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ARGON GAS ANALYSIS TO PREDICT WATER LEAKAGE INTO THE W88

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ABSTRACT

Analyses of the internal argon gas concentrations monitored on surveillance units of the W84 indicates that field aging of this weapon for times up to ~4 years does not lead to important increases in the rate at which water leaks into the interior of the weapon. This implies that the EPDM environmental seals used on the W84 do not age significantly over this time period. By comparing the percentages of oxygen and argon in the internal atmosphere, an estimate of the oxygen consumption rate is made for a typical W84 unit.

The argon gas analysis approach is then applied to the W88, which is sealed with a new EPDM material. Predictive expressions are derived which relate the anticipated argon gas concentrations of future, field-returned units to their water leakage rates. The predictions are summarized in convenient plots, which can be immediately and easily applied to surveillance data as reported. Since the argon approach is sensitive enough to be useful over the entire lifetime of the W88, it can be used to point out leaking units and to determine whether long-term aging has any significant effect on the new EPDM material.

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INTRODUCTION

Environmental o-ring seals are used to protect the interior of weapons from potentially degrading external environments surrounding the weapon during its lifetime. Perhaps the most worrisome environmental factor is water vapor, which can lead to corrosion and degradation of internal components. Ingress of water vapor from the surrounding atmosphere to the weapon interior is due to two phenomena, water permeation through the o-ring seals and water leakage, mainly between the o-ring surface and its mating surface (other leaks, through cracks in connectors for example, are also possible). Internal sources also contribute to water vapor buildup; these come mostly from water dissolved in internal components when the weapon is first sealed. Because of the inevitability of internal water vapor buildup, water dessicants are usually designed into the weapon to keep the internal water vapor pressure at acceptably low levels (typically below a -20°C dew point). The amount of dessicant, which is often limited by weight and space considerations, is chosen based on dessicant properties coupled with reasonable lifetime estimates of the various contributing water sources. These include internally dissolved sources of water, water vapor in the internal atmosphere when the weapon is first sealed and water permeation through the o-ring seals. An excellent report, outlining detailed procedures for accomplishing this goal has recently been published. [1] Unfortunately, one potential contribution to the internal water content, that part due to leakage, is difficult to estimate. Leakage testing is often done when the weapon is first sealed to ensure proper sealing, and the specification for this test has been incorporated in calculations of dessicant requirements. [1] However, the leakage can and does [2] change dramatically with time. Many factors potentially lead to such changes. Aging of the seals can result in sufficient compression stress-relaxation for leaks to open up. Low temperature exposures may cause sufficient stiffening of the o-ring to destroy its sealing properties, leading to leaks. For submarine weapons, the larger pressure differentials during launch tube pressurization cycle testing may open up leaks.

The need to have some reliable method for estimating the integrated lifetime contribution from water leakage led to the development of the argon analysis approach, described in a recent report. [2] It is based on the use of the argon gas concentration in nitrogen backfilled weapons as an internal monitor of lifetime water leakage. Since argon is the third most important constituent of normal air at a concentration of 0.93%, argon leakage into such weapons will parallel water vapor leakage. This fact, coupled with the inertness of argon (no losses due to reaction), allows us to use the argon concentration to derive

reliable estimates of the lifetime water leakage into a weapon. Since the argon concentration is already monitored as part of the normal gas analysis of many field-returned weapons, application of this approach to such weapons is easy. In this report, the argon approach and an oxygen analysis variation of this approach are first applied to surveillance data on the W84 for weapons aged in the field for up to ~4 years. The results allow us to make conclusions about both the importance of water leakage and the typical rate of internal oxygen consumption for this EPDM-sealed weapon. We then apply the argon approach to another EPDM-sealed weapon, the W88. This results in predicted argon versus time curves which will allow water ingress estimates to be made directly and easily from future surveillance reports for W88 units.

ARGON AND OXYGEN ANALYSES OF W84 SURVEILLANCE UNITS

The W84 is a nitrogen backfilled system, sealed with EPDM o-rings which are coated with Krytox grease. Immediately after a weapon is pumped out and backfilled with dry nitrogen, the internal gas phase concentrations of argon and oxygen will be negligible. As the weapon ages either in the field (SLT units) or at Pantex (NMLT units), the argon and oxygen concentrations will build up from both internal sources (air dissolved in various materials inside the weapon) and gas ingress (permeation plus leakage) from the air-containing atmosphere surrounding the weapon. Figures 1 and 2 give W84 surveillance results for the percentage of argon and oxygen found in the interior of units plotted versus time in the field in days. In addition to the 104 data points plotted, there were 4 units which had approximately 0.93% argon and 21% oxygen (i.e., air) and 5 additional units with argon and oxygen concentrations higher than the upper limits plotted in the figures. These large values may indicate either units with severe leaks or gas sampling (e.g., air contamination) errors. The solid curves drawn through the data of Figs. 1 and 2 are visual aids meant to describe the overall trends for the bulk of the data. These curves show that both gas concentrations rise rapidly over the first 100 days to approximately 0.06% argon and approximately 1.1% oxygen; these increases are mainly due to contributions from internally dissolved gases. [2] At longer times, the argon results continue to increase, but typically at a slower rate; these increases are dominated by argon ingress (permeation plus leakage) from the surrounding air atmosphere. [2] On the other hand, the oxygen results tend to decrease after the initial rise; this decrease implies that internal oxidation reactions use up oxygen faster than ingress from the surrounding air atmosphere supplies additional oxygen.

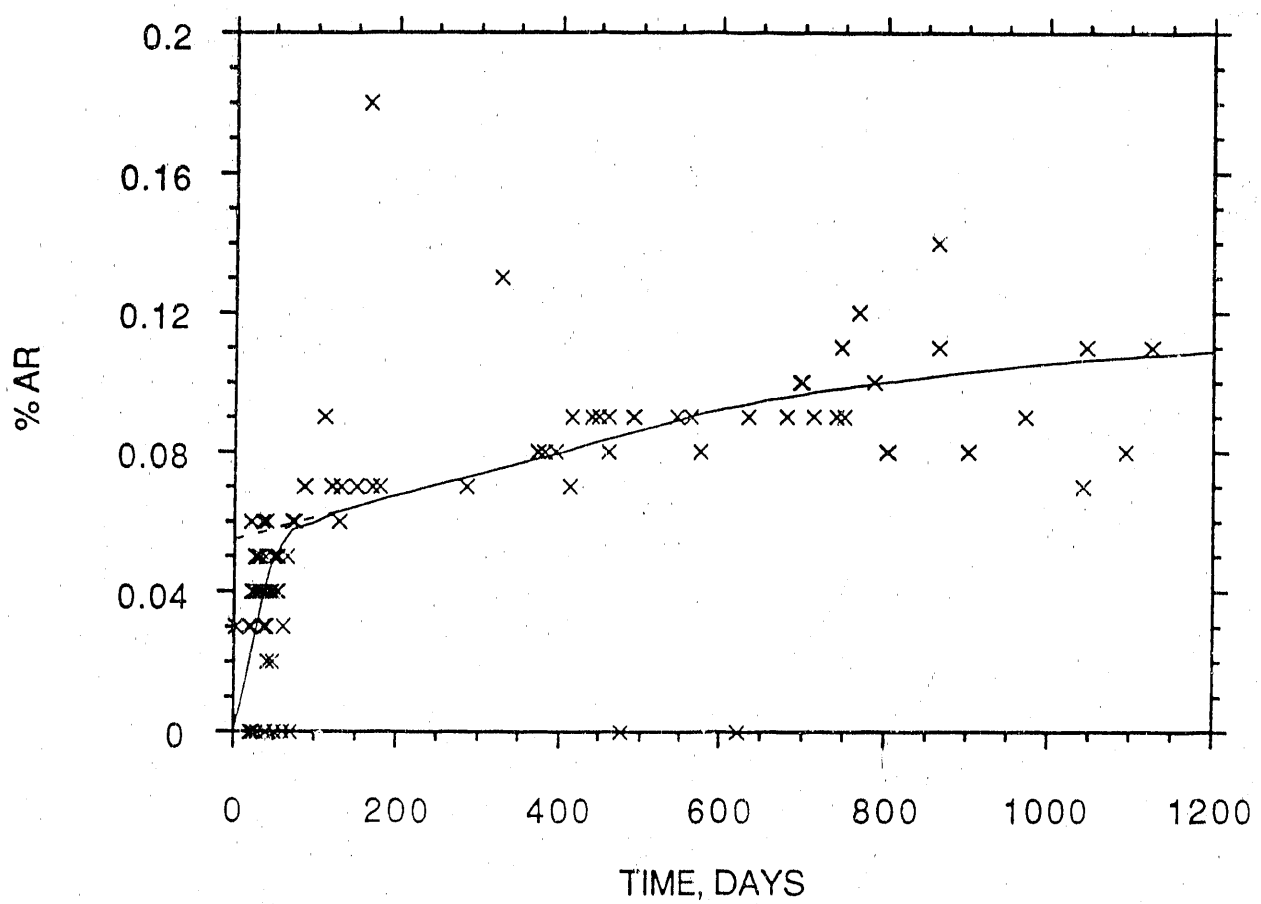

Fig. 1. Percentage of argon gas in the internal atmosphere of W84 surveillance units (SLT and NMLT) versus time in the field.

