (broken down into sub-sections for fine control) to enable bakeout of the entire system at various fixed temperature up to 300 C.

(6) Since the experiments are performed in the cobalt-60 pool, the vacuum system was designed to be inserted into the pool without breaking the vacuum. The mechanical design of the experiment includes a table which supports the entire vacuum system. The vacuum system is fastened to the table and is lifted by an overhead winch suspended from an I-beam in the laboratory. After being properly positioned, the vacuum chamber is lowered into the cobalt-60 region.

VII. Cobalt-60 Irradiation Facility

The cobalt-60 irradiation facility (Winkel Radiation Laboratory) used in this research is located in the basement of the Old Chemistry Building at the University of Cincinnati. The cobalt-60 is contained in 36 pins clad with type 304 stainless steel. At the time of the experiments reported herein (September 14, 1977) the cobalt activity was 1120 curies. The pins are located in a source holder (see Figure 4) at the bottom of a pool of demineralized water. The arrangement of the pins is such as to provide a vertical cylindrical access hole 3 5/8-in-diameter for experimental use. The active source length is approximately 10 inches.

The pool is a concrete pit 9.5 feet deep by 6 ft. by 14 ft. Figure 5 is

a photograph of the facility. The nine feet of water above the source reduces the radiation level at the surface of the pool to well below 0.25 mr/hr. The radiation level in water in the center of the experimental access hole was initially measured in May, 1977 by use of thermoluminescent detectors (TLD). The rad dose as determined by these detectors along the centerline vertical axis of the source is shown in Figure 6. When the vacuum system is inserted into the source, the test insert essentially extends over the bottom 10 inches. Thus it receives an average dose rate of about 0.1 megarad/hr. Detailed in situ dosimetry is reported later in this document.

VIII. Out-of-Pile Thermal Outgassing of Stainless Steel 304

Observations of the system behavior during the initial pumpdown have general interest. The SS-304 vacuum system was cleaned by the fabricator as follows:

(1) Acid etch with mixture of HNO_3, HF, HCl and H_2O

(2) Rinse with tap water

(3) Rinse with distilled water.

Prior to assembly in the Winkel Radiation Laboratory (Cobalt-60 irradiation facility) all parts were cleaned with ethyl alcohol and then dried with a heat gun. For the initial pumpdown of the system, no bakeout was used. After approximately one hour of pumping with the 20 liter/sec diode ion pump, from the ion pump current (2.5 milliamperes at 25 C), the outgassing rate was determined to be 4.0×10^{-8} torr-liters/(cm^2)(sec). This compares favorably with data from Blears[17] who reports values of 10^{-7} to 2×10^{-8} during the first ten hours of pumping on a stainless steel system.

Following the initial pumpdown, outgassing was measured after bakeout at various fixed temperatures up to 300 C. Outgassing measurements were made at

