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FINAL REPORT

RESEARCH ON REMOVAL OF IODINE BY CONTAINMENT SPRAYS CONTAINING TRACE LEVELS OF HYDRAZINE

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ABSTRACT

Four large scale experiments were conducted to determine the effectiveness of boric acid sprays containing 50 ppm hydrazine for removal of iodine from containment atmospheres. For three of these experiments, iodine was released as a simulated burst prior to spraying. Spraying was intermittent over an 8 hr period at an isothermal temperature of 280°F for one test and at 150°F for two tests. The fourth test simulated the temperature-pressure decay (from 280°F) of sprayed containment vessels following a LOCA. Iodine was released over a 1 hr period during continuous spray operation. The fresh spray water contained 1500 ppm boric acid and 50 ppm hydrazine for all tests. The iodine partition coefficients were greater than 10,000 and 100,000, for the instantaneous and pseudo equilibrium coefficients, respectively. The 2 hr dose reduction factor projected from these results was approximately 15 assuming a 4 percent cutoff for "nonreactive" species. It is worth noting that in these experiments less than 0.1 percent of the injected iodine was airborne as "nonreactive" species. These large scale proof tests demonstrated that sprays containing trace levels of hydrazine were as effective for absorbing airborne iodine as had been indicated from earlier equilibrium studies.

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1.0 INTRODUCTION

This report presents the results of large scale proof tests of iodine removal by boric acid sprays containing trace quantities of hydrazine (N_2H_4). The research was undertaken to provide additional data to support calculations of the airborne fission products which could escape from the containment vessel of a pressurized water reactor (PWR) in the event of a postulated, but highly unlikely, loss-of-coolant-accident (LOCA). This work is a sequel to laboratory studies(1) carried out for a consortium of utilities which identified hydrazine as a highly effective additive to boric acid sprays for removal of elemental iodine. The equilibrium distribution of iodine between gas and liquid phases measured in the earlier work showed that hydrazine-containing sprays should be very effective for rapidly removing airborne iodine. The work reported here was designed to answer questions still remaining as to the effectiveness of such sprays under LOCA conditions.

PWR containment vessels are equipped with water spray systems which would operate in the event of a LOCA. The spray would condense steam and limit the pressure buildup within the containment vessel. The sprays would also scrub airborne fission products from the containment vessel atmosphere. Fission products are assumed to become airborne following the postulated rupture of fuel element claddings during a LOCA.

Iodine is the limiting fission product for postulated loss-of-coolant-accidents. Its removal from the gas phase by sprays is attractive because of the fast removal rates which are potentially available and because of the favorable cost and reliability of spray systems. Theoretically, pure water will not absorb iodine to a high degree. For this reason, some spray systems have been designed to include reactive reagents such as sodium hydroxide and sodium thiosulfate. These reagents cannot be used in systems not designed for their use. Also, the use of these reagents may lead to other problems, such as costly corrosion in the event of inadvertent operation of sprays.

In an earlier program of this series,(5) it was demonstrated that the trace level impurities in a boric acid solution served as an effective spray reactant for airborne elemental iodine. This observation, coupled with the need for iodine removal credit for boric acid sprays, led to a subsequent study to identify a trace level chemical which could be added to coolant water to assure an effective spray scavenging of iodine.(1) A spray using trace levels of hydrazine for this purpose was identified from these studies. The present program was a proof test of spray washout under conditions simulating those occurring in the containment vessel of a PWR following a postulated LOCA.

The previous research(1) which identified hydrazine as the most favorable trace additive for the water spray system of a PWR involved primarily equilibrium studies of the partition coefficient between the gas and liquid phase. The equilibrium tests were carried out in a stainless steel pressure vessel 3 ft in diameter and 5 ft in height. The results conclusively demonstrated that a very high liquid-gas partition coefficient existed for 50 ppm of hydrazine in a typical boric acid spray solution. These results together with scoping kinetic studies indicated that the rate of reaction between the iodine and the hydrazine was sufficiently high to rapidly remove iodine from containment atmospheres. However, these studies did not demonstrate the iodine spray removal rate for this solution under conditions occurring in the containment vessel following a postulated LOCA. The present program was designed to provide this demonstration in a large vessel 25 ft in diameter and 67 ft in overall height with a total free gas space of some 26,500 cubic ft, under conditions which closely simulate those occurring following a postulated LOCA. Results from these tests can be used in support of licensing calculations of the dose reduction factors which can be anticipated for specific PWR reactors.

2.0 SUMMARY AND CONCLUSIONS

The absorption of iodine from containment atmospheres by sprays containing trace-level hydrazine (50 ppm) was investigated experimentally. The four demonstration experiments were conducted in the 26,500 ft^3 Containment Systems Experiment (CSE) vessel under a range of conditions simulating those expected following postulated loss-of-coolant-accidents in PWR reactors. Two "burst release" tests were conducted under an isothermal temperature of 150°F; one with 7G-3 spray nozzles* and the other with 1713A nozzles.** A third test was carried out under isothermal conditions at 280°F, 64 psia and used 7G-3 nozzles. The fourth test simulated pressure-temperature decay from 280°F and 64 psia, a prolonged iodine source term, and a continuous spray operation using 1713A spray nozzles. Mathematical models were used to compare theoretical prediction with experimental observation.

The experimental findings support the following conclusions:

- Elemental iodine was scavenged from the gas phase by both a gas to liquid transfer controlled by the gas phase mass transfer coefficient and a gas phase reaction with volatilized hydrazine. The magnitude of the latter was found to increase with increasing airborne iodine concentration. Thus two reactions occurring simultaneously enhanced the spray washout rate which surpassed the perfect sink model predictions.
- The spray washout rates observed for the first fresh spray period (10 min duration) were about 0.4, 0.46 and 0.68 min^{-1} for pre-spray iodine release tests for gas phase concentrations of approximately 3, 45 and 160 mg/M^3 just prior to spraying. The 0.46 and 0.68 min^{-1} rates exceeded the comparable theoretical well-mixed model rates of 0.3 and 0.36 min^{-1} calculated for the prevailing test conditions. Comparable rates for the low concentration run were 0.40 and 0.45 min^{-1} for observed and theory, respectively.