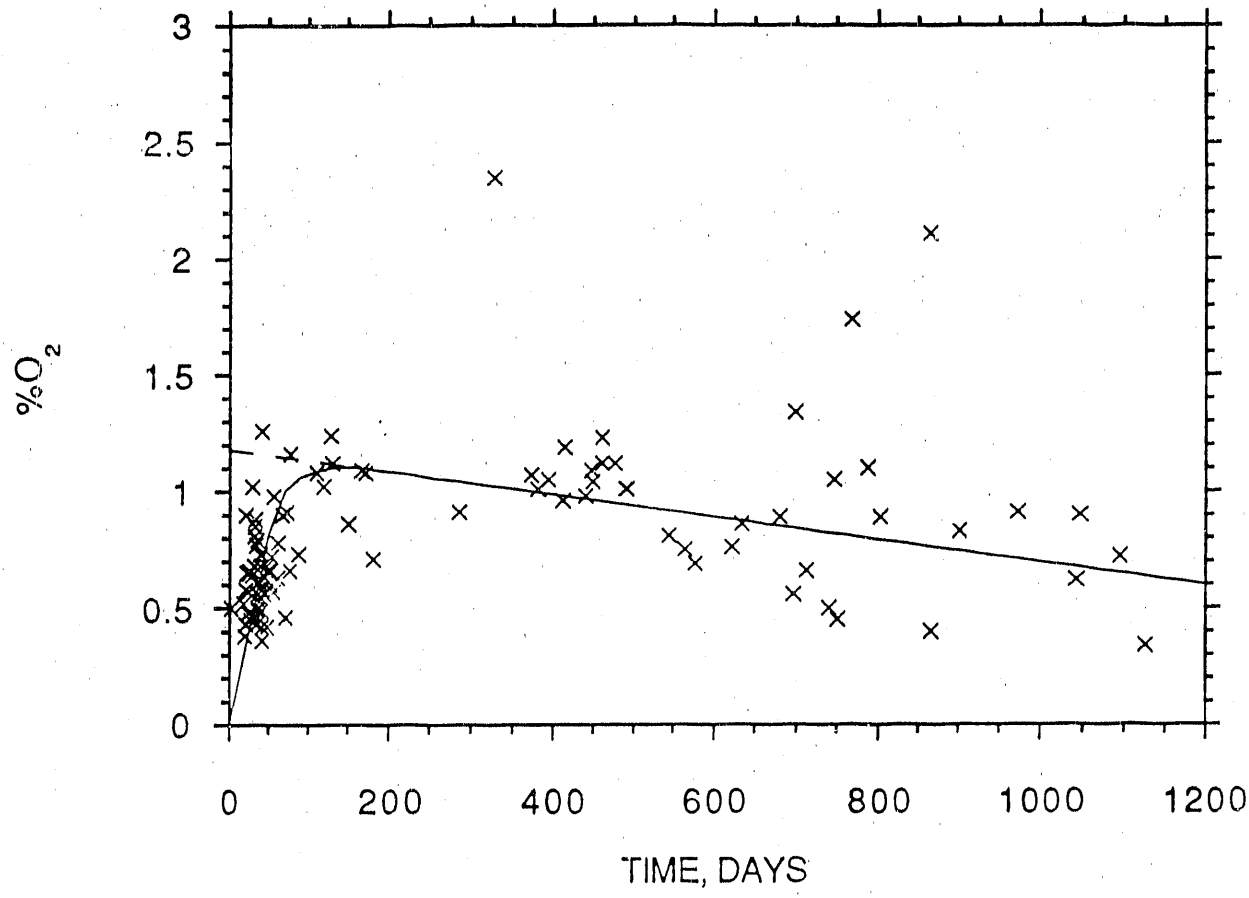

Fig. 2. Percentage of oxygen gas in the internal atmosphere of W84 surveillance units (SLT and NMLT) versus time in the field.

Thus a number of mechanisms can impact the measured gas concentrations. These include (1) early time contributions from gases dissolved internally when the weapon was initially sealed, (2) ingress contributions (permeation and leakage) from the surrounding air atmosphere and (3) for oxygen, decreases due to internal oxidation processes. We will first obtain estimates of the internal and permeation contributions for both argon and oxygen. These will then allow us to estimate both the argon leak rate contributions and the average oxygen consumption rate for a typical W84 unit.

INTERNAL GAS SOURCES

Internal gas sources are due to release of small quantities of argon and oxygen dissolved in various materials and components inside the weapon. Even though the weapon interior is pumped out before the nitrogen backfill, it can take several months for most of the dissolved gases to be removed from certain components.[2] One method of estimating the amount of gas which comes from internally dissolved sources is to extrapolate to zero time the long term (where internal contributions are minor) portions of the curves drawn through the data of Figs. 1 and 2. These extrapolations, shown as dashed lines in the figures indicate that the internal contributions for the W84 average approximately 1.18% for oxygen and 0.055% for argon. Although it is comforting that the ratio of these two contributions (21.5) is close to the ratio of the concentrations of oxygen to argon in air (22.5), this close correspondence should not always be expected. This is because the amount of each gas dissolved in a particular internal component will depend first upon the solubility coefficients for the gases; although often similar, these can differ by up to a factor of ~2 [3,4]. In addition, since many weapons are evacuated for periods of time ranging from hours to days prior to backfilling with nitrogen, differing diffusion constants for oxygen and argon [5,6] can also modify the expected ratio.

GAS PERMEATION THROUGH O-RINGS

For a plane of material of surface area A and thickness ℓ, the permeation flux F of a gas is given by

$$F = \Delta p \; P \; A/\ell \qquad (1)$$

where Δp is the partial pressure differential of the permeating gas across the material and P is the permeation constant for the gas. By assuming that a compressed o-ring can be approximated with a rectangular cross-section of area equal to that of the uncompressed o-ring, [1,2,7] the effective permeation thickness ℓ is given by

$$\ell = \frac{\pi D}{4(1-S)} \qquad (2)$$

and

$$A = D(1-S)L \qquad (3)$$

where S is the fractional strain on the o-ring, D the original cross-sectional diameter of the o-ring and L is the circumferential length of the o-ring. Combining eqs. (1)-(3) gives

$$F = 4\Delta p P \pi^{-1} (1-S)^2 L \qquad (4)$$

Extensive o-ring studies by Parker [7] indicate that the rectangular approximation of eq. (4) modified by an empirical multiplicative factor ranging from ~0.75 to 1 ($S \geq 0.25$) for lubricated o-rings does an excellent job of predicting permeation fluxes. One likely explanation for the small correction factor is the possible formation of single or double equatorial seals. [1] In a recent report, Keenan [1] used finite element models on compressed o-rings to investigate the importance of such equatorial seals and the appropriateness of the rectangular approximation leading to eq. (4). In the absence of equatorial seals, his calculations yield permeation fluxes which are ~10% higher than predicted by eq. (4); the presence of equatorial seals drop the fluxes by ~10-30% in a manner reasonably consistent with the Parker empirical corrections. Given the uncertainty in predicting whether equatorial seals will form for a particular o-ring and given that the range of results from the calculations vary from ~10% greater than eq. (4) to ~20% lower than eq. (4), we will follow Keenan's recommendation and use this equation for estimating permeation fluxes.

In order to apply eq. (4) to gas permeation estimates for the W84, we must obtain estimates of the various parameters in the equation. Following White, [8] we use $S = 0.25$ and assume that the effective circumferential length of o-ring seal (L) is 99 cm. To obtain estimates for the permeation constant (P) and the partial pressure differential (Δp) of the permeating gas, we need to estimate the <u>average</u> as well as the extreme environments seen by units placed in the field. Note that our emphasis is on obtaining the average environment, since we are trying to determine the importance of permeation on the real data of Figs. 1 and 2. Although W84's were kept in various known locations, [8] it is only possible to obtain and analyze extensive meteorological data for locations close to, but not at the weapon's storage site. Because (1) the humidity and temperature may be somewhat different at the weapon's location compared to the meteorological site and (2) both humidity and temperature vary on a daily and seasonal basis, estimates of the effective average conditions experienced by a weapon in various locations can only be approximate. With these qualifiers in mind, we estimate that the average W84 unit saw an effective average environment of 15±2°C and 70% R.H. during its storage lifetime. Weapons in the most and least severe locations were estimated to experience effective average environments of 70% R.H. plus 21°C and 9°C, respectively.

The values of P_{Ar} and P_{Ox} (permeation constants for argon and oxygen, respectively) at 9°C, 15°C and 21°C are obtained from small extrapolations of data taken at higher temperatures. For argon, we use permeation data obtained on two EPR rubber formulations (E692-75 and E529-65) by Parker, [7] with the extrapolated results listed in Table 1. Oxygen permeation results on the EPDM rubber actually used on the W84 (E740-75) were obtained for us at 23°C and 60°C by Mocon/Modern Controls, Inc.; their results are plotted in Fig. 3. Extrapolated results at the temperatures of interest are shown in Table 1.