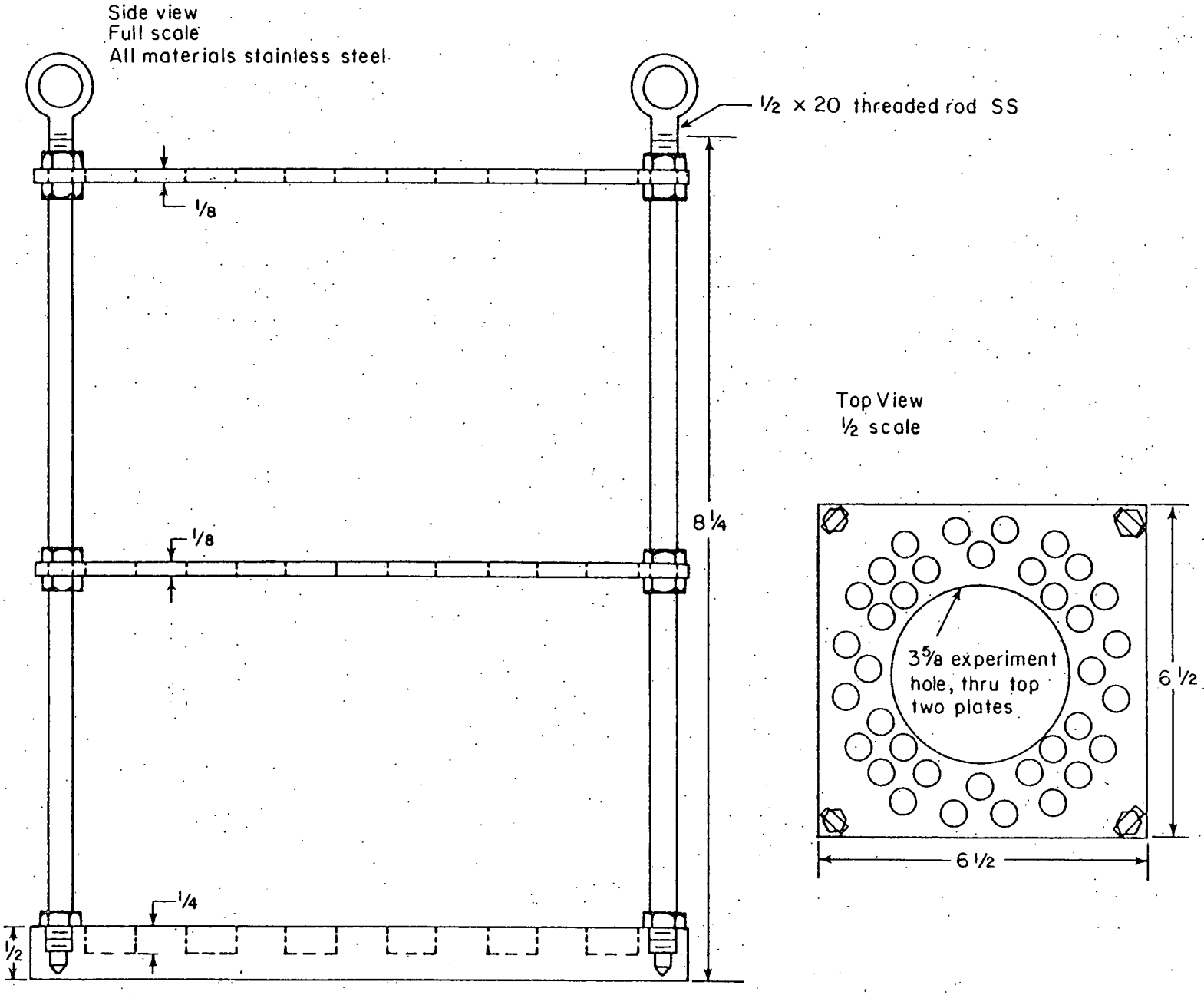
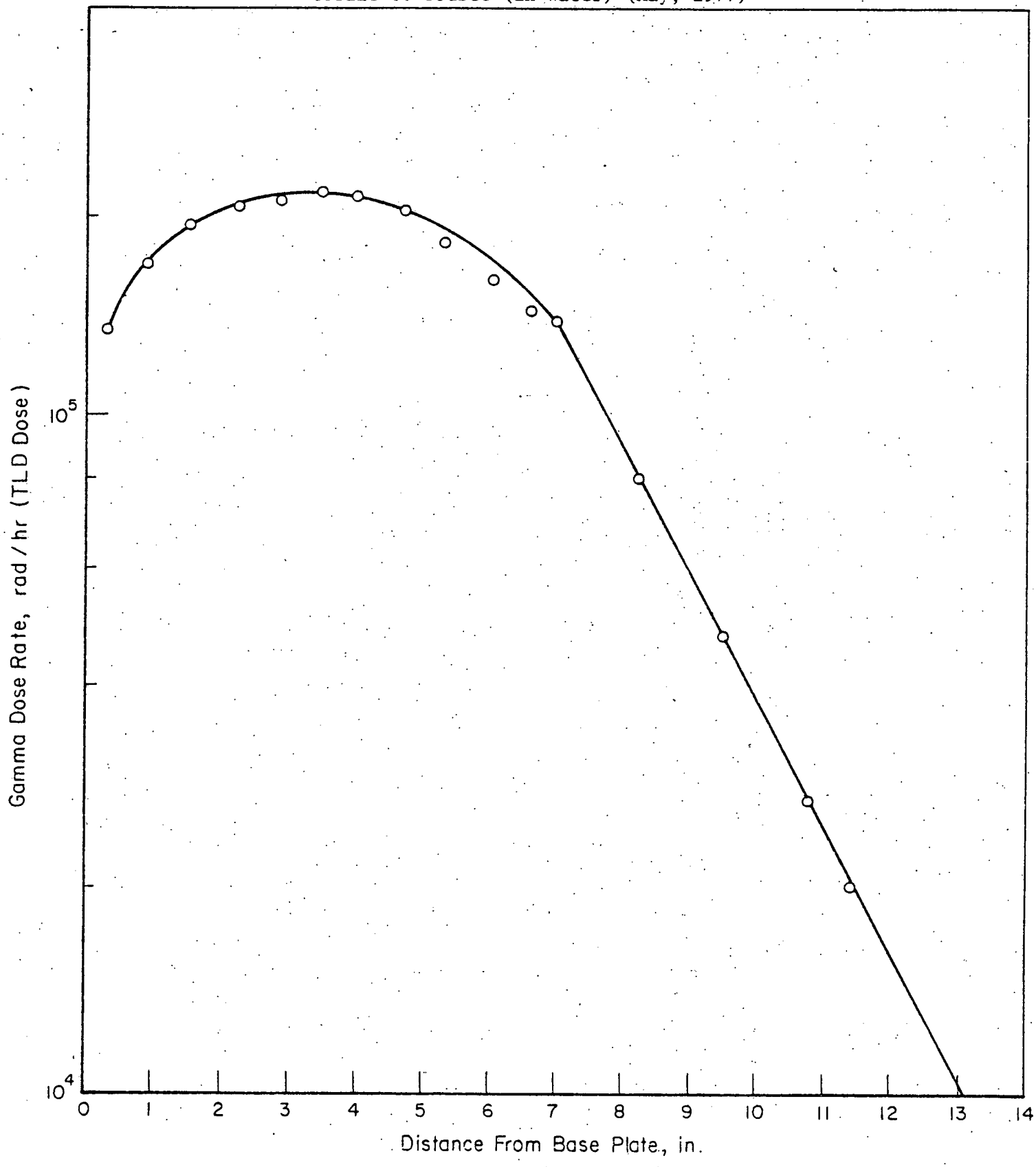


Figure 4
Source Holder for Cobalt-60 Pins

Figure 5. Cobalt-60 Gamma Irradiation Facility at The University of Cincinnati

Figure 6
Gamma Dose Rate Versus Distance Along Centerline Axis of
Cobalt-60 Source (in Water) (May, 1977)



various temperatures following bakeout by the rate-of-rise technique. Typical data are shown in Figure 7. A plot of the outgassing at various temperatures versus temperature checks the validity of Equation (7) and determines the average desorption energy $\bar{Q}$. Typical data are shown in Figure 8.

It is seen indeed that the outgassing obeys the assumed temperature dependency. A summary of the thermal outgassing data is given in Table 5, where the parameters are associated with the assumed model

$$\Delta = \Delta_o e^{-\bar{Q}/RT}$$

This is the outgassing at any temperature T after bakeout at temperature T*.

Table 5

Parameters Fit to the Data for Thermal Outgassing of 304 SS

T*, Bakeout Temperature, C	Δ_o $(\frac{\text{torr-liters}}{\text{cm}^2\text{-sec}})$	$\exp(-\bar{Q}/RT)$ (a)	$\bar{Q}$ $\frac{\text{kcal}}{\text{mole}}$
300	4.27×10^{-5}	$e^{-4650/T}$	9.25
275	1.32×10^{-4}	$e^{-4920/T}$	9.78
200	4.33×10^{-4}	$e^{-5420/T}$	10.8
100	1.76×10^{-3}	$e^{-5869/T}$	11.7

(a) Temperature T in the exponent is the Kelvin Temperature.

It is seen that the average desorption energy $\bar{Q}$ has indeed a value consistent with the data presented in Table 3 and the values fall between the extremes of helium and water. That $\bar{Q}$ decreases as the bakeout temperature increases suggests that more water vapor (the worst offender) is being driven off at the higher temperature. Indeed, the spectrometer data verify this trend.