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*Manufactured by Spraying Systems Co., Bellwood, Illinois
**Manufactured by Spray Engineering Co., Burlington, Massachusetts

- The magnitude of the instantaneous iodine partition coefficient, H_o, inferred from the 10 min fresh spray was greater than 10,000 for all tests.
- The elemental iodine concentration was reduced by factors of 67, 137 and 1170 during the 10 min fresh spray period for starting airbore I_2 concentrations of 3, 45 and 160 mg/M^3. In 2 hrs time the concentration was reduced by factors of 530, 2040 and 4260 for the above respective initial concentrations.
- The gas-liquid pseudo equilibrium partition coefficients (H_e) measured during recirculating spray periods were $>10^5$ for all tests. The pseudo equilibrium partition coefficient in each test increased with spray time and was approaching a maximum value at the end of the 8-hr test period when the less reactive iodine species were predominant.
- The two-hour dose reduction factor based on PWR spray parameters equaled or exceeded the goal set for the trace additive spray. For the AEC-defined 4 percent cutoff for "nonreactive" iodine species in the containment vessel, the 2 hr DRF's were about 15 based on the observed 10 min fresh spray washout rate.
- The maximum organic iodide (CH_3I) gas phase concentration measured during this series of experiments was 0.25 percent of the injected I_2. At the end of the test period, the CH_3I concentration was about 1/10th of that of the start of the first spray period. However, this reduction appears to be an artifact of the sampling system (imperfect discrimination) rather than spray effectiveness.
- The maximum hypoiodus acid (HOI), observed in the 280°F isothermal test prior to spray activation, was 3.7 percent of the injected I_2. For all tests the final HOI concentration ranged between 0.005 and 0.017 percent. The major reduction in gas phase concentration occurred during the fresh spray periods. Thus hydrazine traced spray solutions preclude the evolution of HOI during spray recirculation periods.

- The degradation of hydrazine by oxygen was not deleterious to the scavenging of iodine from the gas phase during fresh or recirculated sprays.
- There was no apparent evolution of iodine species during recirculation even in the one test where the hydrazine concentration had been reduced to less than 0.1 ppm. This supports the formation of an ionic species in the presence of hydrazine that is nonvolatile at the temperatures predicted for PWR's under postulated LOCA conditions.
- Spray removal rates observed for 7G-3 and 1713A nozzles were comparable. Observed differences were caused by differences in drop sizes and in airborne iodine concentrations.

3.0 BACKGROUND

3.1 SIGNIFICANCE OF IODINE REMOVAL BY BORIC ACID SPRAYS

The present guideline for the siting of nuclear power reactors is contained in AEC Regulatory Guides 1.3 and 1.4(2) which spell out assumptions to be used for calculating the site boundary dosages following the design basis LOCA accident. For most reactor sites, the limiting condition for locating a reactor is the 2-hr dose received by an individual located at the site boundary. Analyses made on the basis of these quides show that iodine-131 is the limiting isotope for the internal dose received at the site boundary.

As water reactor technology has matured it has become necessary to provide engineered safeguards to remove airborne iodine from the containment atmosphere in the design bases accident. Accepted iodine removal systems include recirculating charcoal filter systems and high pH sprays. However, the use of high pH sprays has the disadvantage of causing significant corrosion of aluminum components within the containment. Caustic sprays would also cause appreciable damage if operated inadvertantly.

An optimum spray system for iodine removal would use water with a trace level chemical additive to react with iodine and at the same time cause no additional problems in its use. A large economic incentive exists for such a spray solution as a result of savings in both construction costs and operating costs when compared to high pH systems. Such a system would be less costly and much more effective in reducing the 2-hr iodine dose than a charcoal filter system.

3.2 PREVIOUS WORK ON BORIC ACID SPRAYS

Although a cursory look would indicate that boric acid sprays should not be very effective in the removal of airborne elemental iodine, results from several sources have shown rather good removal of iodine via such sprays. As part of the CSE program for the USAEC, one large scale test was made to show the removal effectiveness of boric acid sprays. CSE Run

A-7 showed that boric acid removed airborne iodine as effectively as did high pH sprays(3). Several runs in the nuclear safety pilot plant (NSPP) at Oak Ridge also showed that boric acid worked very well in removing airborne iodine(4). These results led to further study within the CSE vessel, sponsored by a consortium of Utilities. Run C-1 of that study(5) showed that the removal rate was far greater than that predicted by theoretical studies of the equilibrium distribution of iodine which neglect iodine reactions with impurities. This run, together with an accompanying study of equilibrium distribution, pointed to the important role of trace level impurities in determining the effectiveness of boric acid sprays. However, the uncertain existence and nature of impurities under accident conditions limits the confidence one can put in a system which uses boric acid sprays alone. This fact led to the subsequent studies of the addition of a trace level chemical species to the spray solution which would provide a firm basis for the assumption that the boric acid sprays were indeed effective under accident conditions. As a result of this study, four additives were identified as being potentially suitable. These were hydrazine at 50 ppm, sodium thiosulfate at 50 ppm, resorcinol at 50 ppm, and sodium hydroxide at pH 7. Hydrazine was selected for a detailed study as a result of consideration of overall suitability to power reactor spray systems.

The results of the trace level additive study showed that the addition of hydrazine to boric acid would lead to highly effective spray removal of airborne elemental iodine. Its effectiveness was substantially the same as that of caustic sprays (pH 9.5) or sprays containing 1 wt. percent sodium thiosulfate. The appraisal of these results by AEC Regulatory pointed out concerns in three areas. These included the rate of removal of iodine by hydrazine sprays under accident conditions, the degradation of hydrazine and the possible impact on its effectiveness, and the potential for evolution of iodine from the spray solution once the hydrazine has disappeared through reaction with oxygen. These questions and others could be answered only with large scale tests under conditions similar to those predicted for a LOCA. This report presents the results of the large scale tests designed to answer these questions.

3.3 THEORETICAL BASIS FOR IODINE WASHOUT BY TRACE LEVEL HYDRAZINE SPRAYS

The washout of iodine by sprays containing hydrazine is developed in the following paragraphs on the basis of gas absorption theory.

A material balance written for a single airborne species in the main gas volume of a containment system may be expressed as:

$$V \frac{dC_g}{dt} = G + (C_{g2} - C_g) B_{12} - \sum_j [k_g(C_g - C_{gi})A]_j - R_G \qquad (1)$$

in which V = volume of main containment space,
C_g = gas phase concentration of solute in main containment volume,
t = time,
G = generation or addition rate of solute within the main containment volume,
C_{g2} = gas phase concentration of solute in connected volumes,
B_{12} = exchange coefficient for interroom transport,
k_g = mass transfer coefficient at each of "j" deposition surfaces,
C_{gi} = gas phase concentration of solute at each deposition surface,
A = surface area of each surface available for deposition,
R_g = rate of gas phase chemical destruction of a species in the main containment volume.

The left hand side of Equation (1) is the accumulation rate of solute which occurs as a result of generation and depletion. The first term on the right side is the generation rate, or addition rate of solute to the gas phase. The second term is transport from connected rooms. The third term of the right hand side represents deposition of a specie onto j surfaces within the main room. The last term on the right accounts for disappearance of a specie by a homogenous gas phase reaction.