To obtain values for Δp_{Ar} and Δp_{Ox}, we must estimate the difference between the partial pressures for each gas on the outside and the inside of the weapons. Since most W84's were stored at low elevations, perhaps averaging ~200 feet above sea level, we estimate an average air pressure of ~75 cmHg. With argon and oxygen representing 0.93% and 20.95% of air, respectively, this implies argon and oxygen partial pressures surrounding the weapon of ~0.7 cmHg and ~15.7 cmHg, respectively. Over the first few months, the internal argon quickly rises to ~0.055% (Fig. 1) due to internally dissolved argon. Since the internal pressure of W84 units averages ~82.8 cmHg, this corresponds to ~0.05 cmHg of internal argon pressure, leading to a Δp_{Ar} of approximately 0.65 cmHg. Although the value of Δp_{Ar} will drop slowly with time as the internal argon concentration builds up, this has a minor effect on the permeation calculations. We will deal more fully with this complication in later discussions concerning leakage contributions, where the effect can become important. For oxygen beyond the first few months, the internal concentration averages ~0.85%, which corresponds to an internal pressure of ~0.7 cmHg; this gives Δp_{Ox} ~ 15 cmHg.

We can now use eq. (4) to estimate the permeation contributions to argon and oxygen ingress. For argon in an average unit,

$$F_{Ar} = 4(0.65\ \text{cmHg})(1.03\times10^{-9}\ \text{ccSTP/cm/s/cmHg})\pi^{-1}(0.75)^2(99\ \text{cm})$$

$$= 4.75\times10^{-8}\ \text{ccSTP/s} = 1.50\ \text{ccSTP/year}$$

Since the free volume of a W84 unit is estimated to be 6547 cc and typical internal gas measurements are carried out at ~20°C and yield average internal gas pressures of 82.8 cmHg, the volume of internal gas at STP, $V_{int}(STP)$, is approximately given by

$$V_{int}(STP) = 6547\ \text{cc}\ (82.8/76)\ (273.2/293.2) = 6646\ \text{ccSTP}$$

By dividing the flux per year in ccSTP by 6646, we obtain

$$F_{Ar} = 0.0225\%/\text{year}$$

This result and results obtained at 9°C and 21°C using similar calculations are summarized in Table 2. Lines with slopes corresponding to these results (solid at 15°C, dashed at 9°C and 21°C) are added to the estimated average internal contribution of 0.055%/year and plotted

TABLE 1

Permeation Constants

Permeation Constant	Temperature		
	9°C	15°C	21°C
P_{Ar}, ccSTP/cm/s/cmHg	8.0×10^{-10}	1.03×10^{-9}	1.28×10^{-9}
P_{Ox}, ccSTP/cm/s/cmHg	6.3×10^{-10}	8.3×10^{-10}	1.08×10^{-9}
P_{HOH}, ccSTF/cm/s/cmHg	2.53×10^{-8}	3.02×10^{-8}	3.60×10^{-8}

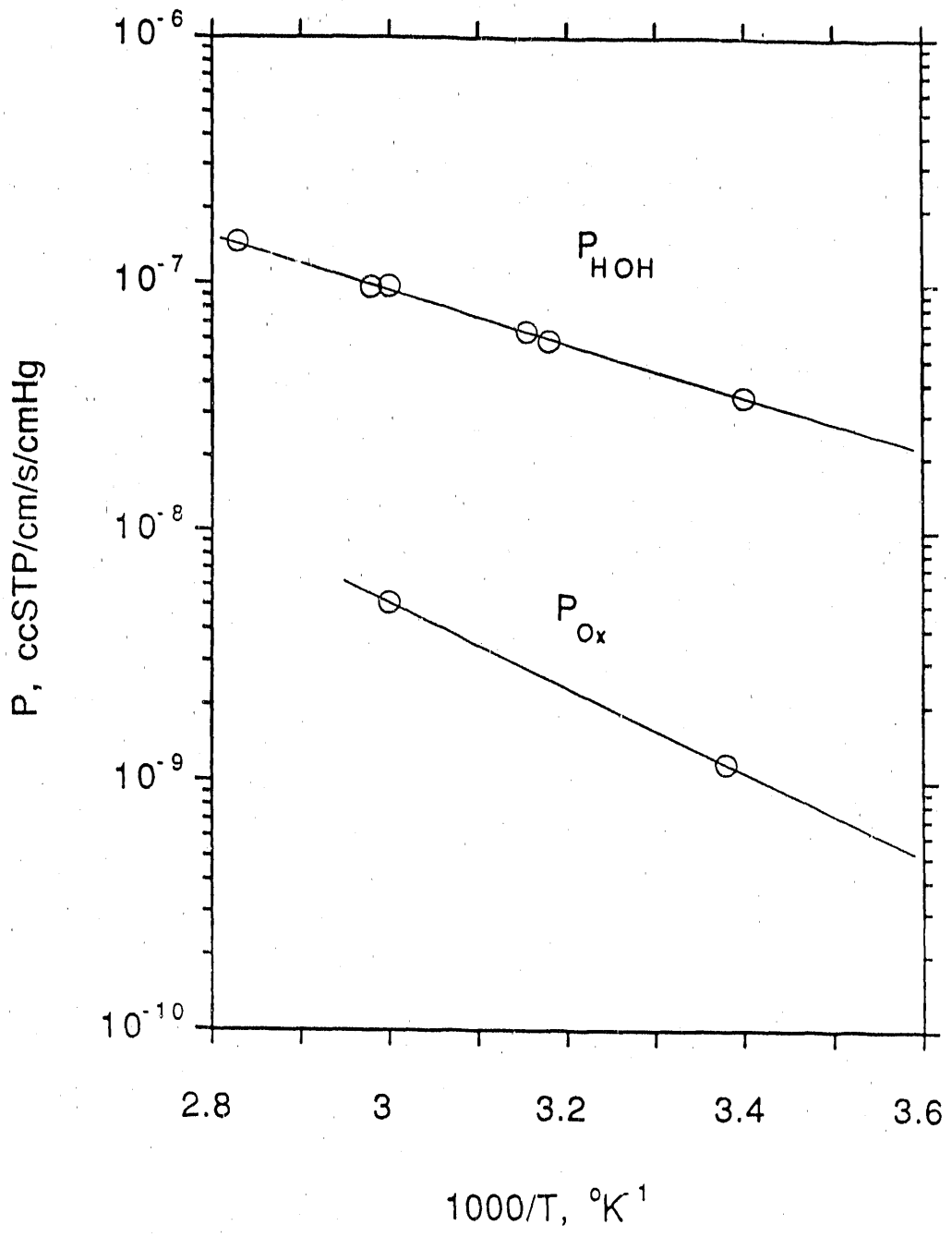

Fig. 3. Oxygen and water permeation constants of an EPDM material (E740-75) versus inverse temperature.

TABLE 2

Permeation fluxes for W84

Flux	Temperature		
	9°C	15°C	21°C
F_{Ar}, %/year	0.018	0.0225	0.028
F_{Ox}, %/year	0.31	0.41	0.54
F_{HOH}, mg/year	29	51	87

on Fig. 4. It is clear from the results of Fig. 4 that the time dependence of the internal argon concentration in most W84 units can be explained as coming predominantly from a combination of dissolved sources and permeation through the environmental o-rings. Very few units have argon concentrations much above the band predicted for permeation, implying that significant argon leakage effects are unusual. In fact, only 5 of the 104 plotted units (the circled points) give some indication of measurable leakage.

The permeation contribution to oxygen ingress can be calculated in a similar fashion. At 15°C, one obtains

$$F_{Ox} = 0.414\%/\text{year}$$

Again this calculated permeation contribution is added to the estimated average internal contribution of 1.18%, yielding the results shown in Fig. 5. As mentioned earlier, the reason that the oxygen tends to drop after its initial rise is due to the fact that it reacts with (oxidizes) internal components and materials. Similar to the argon results, in the absence of reaction, most of the units would have been expected to approximately follow the permeation line. For these units, the amount of drop below the permeation line therefore represents the oxygen consumption rate inside the W84. The results of Fig. 5 indicate that a typical unit consumes ~0.6% oxygen per year (~60 mg). Given (1) the lack of knowledge of the details of the internal oxidation reactions and (2) the sensitivity of these reactions to such things as uncontrolled variables during component preparation and temperature fluctuations during weapon transport and storage, it is not surprising that quite a bit of scatter exists in the oxygen results. On the other hand, the three data points which are circled appear to be far enough removed from the scatter band to implicate measurable leakage for these units. These three units are identical to three of the five units suspected as possible "leakers" based on the argon results of Fig. 4. It is therefore quite possible that the 2 early time units with higher than expected argon concentrations represent anomalous measurements. From Figs. 4 and 5, we can see that oxygen analysis can sometimes complement argon analysis by pointing out potentially anomalous data and by allowing oxygen consumption rates for a weapon to be estimated.