The mass spectrometer data indicate that hydrogen and water are the two major outgassing species after reasonable cleanup of the system. The time evolution of the partial pressures due to hydrogen and water vapor during the process of

Figure 7
Rate-of-Rise Data at Various Temperatures
Following Bakeout at 100 C

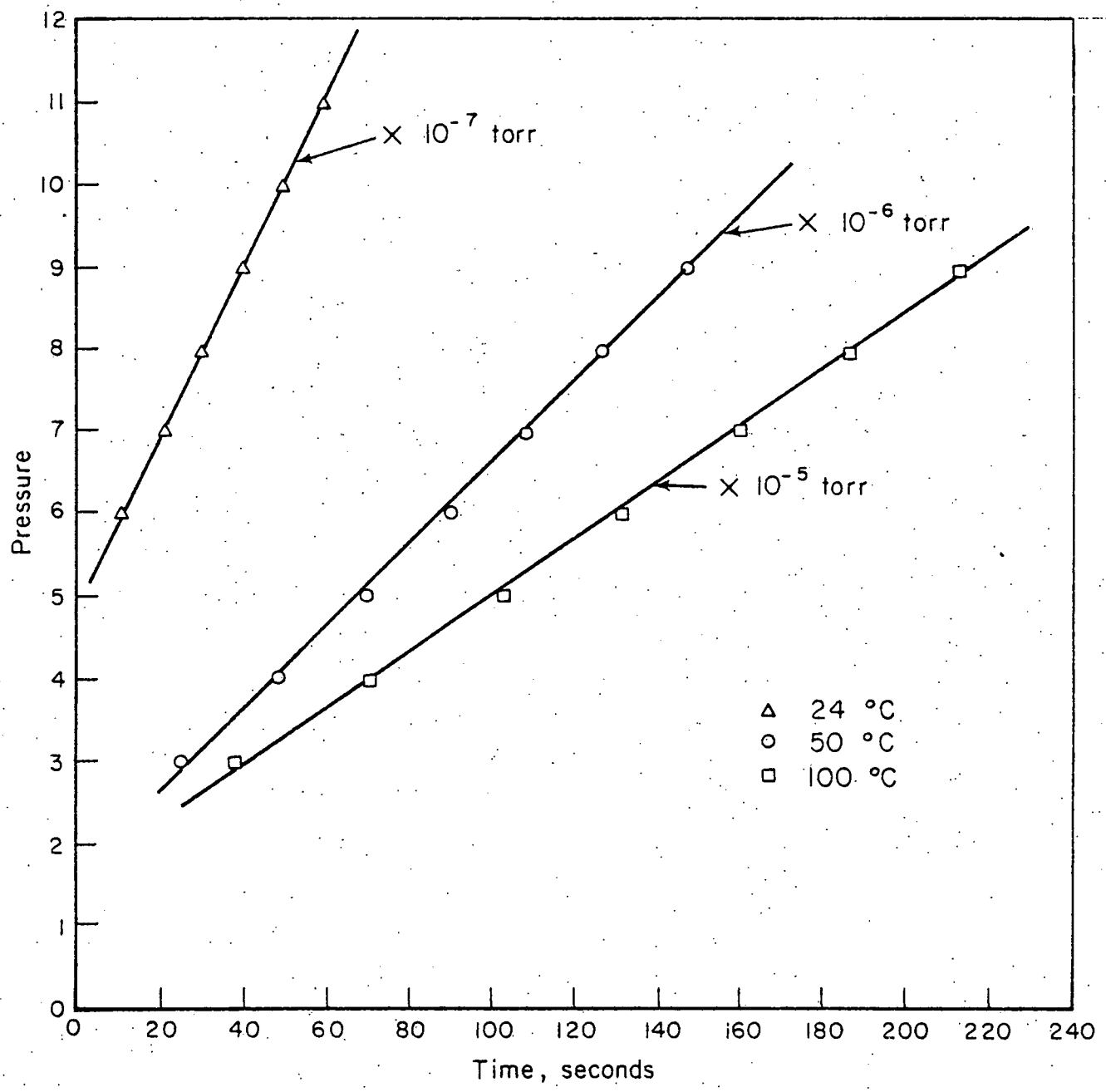
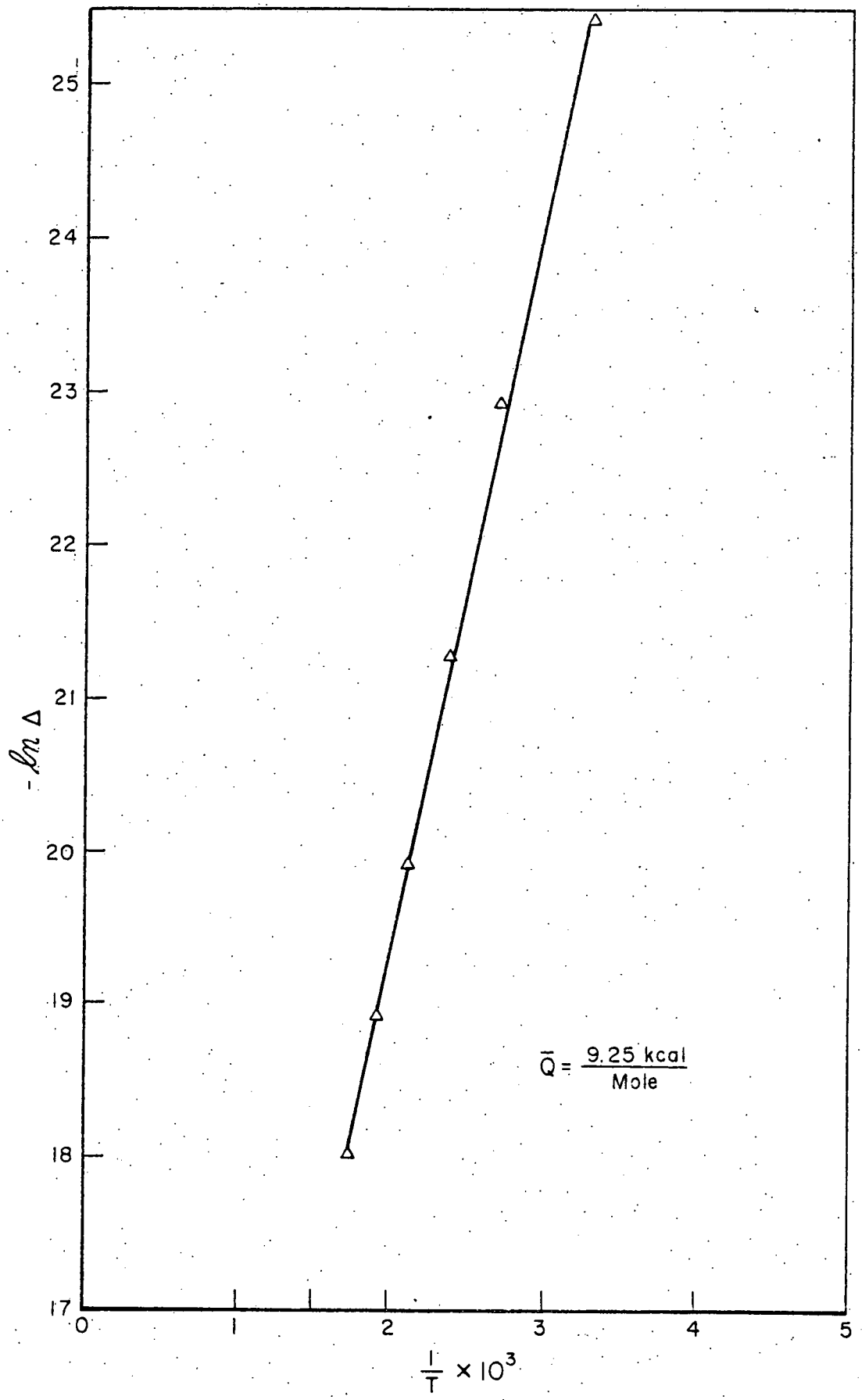