In order to show how the spray solution composition influences the removal rate, one may set G, B_{12}, and R_g equal to zero. Also, the surfaces may be considered to be either spray drops or wall surfaces. For these conditions, Equation (1) becomes

$$-V \frac{dC_g}{dt} = [k_g (C_g - C_{gi})A]_{drops} + [k_g(C_g - C_{gi})A]_{wall} \tag{2}$$

In Equation (2), absorption by both spray drops and wall surfaces is accounted for. Wall film absorption in the containment experiments reported here is accounted for experimentally by measuring $\frac{dCg}{dt}$ before and after spray, operation. The average value of $\frac{dCg}{dt}$ due to wall deposition is then subtracted from the total observed during spray. The net value is that due to spray alone. The function of a chemical additive in enhancing spray washout is to maintain C_{gi} small compared to C_g. The upper limit to washout rate corresponds to the perfect sink case in which the rate of reaction in the liquid phase is sufficiently rapid to maintain interface gas concentration at zero, i.e., $C_{gi} = 0$. The absorption rate due to spray operation, $[k_g(C_g-C_{gi})A]$ drops may be related to single drop absorption. For fresh spray drops which enter the containment vessel, the concentration of iodine at the end of the fall path may be written as

$$C_\ell = H_o E \, C_g \tag{3}$$

where

C_ℓ = conc. in drop at end of fall path,

H_o = equilibrium partition coefficient applicable to spray washout $H_o = \frac{\text{Conc. in liq.}}{\text{Conc. in gas}}\Big|$ at equilibrium,

E = fractional saturation attained by drop.

The total iodine absorption rate is simply FC_ℓ, where F is the spray flow rate. Thus, the spray absorption rate is from Equations (2) and (3),

$$\text{spray absorption rate} = [k_g(C_g - C_{gi})A]_{drops} = F \, H_o E \, C_g \tag{4}$$

The spray washout constant, λ_s, commonly used to describe washout in containment vessels may be written by combining Equations (2) and (4) as

$$\lambda_s = \frac{F\ H_o\ E}{V} \tag{5}$$

where

λ_s = spray washout constant, min^{-1},

F = spray flow rate, $\text{ft}^3\ \text{min}^{-1}$,

V = volume of gas space, ft^3.

For well mixed drops, the fractional saturation may be obtained from solution of a differential equation based on a material balance on the liquid drop. At the gas-liquid interface and throughout the drop the solution is assumed to be in equilibrium with the iodine concentration in the gas, which in turn is assumed to be constant throughout the volume. The resulting equation is

$$E = 1 - \exp\left(\frac{-6k_g t_e}{H_o d}\right) \tag{6}$$

where

$E = \frac{C_\ell}{H_o C_g}$ = fractional saturation,

k_g = gas phase mass transfer coefficient,

t_e = drop exposure time,

H_o = equilibrium partition coefficient,

d = drop diameter.

Equation (6) relates E to spray system parameters and the absorptive capacity of the spray solution given in terms of the equilibrium partition coefficient, H_o. The well mixed drop relationship represents an upper limit to drop absorption because liquid phase mass transfer resistance has been neglected.

A lower limit to drop absorption may be predicted from a stagnant drop model (no liquid circulation in the drop) presented by Danckwerts.$^{(6)}$

$$E = \frac{6h^2}{a} \sum_{n=1}^{\infty} \frac{1 - \exp(-Dt\alpha_n^2)}{\alpha_n^2 \, [a\alpha_n^2 + h(ah-1)]} \tag{7}$$

where

$h = \frac{k_g,}{H_o D}$

D = diffusivity in liquid phase,

a = drop radius,

α_n = nth root of the equation: $(a\alpha)\mathrm{Cot}(a\alpha) + ah - 1 = 0$,

t = exposure time.

Both the upper limit and lower limit to E, Equations (6) and (7) respectively have been evaluated numerically for iodine absorption under LOCA conditions$^{(5)}$. It was found that these equations give predictions which typically differ by less than 30 percent, hence one may carry out a reasonably accurate analysis by considering only the simple expression for well-mixed drops, Equation (6). A more complete discussion of the method of incorporating satisfactory conservatism within the calculations is presented in References 5 and 17.

The spray washout constant, λ_s, may be related to the equilibrium iodine partition coefficient by combining equations (5) and (6).

$$\lambda_s = \frac{FH_o}{V}\left[1 - \exp \; \frac{-6k_g t_e}{H_o d}\right] \tag{8}$$

For large values of H_o (greater than about 5000), the argument of the exponential term becomes small, allowing a simplification using $e^{-\chi} \cong 1-\chi$ for small χ. For large H_o, Equation (8) becomes

$$\lambda_s = \frac{6Fk_g\, t_e}{Vd} \tag{9}$$

Equation (9) is identical to the result predicted on the basis of a perfect sink model. Thus, for H_o greater than about 5000, the precise numerical value of H_o is unimportant because the absorption rate is limited by gas phase mass transfer resistance.

The equilibrium partition coefficient has been subscripted in recognition that the applicable value is that occurring in very short time, a few seconds. Thus, although slow reactions (several minutes) would cause iodine in solution to displace toward iodide, this displacement would not appreciably enhance spray washout.

The rapid washout of iodine by an aqueous spray depends on rapid reactions in solution to destroy dissolved iodine. This may be shown schematically as

$$I_{2(aq)} \xrightarrow{k} \text{nonvolatile products} \tag{10}$$

The instantaneous partition coefficient, H_o, can be translated into a solution reaction rate using a well-mixed drop model if one assumes that the reaction rate is first order. The result is

$$H_oE = H\,(kt_e+1) \tag{11}$$

where

H_o = effective overall partition coefficient,

H = Henry's Law constant = $\frac{[I_2]aq}{[I_2]_{gas}}$,

k = first order solution reaction rate constant, sec^{-1},

t_e = time for drop to fall to floor, sec.

The value of H varies from about 80 at room temperature to 7.5 at 250°F. An estimate for PWR conditions indicates that in order to achieve an H_o of 500, k is required to have a value of 6.5 sec^{-1}. In order to achieve the perfect sink case (H_o >5000), k would need to be greater than 65 sec^{-1}.

In the equilibrium study which was a precursor to this study, H_o could not be precisely determined for times smaller than a few minutes. Thus, the large scale spray tests were considered necessary to demonstrate that the reaction in solution is rapid enough to provide large values of H_o in time periods of the same order as the drop exposure time.