WATER INGRESS ESTIMATES FOR W84 SURVEILLANCE UNITS

Water vapor will permeate through and leak around the environmental seals of a weapon. Similar to argon and oxygen, the water permeation contribution can be estimated from eq. (4). For the EPDM material (E740-75) used for environmentally sealing the W84, we have recently measured the water permeation constant (P_{HOH}) at temperatures ranging from 21°C to 80°C; [9] the results are plotted in Fig. 3. The straight line through the data was extrapolated to the three temperatures of interest, with the resulting values of P_{HOH} shown in Table 1. Assuming

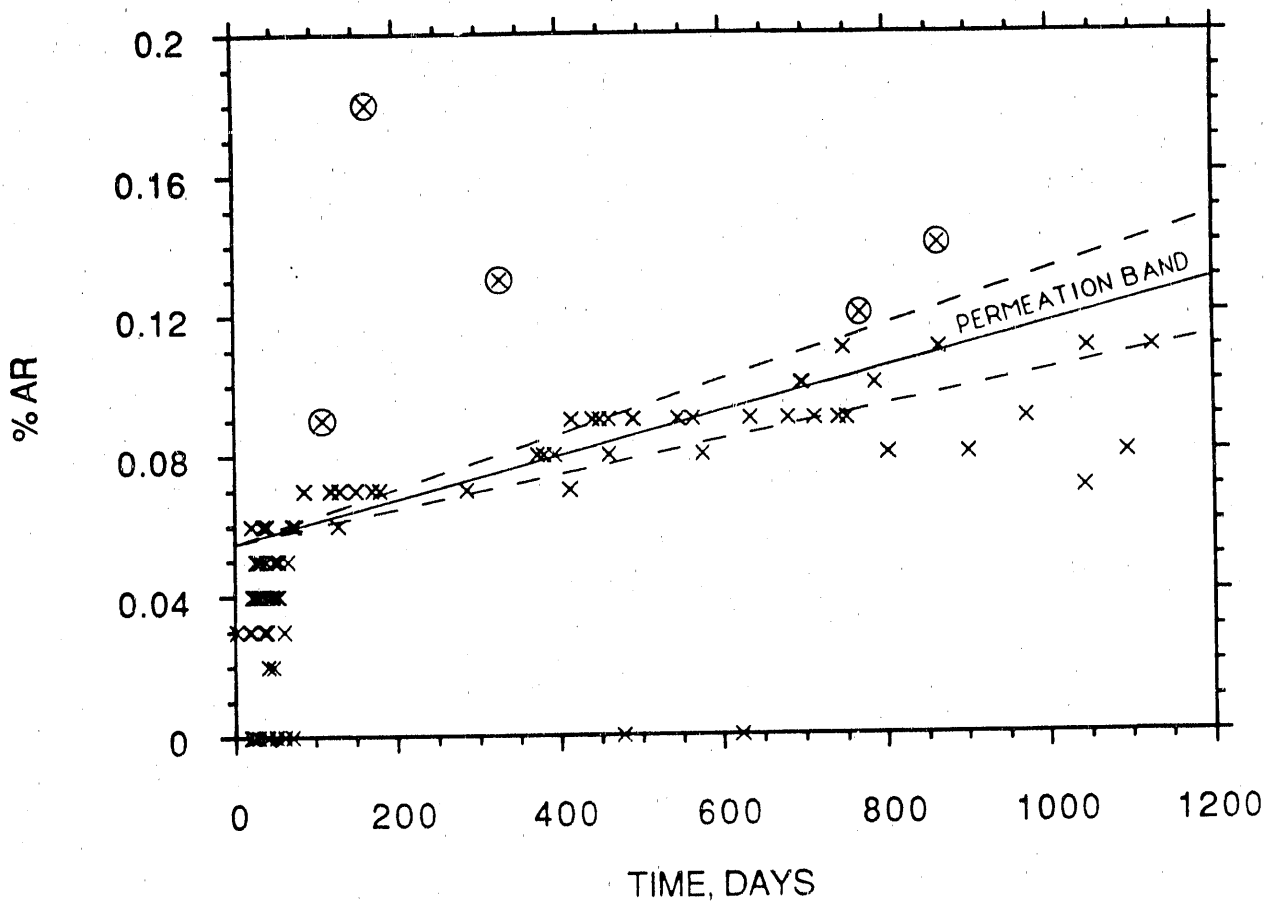

Fig. 4. W84 argon gas data together with predicted contributions from argon permeation. The circled data indicate units where moderate leakage effects may contribute to the argon percentage.

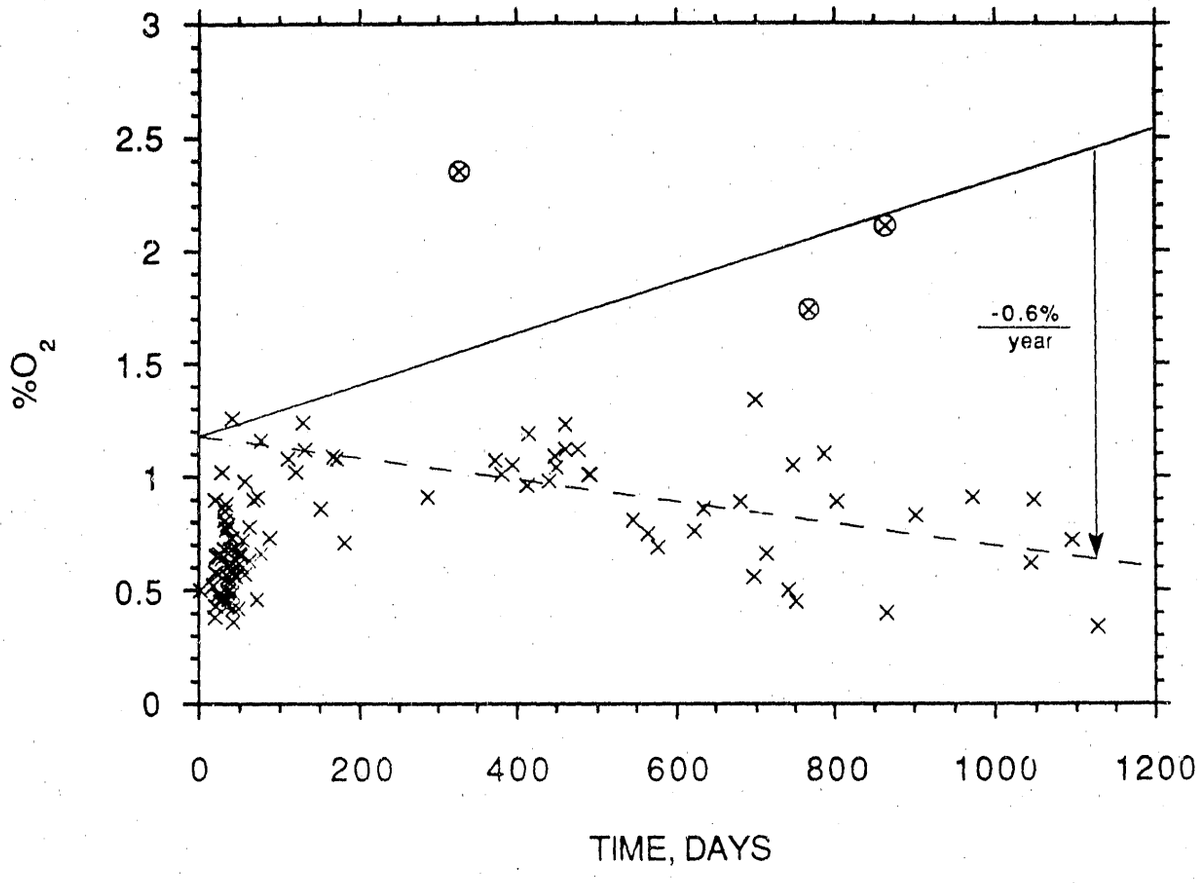

Fig. 5. W84 oxygen gas data together with the predicted contribution from oxygen permeation in the absence of any reactions. The observed data indicate that a typical unit consumes oxygen at the rate of 0.6%/year.

average atmospheric conditions of 70% R.H. at all three temperatures and negligible water vapor pressure inside the dessicated weapon, the Δp_{HOH} values are easily calculated to be 0.64 cmHg, 0.94 cmHg and 1.35 cmHg at 9°C, 15°C and 21°C, respectively. These results lead to the estimated water permeation rates shown in Table 2.

Estimating the water leakage rate into weapons is much more difficult. The main reason for monitoring and analyzing the argon concentration in weapons is to use argon leakage results to estimate the importance of long-term water leakage. [2] Unlike argon, which is inert, water that leaks into a weapon can disappear due to reaction (degradation/corrosion of components) or absorption by dessicant material. Since internal sources of water exist and water permeation through the environmental o-ring seals is expected, dessicants are included inside of weapons to keep the dew point below some specified value (typically -20°C). [1] The amount of dessicant is usually based on the assumption that leakage contributions are small compared to permeation, an assumption easily rationalized because of the small helium leak rate specification allowed for units just prior to initial nitrogen backfill. Unfortunately, many factors can lead to changes in leak rates with time; for instance, aging of the environmental seals may lead to significant compressive stress-relaxation, reducing the sealing forces enough to open up significant leaks. If leaks become significant, the capacity of the dessicant may be overwhelmed, leading to a high humidity internal environment and the possibility of significant degradation of internal components.