Figure 8
Determination of Average Desorption Energy After Bakeout at 300 C



the bakeout at 275 C is shown in Figure 9. It is seen that after the bakeout, hydrogen is the more predominant of the two species. These data have been corrected for the relative sensitivity of the mass spectrometer (provided by the manufacturer: Spectrum Scientific Ltd., Cheshire, England).

IX. Radiation-Induced Outgassing from 304 SS

The Principal Experiment

Following the 300 C out-of-pile bakeout, the system was allowed to return to ambient temperature (26 C). Rate of rise measurements were made during this cooling period. After ambient temperature was reached, pumping continued for 95 hours until an equilibrium pressure was reached. At this point the temperature was increased again to 300 C. It was hoped that this might lower the ultimate pressure significantly. After baking for 4 hours, the system was brought back to ambient temperature and pumping continued for 20 more hours. The decrease in pressure on gauge #2 (located next to the mass spectrometer - see Figure 3) was from 7.6×10^{-8} torr to 3.8×10^{-8} torr as a result of the second bakeout. At this point, after baking twice at 300 C and pumping for 166 hours, the test section was inserted into the Co-60 Facility for a period of 26 hours. Figure 10 shows the pressure vs time for the radiation experiment. The time base in Figure 10 is the total pumping time.

Immediately before removal from the Co-60 facility (26 hours of radiation), a rate of rise measurement was made and the outgassing was calculated. Following the removal from the radiation source, a second rate of rise measurement was made and a second outgassing calculation was made. Figure 11 shows the rate of rise data. From the data of Figure 11, and using a surface area of 4595 cm^2, the radiation-induced outgassing was determined to be 9.48×10^{-13}

Figure 9
Time Evolution of Pressure Due to Hydrogen
and Water Vapor During the Process of Bakeout at 275 C