The effectiveness of hydrazine in the removal of gaseous elemental iodine is due to its ability to remove aqueous iodine from solution by reduction to the iodide ion. The reduction of iodine to the iodide ion may be represented by the half cell reaction

$$I_2 = 2I^- - 2e^- \qquad E^\circ = 0.536V \qquad (12)$$

Thus, any substance whose oxidation potential is greater than -0.536V is a thermodynamically feasible reductant for iodine. In a basic solution, hydrazine may act as a powerful reducing agent as indicated in the following reactions(7):

$$N_2H_4 + 4OH^- = N_2 + 4\ H_2O + 4e^- \qquad E^\circ = 1.16V \qquad (13)$$

$$N_2H_4 + OH^- = NH_3 + \frac{1}{2}N_2 + H_2O + e^- \qquad E^\circ = 2.42V \qquad (14)$$

$$N_2H_4 + \frac{5}{2}\ OH^- + \frac{1}{2}\ N_3^- + \frac{1}{2}\ NH_3 + \frac{5}{2}\ H_2O + 2e^- \qquad E^\circ = 0.92V \qquad (15)$$

In acidic solution, the following half cell reactions take place:

$$N_2H_5^+ = N_2 + 5H^+ + 4e^- \qquad E^\circ = 0.23V \qquad (16)$$

$$N_2H_5^+ = NH_4^+ + \frac{1}{2}\ N_2 + H^+ + e^- \qquad E^\circ = 1.74V \qquad (17)$$

$$N_2H_5^+ = \frac{1}{2}\ NH_3 + \frac{1}{2}\ NH_4^+ + \frac{5}{2}\ H^+ + 2e^- \qquad E^\circ = -0.11V \qquad (18)$$

From a thermodynamic standpoint, any one of these oxidation half-reactions would reduce iodine in solution to the iodide form. The particular reaction which dominated in a certain situation would likely depend on the pH, temperature, and concentrations of the reacting species. The listing of potential reactions represented by equations (13) through (18) supports the feasibility of hydrazine as a spray additive because thermodynamically favorable reactions exist for all of the pH conditions which might be encountered under LOCA conditions.

The mechanism of the reaction between iodine and hydrazine was studied in acid solution by Sen Gupta and Sen Gupta(8). Their work showed that the reacting iodine specie was HOI. A first step in iodine hydrolysis involves formation of HOI.

$$I_2 + H_2O \rightleftharpoons HOI + H^+ + I^- \qquad (19)$$

Destruction of HOI causes this reaction to proceed to the right, which increases the fraction of dissolved iodine present as nonvolatile forms, and thus increases the iodine partition coefficient defined on the basis of the total iodine in solution. Any increase in pH of the solution would also shift reaction (19) to the right, increasing the partition coefficient. Thus in sprays utilizing NaOH as the reactant one would expect HOI to be a major specie in solution, hence its volatility could be important where the iodine partition coefficient is increased by pH shift alone. The fact that HOI is the reacting species represents a potential advantage for hydrazine sprays as compared to caustic since HOI is removed from solution as rapidly as it is formed.

The overall reaction between iodine and hydrazine is expected to be similar to that for the oxygen reaction, which proceeds according to reactions (13) or (16). Thus, the stoichiometry would be represented by

$$N_2H_4 + I_2 = N_2 + 4H^+ + 4I^- \qquad (20)$$

If one assumes that all the iodine postulated to become airborne in the containment vessel (25% of total core inventory) reacts with hydrazine, an estimate of stoichiometric hydrazine can be made. For a 1,000 MW(e) plant having a containment volume of 2,000,000 ft^3, the initial elemental iodine concentration is no greater than 90 mg/M^3. Thus, the total mass of airborne iodine would be 5100 grams, or 20 gram moles. On the basis of Equation (20), this requires 20 gram mols of hydrazine or 640 grams. If this amount of hydrazine is mixed in the emergency spray storage water (400,000 gal), the concentration would be 0.42 ppm. Thus, the amount of hydrazine required to react with all of the released iodine is minimal. The first spray drops entering the containment vessel will be exposed to airborne iodine at a concentration of 90 mg/M^3. Gas phase mass transfer will limit the drop enrichment to less than about 4000. Thus, the maximum amount of iodine which could be absorbed would be (4000) (90 mg/M^3) = 3.6×10^5 mg/M^3 of spray liquid. This is 360 ppm of iodine, which would require 45 ppm of hydrazine. Thus, an initial hydrazine concentration of 50 ppm would theoretically permit complete reaction with iodine in the most concentrated solution which could be formed. The highest concentrations would exist for only tens of seconds, hence the hydrazine would be in <u>great</u> excess for nearly all of the initial two hour period.

It is recognized that hydrazine will react with oxygen within the containment vessel, and be progressively destroyed over a time period of many hours, if hydrazine addition is terminated. A question raised by the DL review of previous work dealt with possible reevolution of iodine if hydrazine is destroyed completely. This question can be answered by considering the reactions which bind iodine in solution.

Eggleton(9) has studied the iodine-water partition in detail. At least eight reactions are involved when elemental iodine is dissolved in water.

$$I_2(\text{gas-phase}) \underset{}{\overset{K_1}{\rightleftharpoons}} I_{2(aq)} \qquad K_1 = \frac{(I_2)_{aq}}{[I_2]_{\text{gas-phase}}} \tag{21}$$

$$I_2(aq) + I^- \overset{K_2}{\rightleftharpoons} I_3^- \qquad K_2 = \frac{[I_3^-]}{[I_2]_{aq}[I^-]} \tag{22}$$

$$I_{2(aq)} + H_2O \overset{K_3}{\rightleftharpoons} H^+ + I^- + HOI \qquad K_3 = \frac{[H^+]\,[I^-]\,[HOI]}{[I_2]_{aq}} \tag{23}$$

$$I_{2(aq)} + H_2O \overset{K_4}{\rightleftharpoons} H_2OI^+ + I^- \qquad K_4 = \frac{[H_2OI+]\,[I^-]}{[I_2]_{aq}} \tag{24}$$

$$3I_{2(aq)} + 3H_2O \overset{K_5}{\rightleftharpoons} IO_3^- + 5I^- + 6H^+ \qquad K_5 = \frac{[IO_3^-]\,[I^-]^5\,[H^+]^6}{[I_2]_{aq}} \tag{25}$$

$$HOI \overset{K6}{\rightleftharpoons} H^+ + IO^- \qquad K_6 = \frac{[H^+]\,[IO^-]}{HOI} \tag{26}$$

$$IO^- + I^- + H_2O \overset{K_7}{\rightleftharpoons} I_2OH^- + OH^- \qquad K_7 = \frac{[I_2OH]\,[OH^-]}{[IO^-]\,[I^-]} \tag{27}$$

$$IO^- + I^- \overset{K_8}{\rightleftharpoons} I_2O^= \qquad K_8 = \frac{[I_2O^=]}{[IO^-]\,[I^-]} \tag{28}$$

The first four of these reactions are known to be fast. The rates of the last four reactions are not well known. The last four reactions would cause displacement of the equilibrium in favor of the liquid phase, hence an assessment which did not include their effect would underestimate the partition coefficient, and therefore would be conservative in terms of spray washout. The overall partition coefficient is defined as the total concentration of iodine in the liquid divided by the concentration of elemental iodine in the gas phase.