We will now derive a general expression which allows predictions of the importance of water leakage to be obtained from argon analysis data. We start by noting that the rate of leakage of argon (L_{Ar}) is proportional to the argon partial pressure difference across the leak

$$L_{Ar} = C_{L\text{-}Ar} \Delta p_{Ar} \qquad (5)$$

where the proportionality constant, $C_{L\text{-}Ar}$, is referred to as the conductance of the leak. If we use eq. (4) and define the permeation conductance for argon as

$$C_{P\text{-}Ar} = 4\, P_{Ar}\, \pi^{-1}\, (1\text{-}S)^2\, L \qquad (6)$$

then the total rate of argon ingress from permeation plus leakage can be written

$$\frac{dAr}{dt} = (C_{P\text{-}Ar} + C_{L\text{-}Ar})\, \Delta p_{Ar} \qquad (7)$$

As opposed to the earlier discussions in which changes in Δp were minor and therefore neglected, when substantial leaks occur Δp can decrease significantly with time, forcing us to deal with this time dependence in the current analysis. We can write

$$\Delta p_{Ar} = v_{ext} - v_d - v_{P+L} \qquad (8)$$

where the three terms on the right hand side of the equation refer to the argon partial pressures in the surrounding air atmosphere, in the interior due to release of dissolved argon and in the interior due to argon ingress (permeation plus leakage) from the surrounding air atmosphere, respectively. We now simplify the analysis by assuming (1) v_d is at equilibrium at time zero (the dissolved argon is released quickly relative to the time frames of interest) and (2) the total internal pressure at 20°C (the approximate gas analysis temperature at Pantex) equals the external atmospheric pressure, P_{atm}. This allows us to write

$$\Delta p_{Ar} = \Delta v_o - v_{P+L} = (\Delta f_o - f)\, P_{atm} \qquad (9)$$

where Δv_o is the initial partial pressure difference at time zero. When P_{atm} is separated from Δv_o in the second part of eq. (9), we are left with Δf_o representing the initial partial pressure difference across the o-rings expressed as a fraction of the total atmospheric pressure. Similarly f represents the time dependent argon ingress contribution (permeation plus leakage) expressed as a fraction of the total atmospheric pressure. Analyzing the results in this fashion is convenient since surveillance data are reported as fractions of the total internal atmosphere. We now insert eq. (9) into eq. (7) and divide both sides of the resulting equation by $V_{int}(STP)$, the volume of internal gas at STP. Since dAr/dt is given in units of ccSTP/s, the argon gas flux due to permeation plus leakage will then be converted to the fractional flux, df/dt

$$\frac{df}{dt} = \left(P_{atm}/V_{int}(STP) \right) \left(C_{P\text{-}Ar} + C_{L\text{-}Ar} \right) [\, \Delta f_o - f \,] \qquad (10)$$

Since

$$V_{int}(STP) = V_{free}\, P_{atm}\, T_{std} \,/\, (P_{std}\, T) \qquad (11)$$

with V_{free} representing the free internal volume of the weapon, P_{std} and T_{std} given by 76 cmHg and 273.2K, respectively and T equalling ~293K, eq. (10) becomes

$$\frac{df}{dt} = (\, 81.5/\, V_{free}) \left(C_{P\text{-}Ar} + C_{L\text{-}Ar} \right) [\, \Delta f_o - f \,] \qquad (12)$$

This expression is easily integrated to solve for the time dependence of f, yielding

$$f = \Delta f_o \left(1 - \exp\, [-(\, C_{P\text{-}Ar} + C_{L\text{-}Ar})\, (\, 81.5 \,/\, V_{free})]\, t \right) \qquad (13)$$

Since we are interested in relating the argon data to the importance of water leakage, we note that the rates of argon and water leakages are related by [1,2]

$$L_{Ar} = [\Delta p_{Ar} / \Delta p_{HOH}]\ [18/40]^{0.5}\ L_{HOH} \qquad (14)$$

which, when combined with eq. (5) gives

$$C_{L\text{-}Ar} = 0.671\ L_{HOH} / \Delta p_{HOH} \qquad (15)$$

To maintain consistency with our earlier units (Table 1), the units of L_{HOH} and Δp_{HOH} appropriate to eq. (15) are in ccSTP/s and cmHg, respectively. When describing water leakage, however, units of mg/year are more convenient than ccSTP/s. Since 22,400 ccSTP of water vapor contains 1 mole of water (18,000 mg), eq. (15) can be rewritten as

$$C_{L\text{-}Ar} = 2.65 \times 10^{-8}\ L_{HOH} / \Delta p_{HOH} \qquad (16)$$

where the units of L_{HOH} are now in mg/year.

By using eqs. (6), (13) and (16), one can determine the relationship between water leakage and argon results. As an example for the W84,

$V_{free} = 6547$ cc; $S = 0.25$; $L = 99$ cm; $\Delta f_o = 0.0093 - 0.00055 = 0.00875$

This gives for the W84

$$f = 0.00875\left[1 - \exp[-(0.883\ P_{Ar} + 3.3\times10^{-10}(L_{HOH}/\Delta p_{HOH}))t]\right] \qquad (17)$$

where the units of f, P_{Ar}, L_{HOH} and Δp_{HOH} are s^{-1}, ccSTP/cm/s/cmHg, mg/year and cmHg, respectively. Values of f from this equation (permeation plus leakage contributions) are added to the internal contribution (0.00055) in order to obtain the overall expected fractional argon contribution to the internal weapon atmosphere. Figure 6 shows curves generated in this fashion assuming average storage conditions of 15°C plus 70% R.H. ($P_{Ar} = 1.03\times10^{-9}$ ccSTP/cm/s/cmHg, $\Delta p_{HOH} = 0.94$ cmHg) for water leakage values of 0, 3, 10, 30 and 100 mg/year. As the internal argon concentration builds up towards its limiting value of 0.93%, the rate of argon buildup will slow down, leading to the deviations from linear behavior most noticeable at higher water leak rates. Note, however, that the water leak and permeation rates do not slow down since the dessicator keeps the interior water concentration at low levels. The curve labelled 10 mg/year is for average storage conditions. It is easy to show that this same curve would be valid for 13.5 mg/year of water leakage for units which experienced worst case (21°C) storage conditions. Similarly, units which saw the most benign conditions (9°C) would follow this curve if they experienced water leak rates of 7.3 mg/year.

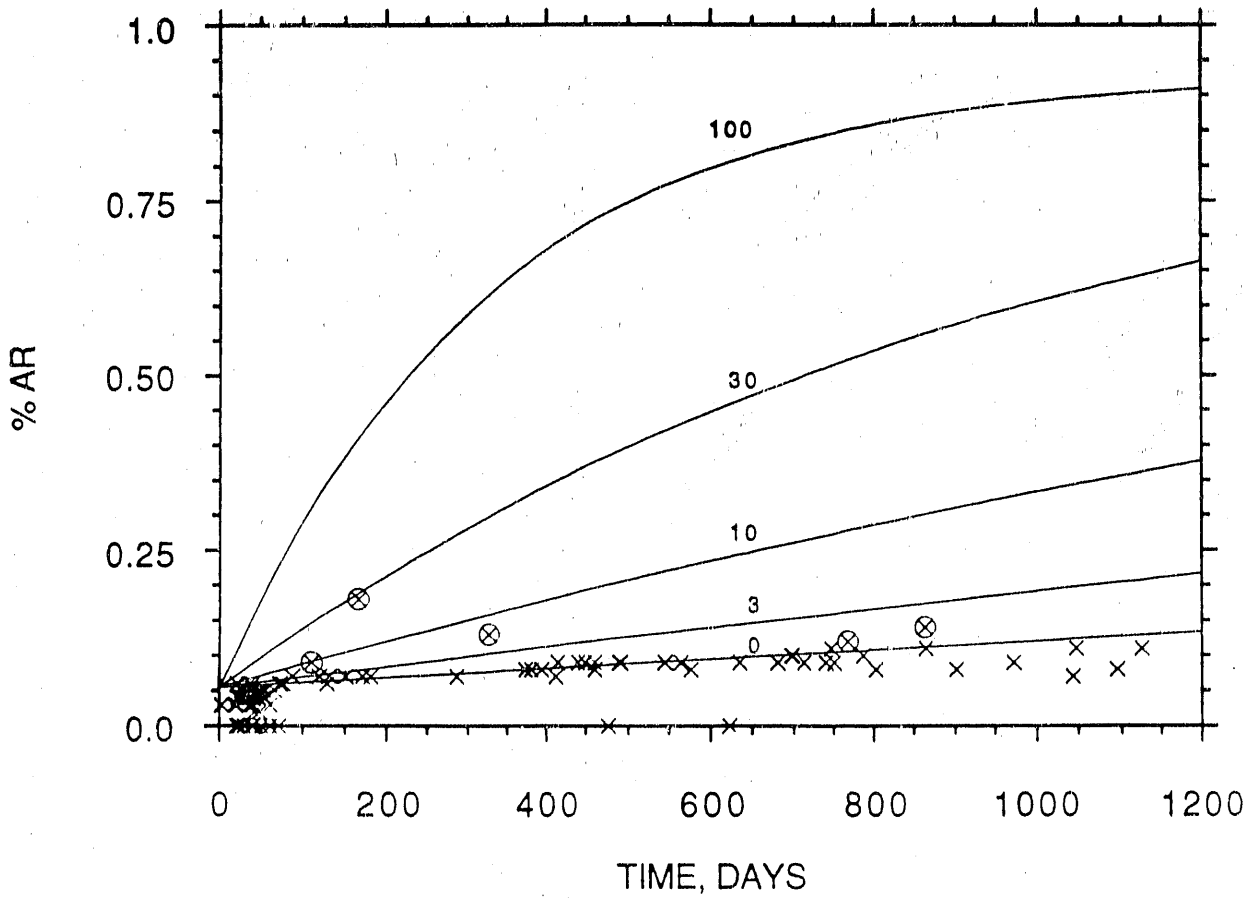

Fig. 6. W84 argon gas data together with predicted argon curves which would correspond to 0, 3, 10, 30 and 100 mg/year of water leakage.