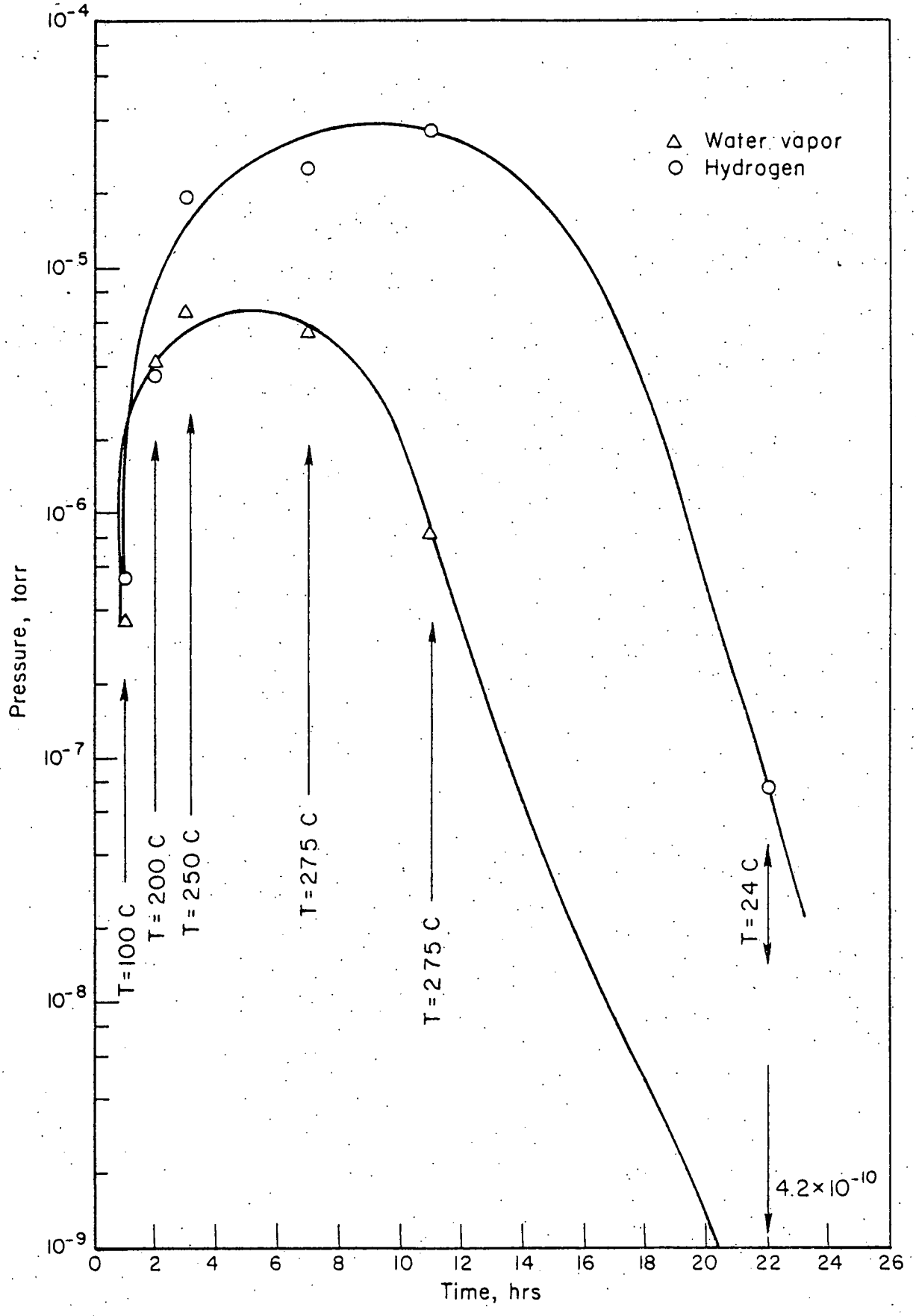
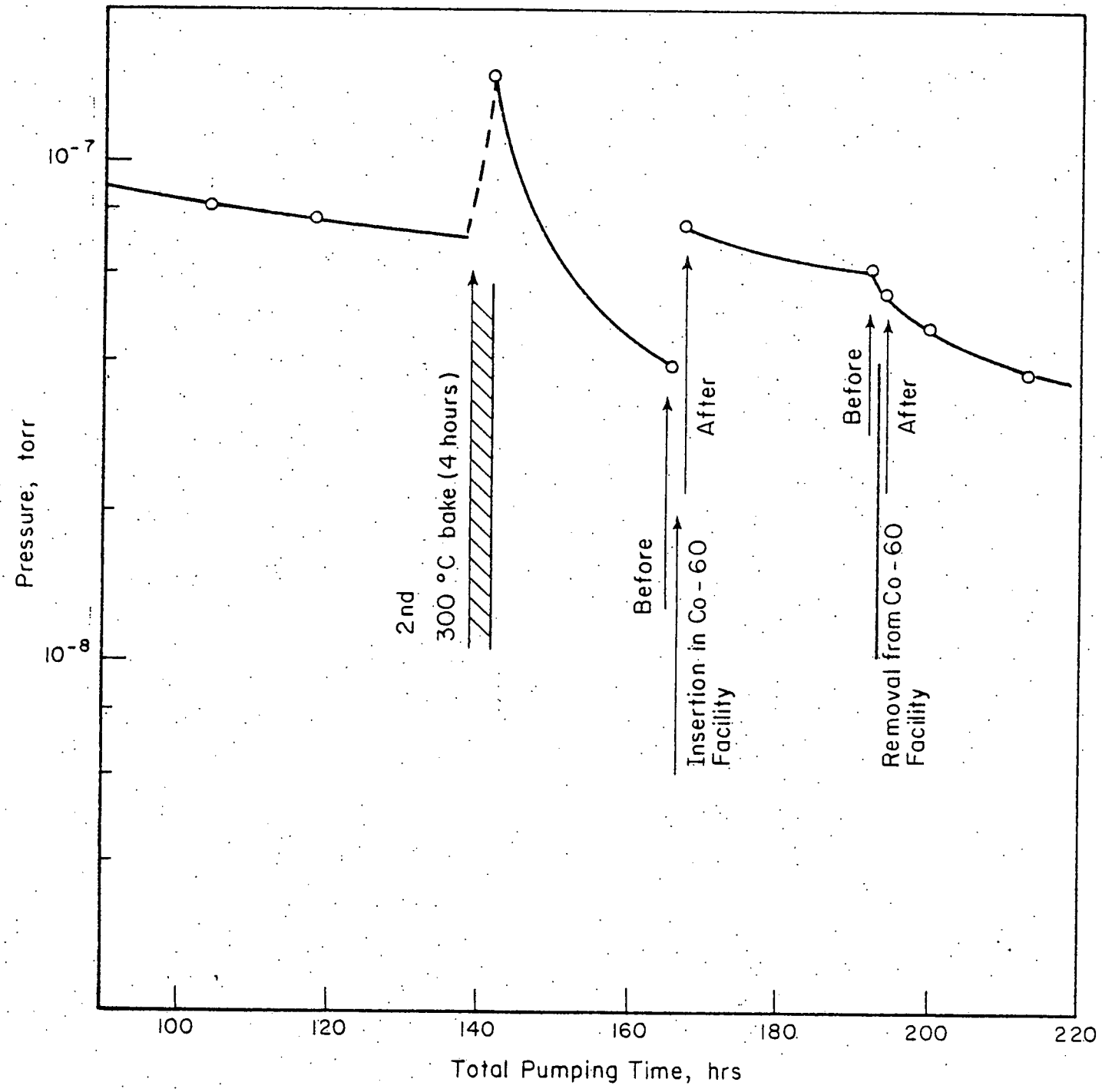


Figure 10
Pressure Versus Time Curve Following Bakeout at 300 C
(Including Irradiation)