Only two molecular species are included in the equilibria. These are $I_{2(aq)}$ and HOI. Since ionic forms are not volatile, the gas phase could contain only I_2 and/or HOI. On the basis of available literature and the results reported herein, it may be stated that I_2 will be the dominant species in the gas phase. Hydrazine works by destroying HOI formed by Equation (23). The probable stoichiometry of this reaction is as follows.

$$2HOI + N_2H_4 = N_2 + 2H_2O + 2HI \tag{29}$$

Thus, the overall partition coefficient is increased because the HOI concentration is reduced. Equation (29) would not be reversible to an appreciable extent because of the free energy change. This is well known because one analytical method for hydrazine is based on quantitative titration with iodine. Thus, if one removed excess hydrazine at some point before all HOI were destroyed, the equilibrium position would not change unless additional iodine were added.

If the pH of the solution were raised subsequent to the destruction of hydrazine, $[H^+]$ would decrease, causing reaction (23) to shift to the right. This would increase the overall partition coefficient. The effect of lowering the pH is considered academic because spray systems will be designed to insure a controlled pH higher than 7.0 for the long term case.

All studies of the removal of iodine from gas phase by absorption have noted the presence of unreactive forms of iodine. These are believed to be primarily organic iodides, typified by methyl iodide CH_3I, and possibly gaseous HOI. Methyl iodide has a low solubility in water and is comparatively unreactive in aqueous solution. Therefore it is very slowly removed by aqueous sprays. The presence of N_2H_4 at the proposed concentration levels would have little effect on the rate of methyl iodide removal from the containment atmosphere. However, as noted above, it is postulated and is shown herein that hydrazine sprays will be effective in removing HOI. As was pointed out in the studies summarized in Reference 1, the assumed concentrations (conservative concentrations assumed by AEC-DL) of organic iodides and particles in containment atmospheres will be the limiting factor in the two-hour dose reduction factor (DRF) that can be achieved through the use of hydrazine sprays.

3.4 HYDROGEN FORMATION FROM HYDRAZINE DEGRADATION

Since radiolysis of spray liquid leads to eventual destruction of residual hydrazine and production of hydrogen, Postma(1) made a thorough analysis of degradation of hydrazine by oxidation, iodine reactions, thermal degradation and radioalysis. Of these reactions only radiolysis results in the production of hydrogen. By assuming that all the hydrazine was destroyed radiolytically, Postma showed that for a reference sized PWR plant and a hydrazine concentration of 50 ppm, that only 1.77 lbs of H_2 would be produced. This mass would be less than 0.03 volume percent in the containment vessel which is negligible compared to hydrogen produced by other sources.

3.5 SPECIFIC QUESTIONS ADDRESSED IN THIS PROGRAM

A letter from AEC Regulatory following review of the work summarized in Reference 1 raised five questions with respect to the relevancy of the results under actual LOCA conditions. The tests reported here were scoped to answer these questions which are detailed in the following sections.

3.5.1 Spray Removal Rate

The need to demonstrate that the solution reaction rate is adequate to achieve the observed high distribution coefficients of the equilibrium tests during the short drop-fall period was pointed out by DL. Tests at two temperatures were run to demonstrate the adequacy of this solution reaction rate. The high temperature test was run at 280°F which approximated the upper limit of temperature in the containment during a LOCA. A low temperature test was run at 150°F which is believed to be the minimum temperature of interest in a LOCA. In both tests the solution reaction rate was fast enough to produce the expected high "instantaneous" distribution coefficients.

3.5.2 Formation of HOI in Containment

Work at ANC(10) has led to the hypothesis that some of the nonremovable specie may be HOI rather than CH_3I. From the reaction kinetic study of Sen Gupta(8) any HOI formed by hydrolysis should be destroyed by hydrazine. The amount of HOI in the gas phase was determined using ANC(10) samplers and associated materials which were more specific for HOI measurements than the standard Maypack. The reduction of HOI during spraying and the resultant very low equilibrium concentration supported the conclusions based on the Sen Gupta(8) and the equilibrium study data.

3.5.3 Thermal Degradation of Hydrazine Under LOCA Conditions

The peak temperature of 280°F is somewhat higher than the experimental maximum temperature of 250°F used in the study reported in Reference 1.

Although, we did not anticipate a significant increase in the rate of degradation of N_2H_4 effectiveness over the 10-second exposure time of the droplets to the atmosphere, the hydrazine concentration in the liquid was measured periodically. The decrease in the hydrazine concentration in the vessel sump by a combination of oxidation and iodine reaction did not discernably alter the spray effectiveness or the long term equilibrium iodine partition coefficient.

3.5.4 Evolution of Absorbed Iodine During Recirculation

This question arises because the N_2H_4 will be slowly removed from the spray solution as a result of reactions with oxygen. As a consequence, the effectiveness for iodine removal will decrease over extended periods. However, on the basis of a discussion presented in Section 2.3, one would expect insignificant evolution of the iodine into the gas phase since there will be no oxidant present to convert the iodide ion to elemental iodine in solution and thence its desorption into the gas phase. Nevertheless, to answer this question all four tests were continued over an 8-hour period during which the spray solution was recirculated through the containment volume. No significant increases in the gas phase iodine concentration over the 8-hour period were observed in any of the four tests.

3.5.5 Effect of pH on Iodine Removal

As a result of concern over the possibility of intergranular corrosion by low pH boric acid solutions, AEC Regulatory has imposed criteria that such spray systems be equipped to raise the pH of the recirculating spray to the range of pH 7 to pH 8 after some period following a LOCA to suppress this corrosion phenomena. Two questions raised concerning a change in pH were related to possible iodine evolution and possible enhancement in the reaction rate with oxygen. For the reasons previously put forth in Section 2.3, we did not anticipate any increase in iodine evolution. The fourth test was designed to demonstrate this, which it did unequivocally.

4.0 EXPERIMENTAL CONDITIONS

This section describes the experimental facility, including the vessel and ancillary equipment, the iodine generating system, and the method of sampling and analysis. This is followed by a synopsis of the test conditions and a description of the experimental procedure.

4.1 EQUIPMENT DESCRIPTION

The experimental equipment used for the large-scale demonstration tests was essentially the same as that used in previous AEC-sponsored experiments in the Containment Systems Experiment (CSE) program. The equipment is described in detail by Linderoth(11), Hilliard, et al.(12), Coleman(13), and McCormack(14). A brief description is included in the present report.

4.1.1 Vessel and Ancillary Equipment

Figure 1 is a schematic drawing of the containment vessel arrangement. The containment vessel is composed of three interconnected vessels. An outer vessel, called the main containment vessel, an inner vessel, called the drywell, and the compartment composing two-thirds of the annular space between the drywell and the main containment vessel, called the wetwell. The main containment vessel is 25 ft diameter, 66.7 ft overall height, with a total volume of 30,680 ft^3. The interior surfaces are coated with a modified phenolic paint, Phenoline 302*.