It should be noted that the results given in Fig. 6 should be viewed as worst-case (e.g., conservative) results, since certain leak scenarios may result in substantial argon concentrations coupled with lower than predicted (from Fig. 6) water leaks. For instance, a unit might leak during a low temperature exposure (to say -30°C) due to stiffening of the o-ring and then reseal when the temperature increases. At the low temperatures, argon leaks would occur with the normal Δp_A of ~ 0.7 cmHg; parallel water leakage, however, would be driven by the very low value of Δp_{HOH} characteristic of the low water vapor pressure existing at such a low temperature.

It is evident from the results of Fig. 6 that the vast majority of W84 units have water leaks less than a few mg/year. Since permeation accounts for ~60±30 mg/year (see Table 2), leakage effects in most units are unimportant. It is also clear from these plots that the argon approach offers a very sensitive method for determining units which may have significant water leaks.

ARGON ANALYSIS APPLIED TO THE W88

The W88 is a submarine-based weapon (e.g., P_{atm} = 76 cmHg) which is initially backfilled with 76 cmHg of dry nitrogen. It is sealed with environmental o-rings made from a new EPDM material jointly developed by KCD and the Institute of Polymer Science, University of Akron. A summary of the W88 o-ring dimensions and o-ring groove sizes is given in Table 3. Also listed are the circumferential lengths for each o-ring and values of S (the fractional strain) obtained from the nominal groove depths compared to the cross-sectional diameter of the o-ring. Because of slight variations in S among the o-rings, eq. (4) for the permeation flux must be generalized to

$$F = 4\Delta p P \pi^{-1} \sum_{i=1}^{n} (1-S_i)^2 L_i \qquad (18)$$

where we sum over the various o-rings in Table 3. This gives

$$F = 151.2\ \Delta p P \qquad (19)$$

We will assume for the calculations in this section that the average environment for the submarine-based W88 is 20°C and 50% R.H.; the calculations can be easily modified for other choices of average environment. Our environmental choice gives Δp_{HOH} = 0.88 cmHg. The water permeation constant (P_{HOH}) at 20°C is 3.3×10^{-8} ccSTP/cm/s/cmHg. This was obtained from Fig. 7, which summarizes recent measurements made on the new EPDM material selected for use on the W88. [9] Substituting these values in eq. (19) leads to an expected water permeation contribution for the W88 of

$$F_{HOH} = 111 \text{ mg/year}$$

TABLE 3

W88 O-Ring and O-Ring Groove Data

O-Ring	D in.	i. d. in.	L cm	Groove Depth in.	S
S/C	0.103	15.46	124.2	0.077	0.252
FWD	0.103	7.88	63.7	0.077	0.252
CABLE	0.070	1.239	10.44	0.052	0.257
RF	0.070	0.301	2.98	0.050	0.286
RF	0.070	0.301	2.98	0.050	0.286
RF	0.070	0.301	2.98	0.050	0.286
P/V	0.070	0.739	6.46	0.050	0.286
TOTAL			214		

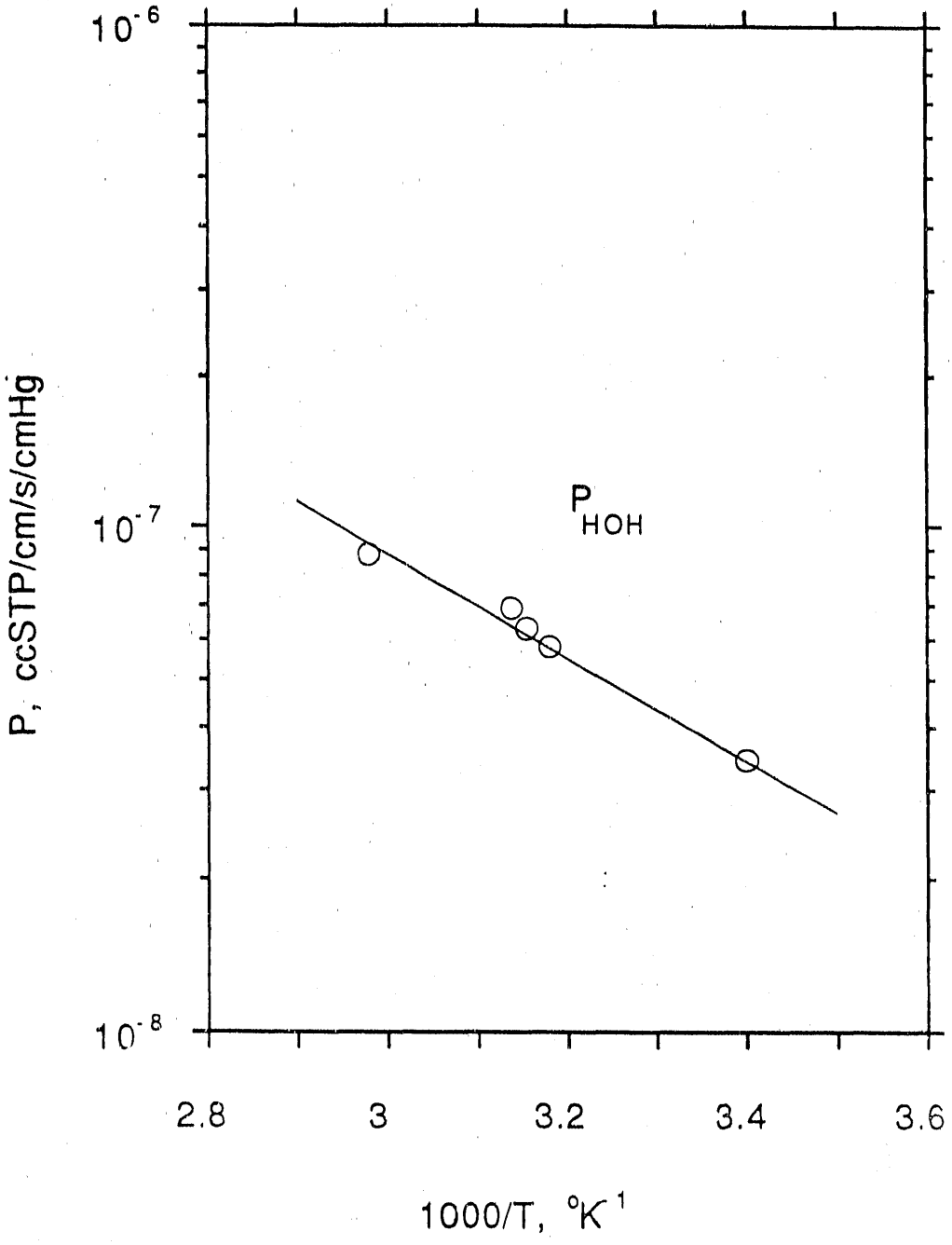

Fig. 7. Water permeation constants versus inverse temperature for the new EPDM material to be used for the environmental seals of the W88.

To relate the leakage of water to the argon gas percentage data as the latter become available, we apply eq. (13) to the W88. Early NMLT unit data (up to 6 months), obtained courtesy of W. L. Black, Jr. of Pantex, indicate that internal argon sources yield a contribution of ~0.015%±0.001%. This gives $\Delta f_o = 9.15\times10^{-3}$. For the W88, V_{free} equals approximately 27,600 cc. From eqs. (7) and (19),

$$C_{P\text{-}Ar} = 151.2\ P_{Ar} \qquad (20)$$

where P_{Ar} is taken equal to 1.24×10^{-9} ccSTP/cm/s/cmHg. [7] With $C_{L\text{-}Ar}$ of eq. (13) taken from eq. (16), we obtain the following result for the W88

$$f = 0.00915\left[1-\exp[-(5.54\times10^{-10} + 8.9\times10^{-11}L_{HOH})t]\right] \qquad (21)$$

W88 at 20°C plus 50% R.H.

where the units of L_{HOH} and t are mg/year and seconds, respectively. Values of f from this equation (permeation plus leakage) are added to the preliminary estimate of the internal contribution (0.00015) in order to obtain the overall expected argon contribution of the internal weapon atmosphere. The solid curves in Fig. 8 give results out to 25 years corresponding to an average environment of 20°C plus 50% R.H. and water leakage values of 0, 10, 30 and 100 mg/year. It turns out that the argon predictions of Fig. 8 are fairly insensitive to the postulated average environmental conditions assumed for the calculations. For instance, if the average conditions were chosen to be 23°C plus 50% R.H., P_{Ar} in eq. (20) would equal 1.4×10^{-9} ccSTP/cm/s/cmHg and Δp_{HOH} would equal 1.053 cmHg, leading to

$$f = 0.00915\left[1-\exp[-(6.26\times10^{-10} + 7.44\times10^{-11}\ L_{HOH})t]\right] \qquad (22)$$

W88 at 23°C plus 50% R.H.

The dashed curves in Fig. 8 show predicted argon curves generated from eq. (22) for L_{HOH} values of 0, 10, 30 and 100 mg/year. The relative insensitivity to the postulated average environment seen by the weapon implies that curves such as those shown can be used to accurately estimate the importance of water leakage effects even in the absence of detailed knowledge of the environmental history seen by each individual unit.