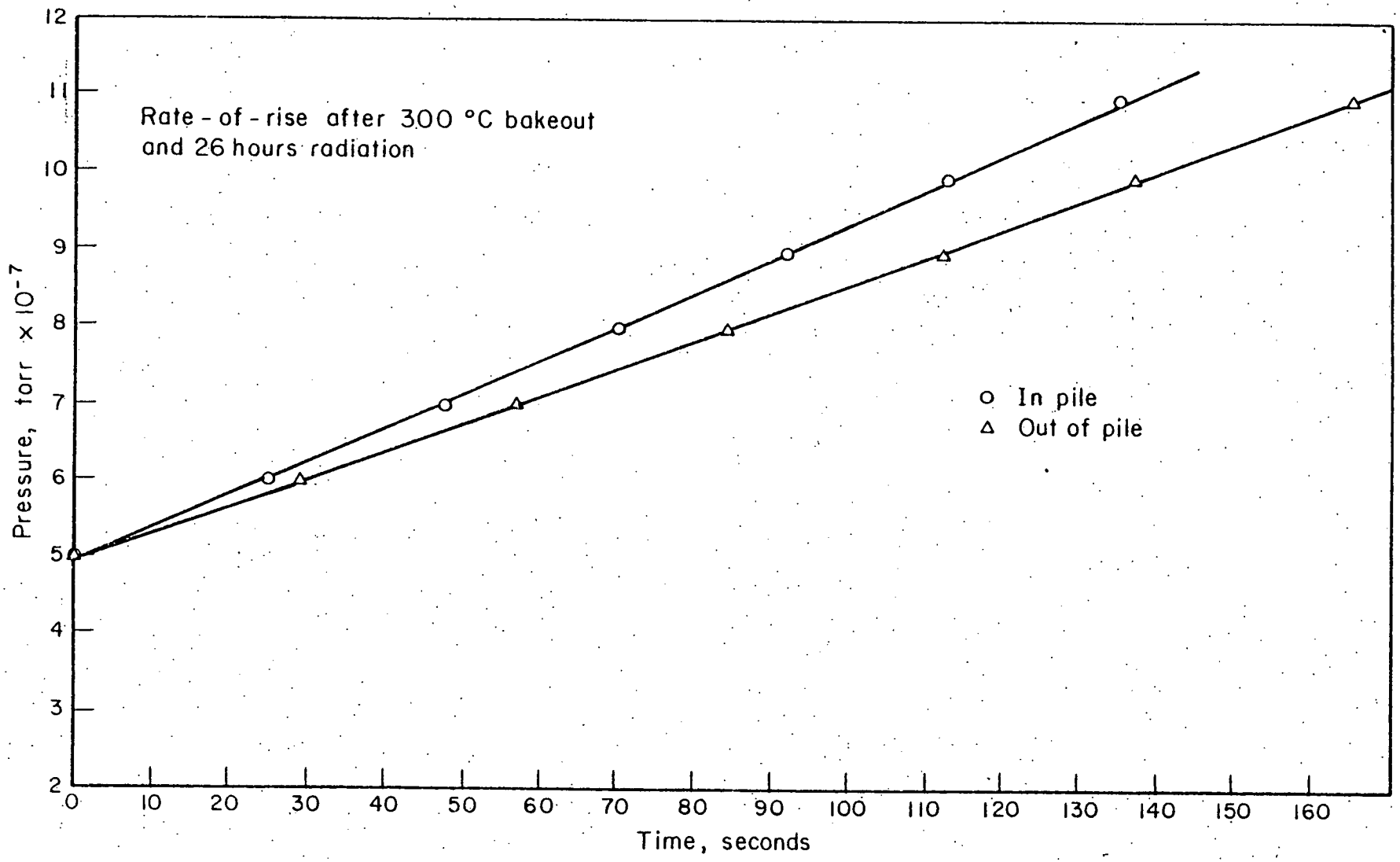


Figure 11
Rate-of-Rise Data Used to Determine Radiation-Induced Outgassing

torr-liters/(cm^2)(sec).

Mass spectrometer data were taken during the irradiation of the test section. No significant change in the gas composition occurred during the radiation. The pressure in the system at this time was almost entirely from hydrogen.

In Situ Dosimetry

The radiation dose rate received by the SS-304 test insert was measured on November 11, 1977 using micro thermoluminescent dosimeters (TLD) (CaF_2:Mn) which are manufactured by Victoreen of Cleveland, Ohio. The microdosimeters were placed on the center line of the test insert and the test chamber was inserted into the Co-60 radiation field.

Figure 12 displays the data from the dosimeters. (The curve below 2 inches was extrapolated using calibration data of July 1, 1977). Using these data, the average dose rate over the test chamber was calculated to be 131.5 krad/hr. Correcting for the decay since the time of the outgassing measurement (September 14, 1977) yields a value of 132.8 krad/hr. However, this value is the average dose rate received by the TLD's. This must be corrected to the average dose rate $\dot{D}_{SS}$ received by the SS-304. This corrected value can be found as follows:[18]

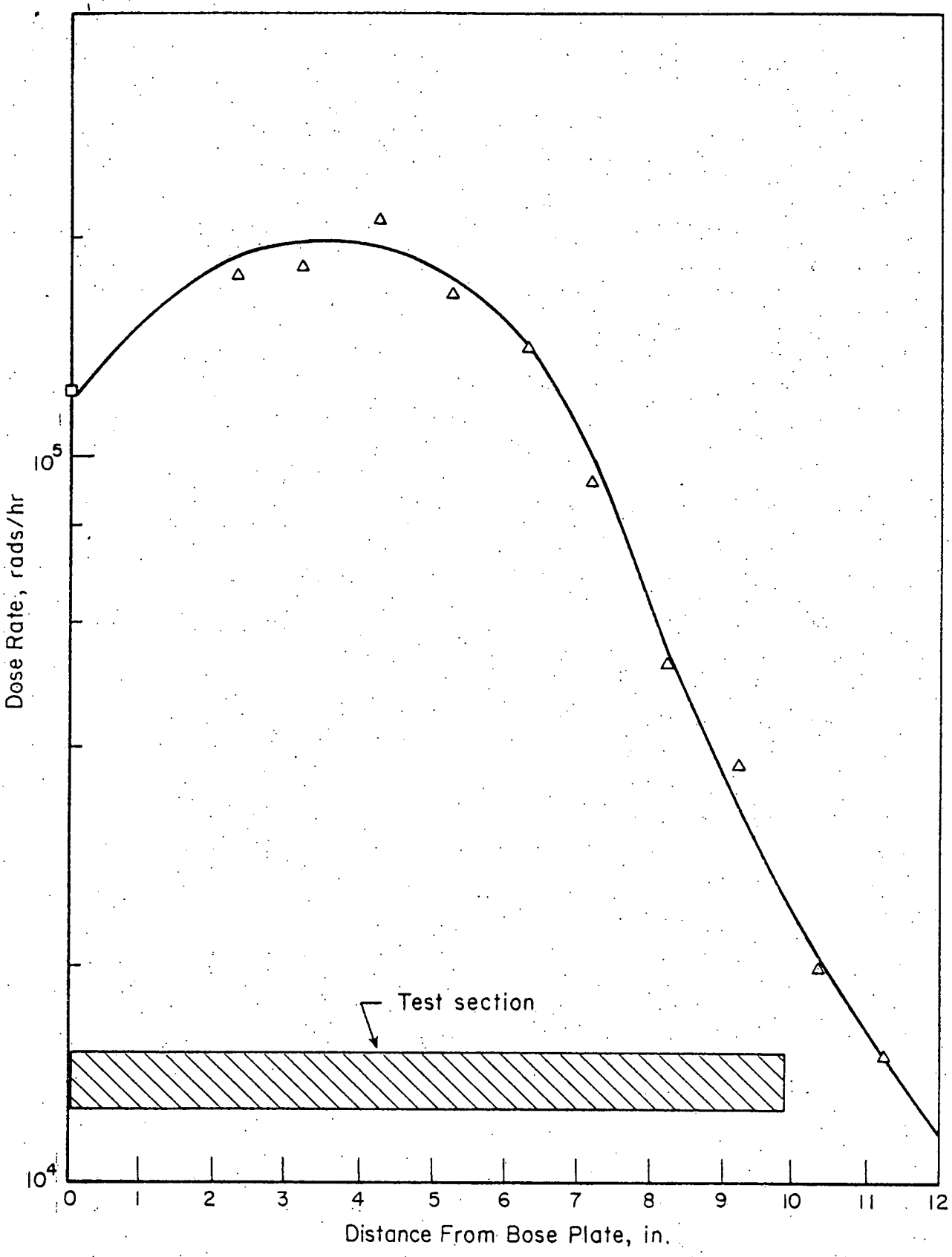
$$\dot{D}_{SS} = 0.869\ (\mu e/\rho)\ ss/(\mu e/\rho)_{air} \cdot \dot{X} \qquad (10)$$