The top of the wetwell forms a solid deck which effectively separates the contained gases into what is termed the "main room" above the deck and the lower rooms below the deck. The lid of the drywell was raised so that its volume was common to the main room. The combined volume of this "main room" is 21,005 ft^3. One-third of the annular space between the drywell and main containment vessel is a small access area called the "middle room," 2089 ft^3 in volume. Below the middle room, drywell, and wetwell is a third

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*Phenoline 302, manufactured by Carboline Corp., St. Louis, MO

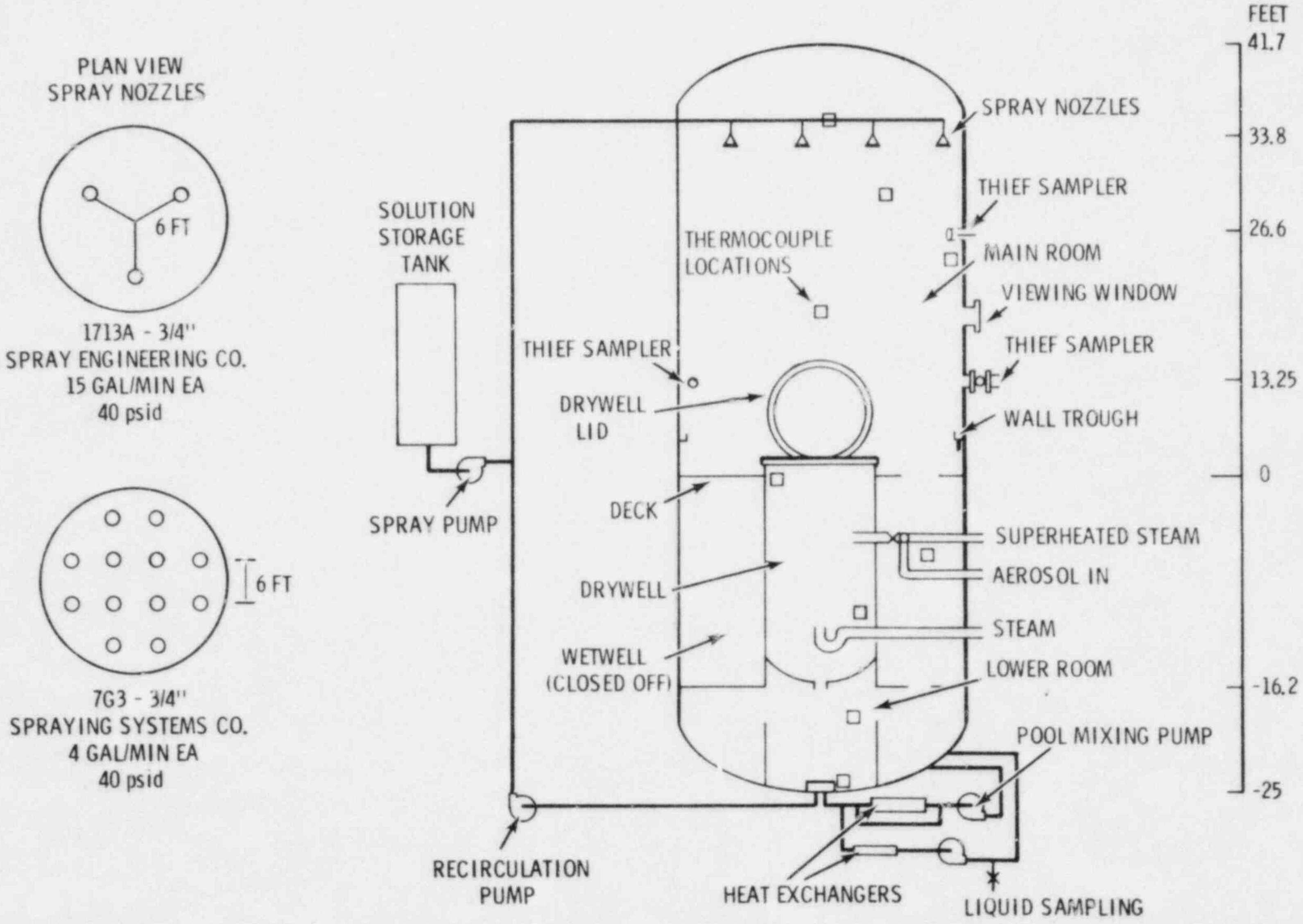


FIGURE 1. Schematic Drawing of Containment System

space called the "lower room," 3380 ft^3 in volume. The wetwell volumes were sealed off and not exposed to steam or fission product simulants in the spray experiment. Two 4 ft diameter holes in the deck connect the main room to the middle room. One 4 ft diameter opening connects the middle room to the lower room.

Steam condensate and spray liquid accumulated in two locations: the main vessel pool located in the lower room (C.V. Sump), and on the flat deck of the main room. The C.V. sump was stirred continuously, sampled at designated intervals, and the liquid volume monitored. The drywell drained continuously and directly to the C.V. pool and the wall trough drained to the deck of the main room. The liquid on the deck was not monitored. Spraying tests during shakedown showed that the volume held by the deck varied with spraying time and flow rate. The deck volume remained constant after 2 hrs of spray time at 48 gallons per minute. Thus the liquid iodine and hydrazine concentration early in the first spray periods was biased to the low side due to holdup of the undiluted spray on the deck and dilution in the vessel sump steam condensate. The short intermittent spray operations, principally the 10 and 30-min spray periods produced distortions in the liquid volume as a function of time. Consequently, truly representative samples of spray liquid were obtained only during the spray recirculation period.

A pipe from the plant steam boiler, terminating near the bottom of the drywell, provided steam input to heat the vessel and its atmosphere. A steam flow meter was provided.