The predicted argon curves labelled 0 rise due to argon permeation only (no leakage). As calculated earlier, the corresponding water permeation rate for the estimated environmental conditions of 20°C and 50% R.H. is 111 mg/year; similar calculations at 23°C plus 50% R.H. yield 145 mg/year. These water permeation contributions are present regardless of the water leakage rate. The curves labelled 10 therefore give the anticipated argon results which would correspond to a water

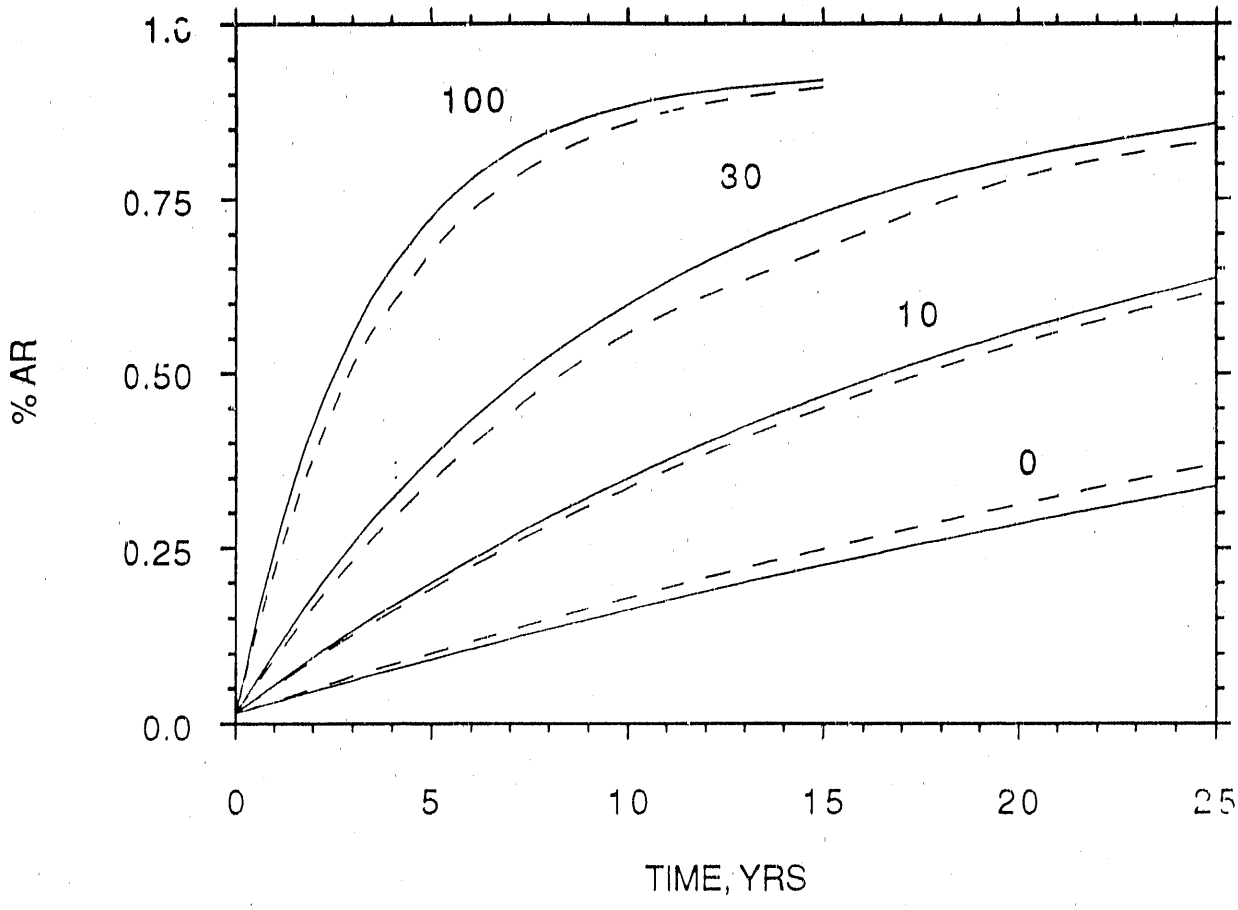

Fig. 8. Predicted argon versus aging time curves for the W88 assuming water leakage rates of 0, 10, 30 and 100 mg/year. The solid curves assume average environmental conditions of 20°C and 50% R.H., whereas the dashed curves assume 23°C plus 50% R.H.. The water permeation contributions under these two conditions are 111 mg/year and 145 mg/year, respectively.

leakage rate (10 mg/year) representing less than 10% of the expected water permeation rate. Thus, it is clear that the argon results represent an extremely sensitive method of determining when important water leaks (relative to water permeation) have occurred during a weapon's long-term field exposure. Since the percentage of argon in the internal atmosphere of each surveillance unit of the W88 will be reported, use of the results shown in Fig. 8 will offer an extremely simple method for immediately determining the importance of leakage effects. As more and more data are collected, it will become apparent if important aging effects (e.g., leakage problems developing with older units) occur for the new EPDM material.

Since the results from Fig. 8 now allow us to estimate the integrated water leakage of W88 units after extended periods of time in the field, it is interesting to estimate the approximate water leakage rate when units are first backfilled with dry nitrogen. To accomplish this, we will use results from helium leak rate testing done on new units just prior to nitrogen backfill. After W88 units are first assembled, helium leak rate testing is done on the entire unit to check both the environmental o-rings and their installation. The procedure first involves evacuating the inside of the unit, then backfilling the unit with helium to a pressure of 28.588 inHg (72.6 cmHg). After monitoring the helium pressure for 10 minutes to assure that no gross leaks exist, the unit is then pumped down to 0.1 psia or less and held at this pressure for a minimum of 5 minutes. The inside is then repressurized with helium to 14 ± 0.1 psia (73.4 cmHg), held for 10 more minutes and finally readjusted to 14 ± 0.1 psia. The unit is then moved to a large vacuum chamber, where the outside of the unit is pumped down sufficiently for a leak test to be conducted. No time interval is recorded between final helium pressure readjustment and the leak test but, according to William Black of Pantex, 30 minutes is a typical number; if problems with pump-down or with the leak rate detector occur, the times can be longer. Thus, we can conclude that a typical unit is exposed to 73.4 cmHg of helium for ~40 minutes before the helium leak rate measurement is taken (we ignore the earlier exposure to helium).

Two mechanisms can in general contribute to the measured helium "leak rate", true leakage between the surfaces of the o-rings and their metal mating surfaces and permeation of helium through the o-rings. When helium is first introduced into the unit, permeation of helium does not contribute. As time progresses, the permeation contribution increases until it eventually reaches its equilibrium value. Two factors determine the importance of the permeation contribution, its equilibrium value and its time dependence. Using eq. (19), where Δp_{He} = 73.4 cmHg and $P_{He} = 2\times10^{-9}$ ccSTP/cm/s/cmHg, [10] we estimate the equilibrium helium permeation contribution to be

$$F_{He} \sim 2.2\times10^{-5} \text{ ccSTP/s}$$

Since this value is significant relative to the helium leak rate specification of 5×10^{-5} ccSTP/s, it is important to determine the time-dependence of the permeation in order to estimate how important this contribution is for typical leak rate measurements.

To estimate the time dependence of the permeation contribution, we use the classical analysis for a slab of material of thickness ℓ. [11] If at time zero, gas is introduced on one side of the slab and the slab initially is devoid of penetrant, then Q, the total amount of gas to permeate the membrane, is given by

$$Q = F_e t - \frac{F_e \ell^2}{6D_s} - \frac{2F_e \ell^2}{\pi^2 D_s} \left(\sum_{n=1}^{\infty} \frac{(-1)^n}{n^2} \exp\left(-D_s n^2 \pi^2 t/\ell^2\right) \right) \qquad (23)$$

where F_e is the equilibrium permeation flux, D_s is the diffusion constant of the gas through the slab and t is the time. If we differentiate eq. (23) with respect to time and then divide both sides of the resulting expression by F_e, we get

$$F(t)/F_e = 1 + 2\sum_{n=1}^{\infty}(-1)^n \exp\left(-D_s n^2 \pi^2 t/\ell^2\right) \qquad (24)$$

$F(t)/F_e$ represents the ratio of the time dependent permeation flux to its equilibrium value. Figure 9 plots this ratio versus the quantity $D_s t/\ell^2$.

To apply eq. (24) to the W88, we assume $D_s = 7 \times 10^{-6}$ cm^2/s, a value determined by Keenan [10] for room temperature permeation of helium through an EPDM material. The values of ℓ in eq. (24) can be estimated from the o-ring approximation derived in eq. (2). Since the W88 has 0.103 in and 0.070 in diameter o-rings (Table 3), the individual time dependencies for each o-ring must be calculated and multiplied times its equilibrium contribution before finally adding together all the individual contributions. This leads to the predicted overall time dependence shown in Fig. 10. Since we determined earlier that the typical time interval between the time the helium reaches 14 psia and the leak rate measurement is approximately 40 minutes, an arrow corresponding to this time interval is noted on the figure. The results in Fig. 10 show that permeation reaches approximately 90% of its equilibrium value and can be expected to contribute approximately 2×10^{-5} ccSTP/sec to the leak rate measurement for typical test conditions.