where $\dot{X}$ is in Roentgen/hour, and $(\mu e/\rho)$ is the mass absorption coefficient. However, the Victoreen TLD's are calibrated to read Roentgens in air[19] and $\dot{D}_{TLD} = 0.869\ \dot{X}$.

Thus, the appropriate correction is given as:

$$\dot{D}_{SS} = \frac{(\mu e/\rho)SS}{(\mu e/\rho)_{air}}\ \dot{D}_{TLD} \qquad (11)$$

Figure 12
In Situ TLD Dosimetry Along Centerline of Test Insert



Using values for the energy absorption coefficients of 0.0246 for stainless steel and 0.0268 for air[20] yields an average absorbed dose in the test insert at the time of the outgassing measurement of 121.9 krad/hr

Final Result and Error Analysis

From the measured outgassing of 9.48×10^{-13} torr-liters/(cm^2)(sec) using a surface area of 4595 cm^2, and from the dosimetry results of 121.9 krad/hr, one thus arrives at the final result for the radiation-induced outgassing for 304SS after bakeout at 300 C of

$$\Delta = 7.78 \times 10^{-12} \text{ torr-liters/}(cm^2)\text{(sec) per megarad/hr}$$

As given from Equation (9) this number is derived from

$$\Delta = \frac{(Q' - Q)}{A_R \dot{D}_{SS}} \tag{12}$$

The mean error $\delta\Delta$ in the derived value is taken as

$$\delta\Delta = \frac{\Delta_{max} - \Delta_{min}}{2} \tag{13}$$

where

$$\Delta_{max} = \frac{(Q' + \delta Q') - (Q - \delta Q)}{(A_R - \delta A_R)(\dot{D}_{SS} - \delta \dot{D}_{SS})}$$

and

$$\Delta_{min} = \frac{(Q' - \delta Q') - (Q + \delta Q)}{(A_R + \delta A_R)(\dot{D}_{SS} + \delta \dot{D}_{SS})} \tag{14}$$

where the δ's are the estimated errors in the parameters. Table 6 summarizes the estimated errors.

Table 6

Estimated Errors in Properties Determining Δ

Property	Estimated Error, Per Cent
Δ P, pressure rise	3
Δ t, time measurement	1
V, volume	1
A_R, area	1
$\dot{D}_{SS}$, dose rate	5

From these estimated errors, one determines the final value of the radiation-induced outgassing for 304 SS after bakeout at 300C to be

$$\Delta = (7.78 \pm 4.36) \times 10^{-12} \frac{\text{torr-liters}}{(\text{cm}^2)(\text{sec})(\text{megarad/hr})}$$

As discussed in an earlier section of this report, the proposed model for radiation-induced outgassing predicted an outgassing rate of 8.3×10^{-12} torr-liters/(cm^2)(sec) per megarad/hr. Considering the crudity of choice of the atom desorption yield by electrons, the agreement is striking. One must conclude that, at least to a first approximation, the model predicts the real phenomena for 304SS. The predicted value by this model for aluminum, however, is in disagreement with the available data.

Radiation Induced Outgassing With No Bakeout

The system was pumped down at room temperature for 122 hours. At this point the test section was inserted in to the Co-60 facility and pumping continued for 46 more hours. After 46 hours of irradiation, the test section was removed from the Co-60 and pumping continued for an additional 45.5 hours.

Table 7 shows the pressure of the system which was measured on gauge 2 and gauge 3 at various important times during the experiment. Gauge 3 is located near the test insert at the base of the assembly (see Figure 2).