4.1.2 Fission Product Simulant Generation

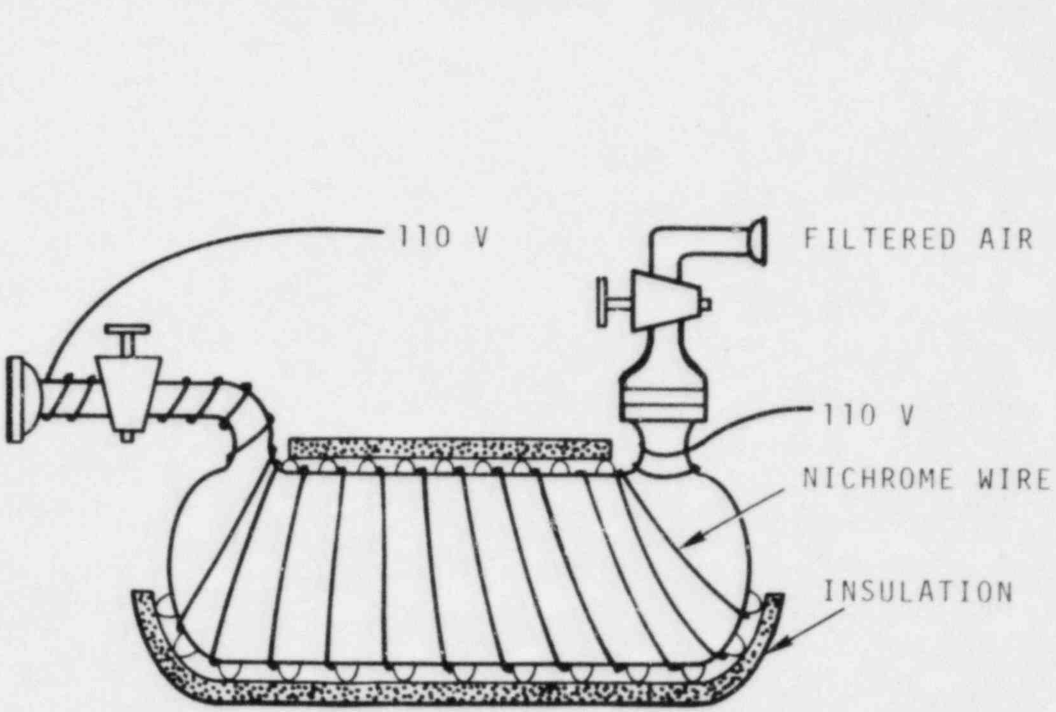
Two hundred grams of stable elemental iodine equilibrated with a known quantity of ^{131}I tracer (about 1 curie) was the fission product simulant. Equilibration was made in the same apparatus used to generate the aerosol via isotopic exchange at 130°C for two hours as described in detail by Coleman(13). When release was desired, the flask was heated electrically and air carried the elemental iodine via a 2-in. ID injection line through a penetration in the main CSE vessel into the vapor space of the drywell. The motive force for injection was provided by a steam jet operated with 225 psig steam. The transfer line is electrically heated to 280°F to prevent condensation.

The original CSE program utilized four separate materials to simulate the fission product release; elemental iodine, methyl iodide, cesium, and particulates formed by melting unirradiated zircaloy-clad UO_2.

In the present program interest was focused on elemental iodine because it is the dominant specie from a dose calculation standpoint. The presence of other aerosol components does not influence the elemental iodine washout rate, hence only elemental iodine was injected into the vessel in this series of tests. Figure 2 is a schematic drawing of the iodine generation equipment and injection system.

4.1.3 Iodine Sampling and Analysis

Sampling of the containment volume was done at three locations, shown in Figure 1, via "thief" Maypack samplers. The Maypacks and ANC samplers were initially preheated to above the containment temperature and then manually inserted through airlocks into the containment atmosphere. Flow through the three samplers, (samples withdrawn simultaneously) was controlled at 0.5 ft^3/min (STP) dry air for 3-min duration for Maypacks and 0.25 ft^3/min for 6 min for the ANC's. The samplers were then immediately withdrawn for analysis. Sampling error was determined to be <10 percent at the 68 percent confidence level. The original CSE program made use of a more extensive sampling system consisting of 14 Maypack clusters located throughout the vapor space. However, the results of that program demonstrated that mixing within the containment volume was nearly complete and hence the large number of samples was redundant. The thief samples avoided the possibility of leakage into the samples either before or after the collection of the sample and simplified the run operation. Figure 3 is a schematic of the thief sampling arrangement.



EQUILIBRATION AND GENERATOR APPARATUS

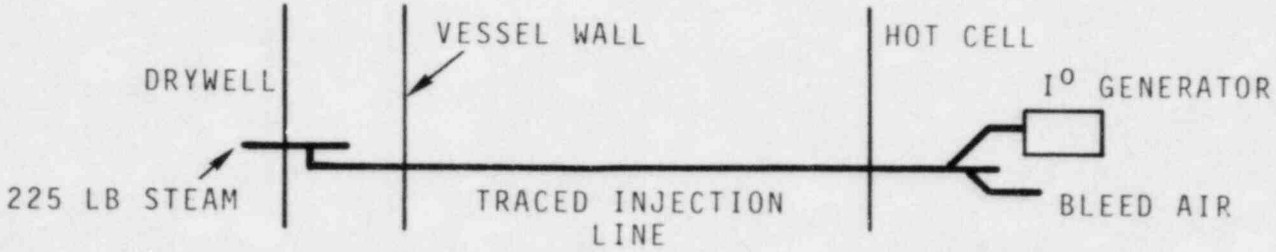


FIGURE 2. Schematic Drawing of Iodine Aerosol Generating Equipment and Injection System