Of the W88 production units which have been helium leak rate tested to date, more than 95% have measured leak rates which are less than 2.5×10^{-5} ccSTP/s. This indicates that for a typical unit, it is likely that (1) the leak rate measurement is dominated by permeation and (2) the most important parameter influencing the "leak rate" measurement is the time interval between helium backfill and leak testing. From the above discussion, one can conclude that a typical unit has a true helium leak rate of less than 1×10^{-5} ccSTP/s. This estimate can be used together with the analogue of eq. (14),

$$L_{HOH} = [\, \Delta p_{HOH} / \Delta p_{He} \,]\, [4/18]^{0.5}\, L_{He} \qquad (25)$$

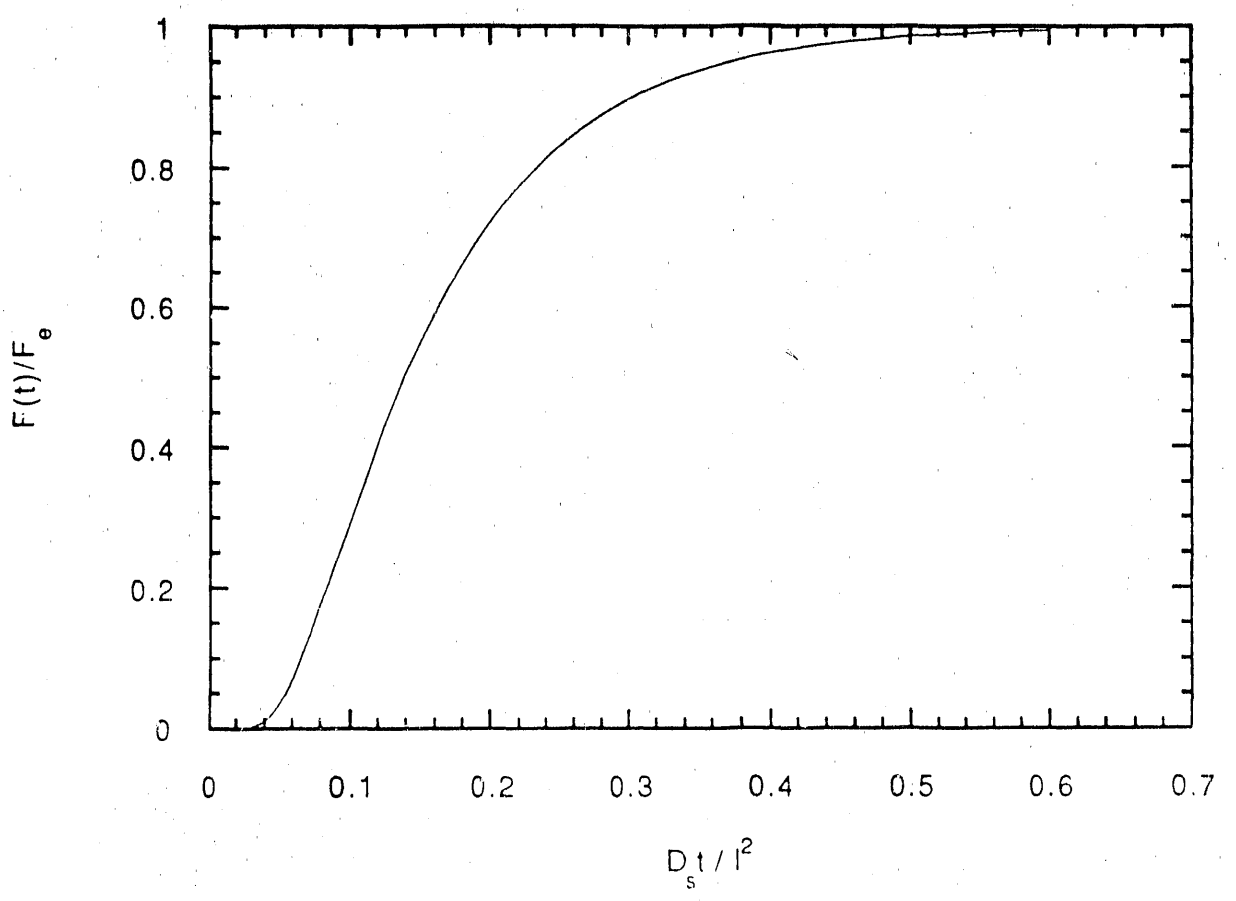

Fig. 9. Plot of the ratio of the time dependent flux to the equilibrium flux versus $D_s t/\ell^2$ according to eq. (24).

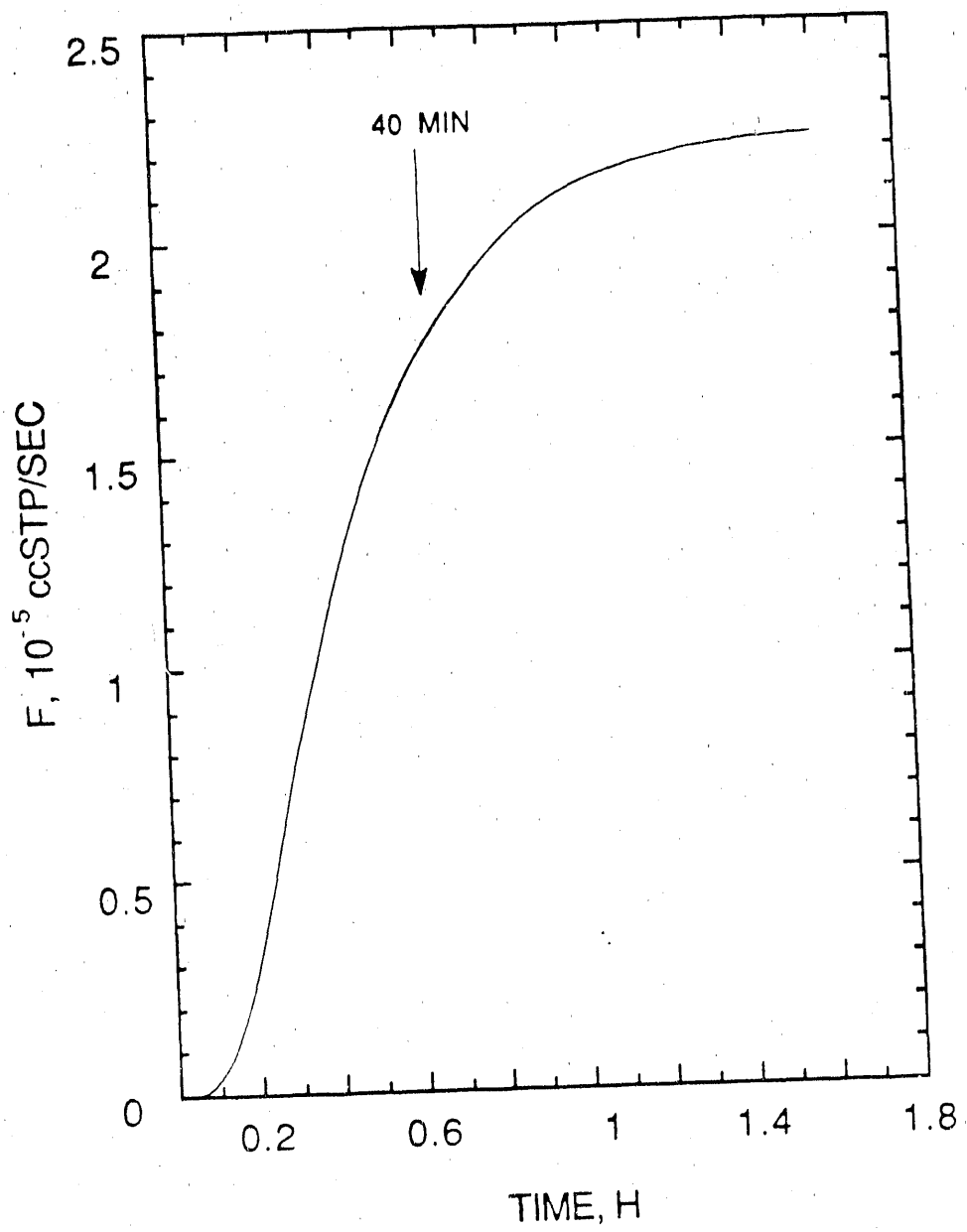

Fig. 10. Predicted helium permeation contribution to the helium leak rate measurements for the W88 versus the time interval between helium backfill and leak rate measurement.

to estimate that the initial water leak rate for a W88 is typically less than 2 mg/year. Thus, if leaks do not increase substantially with time in the field, one would expect that the argon results for field returned units would not deviate much from the permeation-only line of Fig. 8.

CONCLUSIONS

Analyses of the internal argon gas concentrations in field-returned units of the W84 indicate that water leakage effects appear to be unimportant for this EPDM-sealed weapon for times up to 4 years in the field. It is shown that comparisons of oxygen and argon gas results can be used to (1) eliminate anomalous data points from consideration and (2) estimate the oxygen consumption rate for a typical unit.

Application of the argon gas analysis approach to the W88 led to predictions relating the anticipated argon gas concentrations of future field-returned units to water leakage rates. The predictions are summarized in Fig. 8, which can be conveniently and directly applied to surveillance data to estimate the amount of water leakage occurring in a given unit. If aging or other problems lead to important water leakage contributions, they will be immediately recognized. Calculations also show that the helium leak rate test used during W88 production is dominated by permeation effects.

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