Table 7

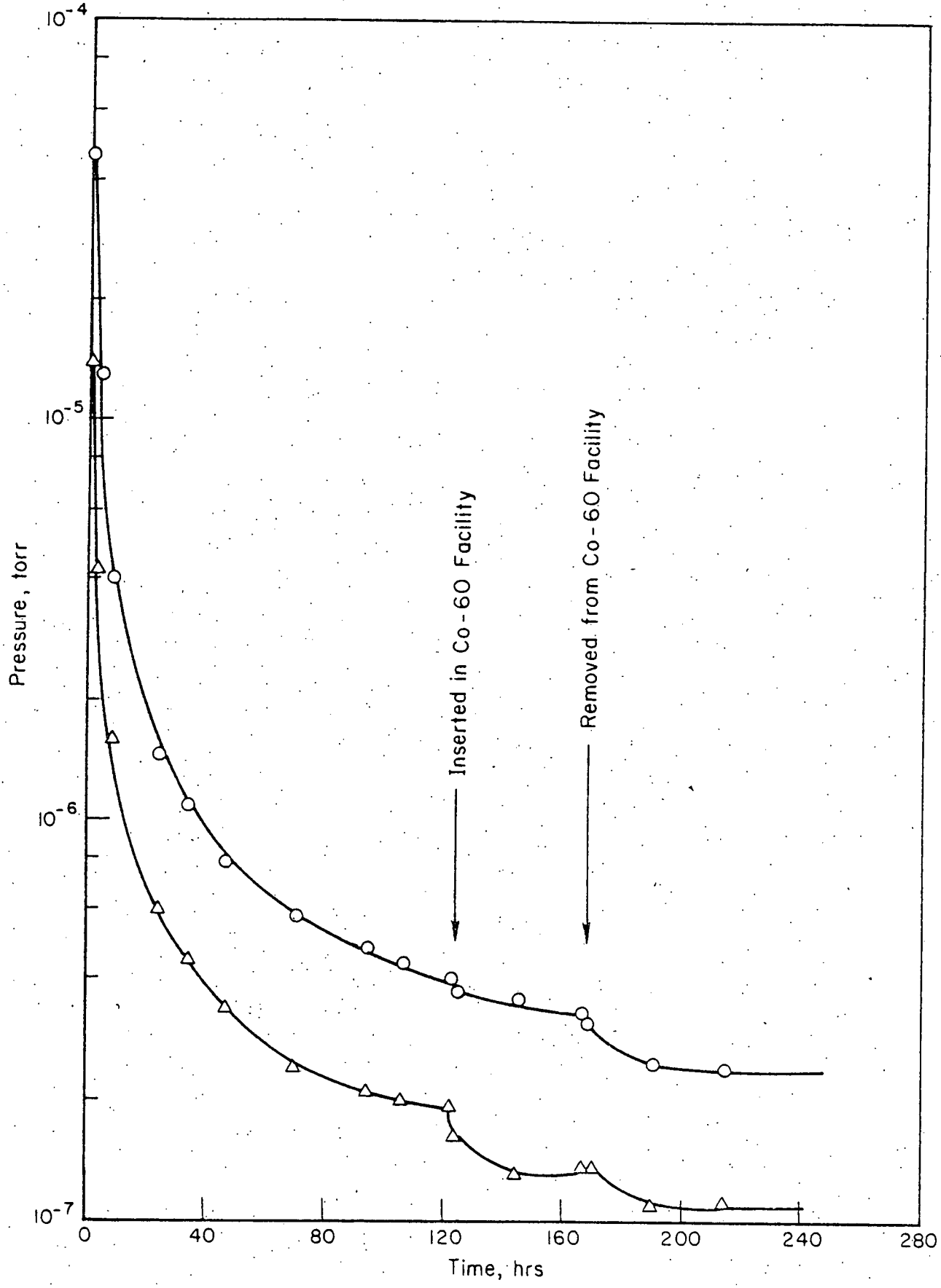
System Pressures at Various Times During the Experiment on Radiation-Induced Outgassing With no Bakeout

Total Pumping Time (hours)	Radiation Time	Pressure (torr) Gauge 2	Gauge 3
121	t=0 (before insertion in Co-60)	1.9×10^{-7}	3.9×10^{-7}
122	t = 1 hour (after insertion in Co-60)	1.65×10^{-7}	3.75×10^{-7}
145	t = 23 hours	1.35×10^{-7}	3.6×10^{-7}
168	t = 46 hours	1.38×10^{-7}	3.2×10^{-7}
169	t = 47 hours (test section removed from Co-60)	1.4×10^{-7}	3.1×10^{-7}
191	t = 22 hours after radiation	1.1×10^{-7}	2.5×10^{-7}
214.5	t = 45.5 hours after radiation	1.1×10^{-7}	2.4×10^{-7}

Figure 13 shows the pressure versus time for the entire experiment.

Rate of rise measurements were made immediately before removal from the Co-60 and immediately after removal. In both case the pressure was allowed to increase from 5×10^{-7} to 12×10^{-7} torr. The "in pile" time was 75 seconds and the "out-of-pile" time was 76 seconds. This difference is too small to make a meaningful determination of the radiation-induced outgassing. The conclusion is that the radiation outgassing to too small in comparison with the "ordinary" outgassing to be measured at this base pressure. However, the data from Figure 13 indicate that the radiation does help in the total reduction of the pressure, although not as dramatic as illustrated in Figure 1 for the original experiment. It should be pointed out that the system had been previously baked out in the many out-of-pile experiments, i.e. the surfaces were not "fresh" as they were in the experiment of Figure 1. Since

Figure 13
Pressure Versus Time Curve for
Irradiation Experiment With No Bakeout



ordinary outgassing from a fresh stainless steel surface is even larger, determinations of the radiation-induced outgassing for fresh surfaces is precluded with this system.

Again, the principal gases at the start of the experiment were water vapor and hydrogen, and after the base pressure was reached the primary residual gas was hydrogen.

X. Conclusions and Recommendations

The principal conclusions from this research are as follows:

(1) Radiation can indeed induce outgassing in a vacuum system.

(2) The magnitude of the radiation-induced outgassing for 304 stainless steel after bakeout at 300 C is $(7.78 \pm 4.36) \times 10^{-12}$ $\frac{\text{torr-liters}}{(\text{cm}^2)(\text{sec})}$ per megarad/hr.

(3) The analytical model proposed predicts the measured value of radiation-induced outgassing for 304 SS but apparently overestimates that for aluminum.

(4) After bakeout at temperature T*, thermal outgassing obeys the relationship $\Delta = \Delta_o \bar{e}^{\ \bar{Q}/RT}$, where both Δ_o and $\bar{Q}$ are functions of T*.

(5) The average desorption energy $\bar{Q}$ for molecules on 304 SS decreases with increasing bakeout temperature, varying from 11.7 kcal/mole after bakeout at 100 C to 9.25 kcal/mole after bakeout at 300 C.

(6) Water vapor and hydrogen are the principal residual gases in a 304 SS vacuum system, with hydrogen being dominant at low pressures after bakeout.

The following recommendations are made to extend this research.

(1) With 304 SS, vary the surface-to-volume (S/V) ratio of the test insert (still with a square array), to determine the sensitivity of the measured outgassing to this parameter.

(2) With 304 SS, at fixed (S/V) ratio, change the array of pins in the test insert to hexagonal, to determine the sensitivity of the measured outgassing to this parameter.

(3) Under the same conditions as for the present research, replace the 304 SS test insert with other materials. Suggested materials are 316 SS, copper, aluminum, and carbon. (The aluminum data will check consistency with the NBS result).

XI. Acknowledgement

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