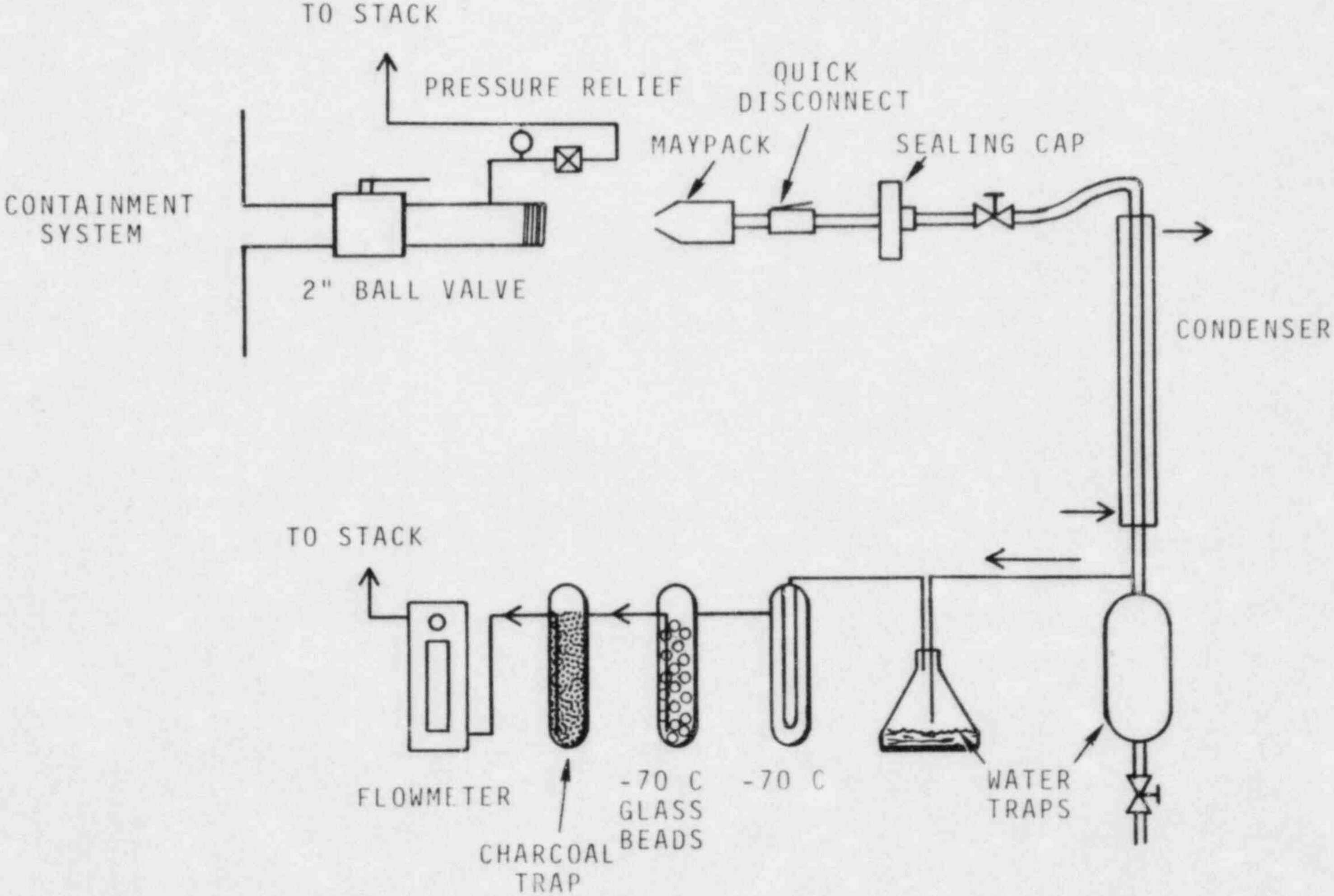


FIGURE 3. Schematic of the Thief Sampling Arrangement

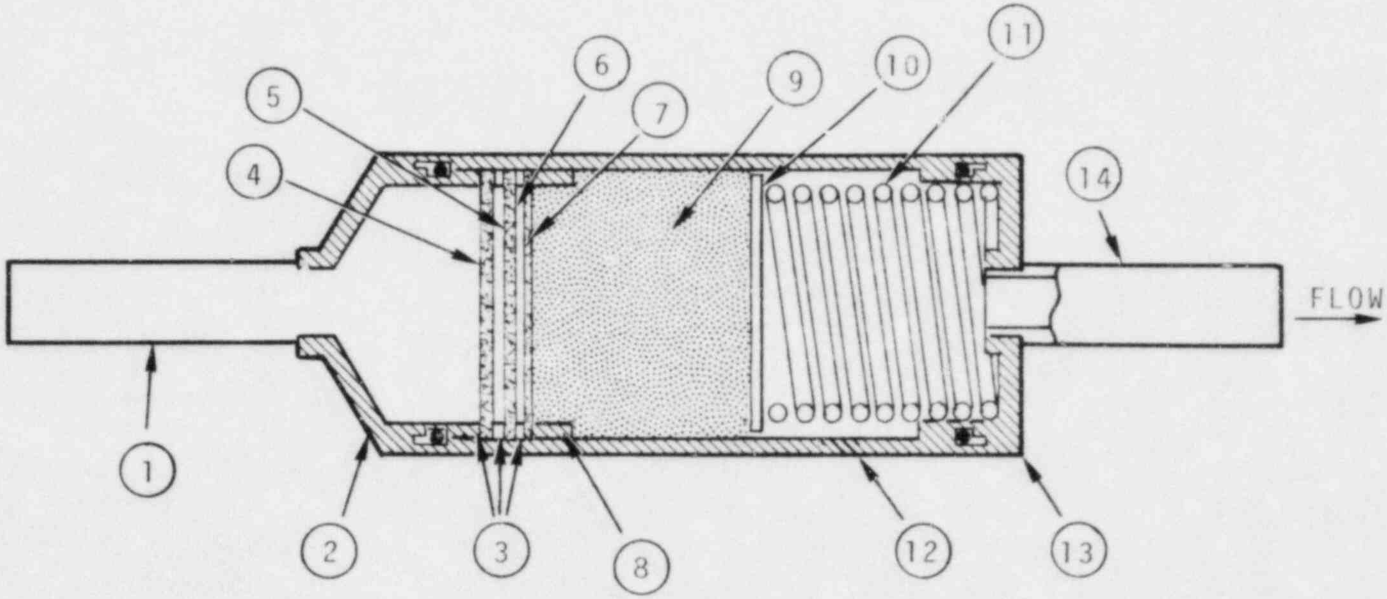
Figure 4 shows a sectional view of the Maypack. Five samples were obtained from each Maypack.

- Filters (2 Gelman Type A)
- Silver membrane, 5μ pore size)
- Silver screens (3)
- Charcoal filter paper (Gelman Type AC)
- Charcoal granules (2-in. activated coconut, 8-14 mesh KI impregnated)

The iodine activity on the inlet surfaces of both the Maypack and ANC samplers was < 0.5 percent of the total I_2 and was not routinely measured in these tests.

The Maypack is not a perfect discriminator of iodine forms, but extensive calibration has shown that reliable classification of the elemental and methyl iodide forms were obtained.(5) Iodine associated with particles and other inorganic and organic forms are less reliably identified. An example of data obtained by the Maypack sampler are shown in Figure 5.(5) Methyl iodide was released 1 hr before the elemental iodine was released. More than 95 percent of the methyl iodide was found on the charcoal bed at times previous to release of elemental iodine, with only 0.1 percent being found on the silver components. Immediately after 100 grams of elemental iodine was released, 92 percent of the total gasborne iodine was found on the silver surfaces, while the charcoal granules showed only a slight increase. The iodine on the thin charcoal paper may be a mixture of HOI, I_2, and CH_3I. However, after severe depletion of the I_2 by spraying its contribution to the charcoal paper would be insignificant.

Special iodine samplers developed at Idaho Falls(10) were used to better define the presence of HOI. The samplers, shown in Figure 6, were used only at selected times, due to their limited number, at one of the +13 ft level sampling stations. The materials for the samplers were prepared and proof tested by personnel of the Radiochemistry Section, Chemistry and Research Engineering Branch, Allied Chemical Company, Idaho Falls, Idaho.



1 - INLET
2 - NOSE CONE
3 - TEFLON GASKET
4 - TWO PARTICLE FILTERS
5 - SILVER MEMBRANE FILTER
6 - THREE SILVER PLATED SCREENS
7 - CHARCOAL LOADED FILTER
8 - STOP RING
9 - CHARCOAL BED
10 - SCREEN
11 - SPRING
12 - BODY
13 - END CAP
14 - OUTLET

FIGURE 4. Sectional View of Maypack Sampler

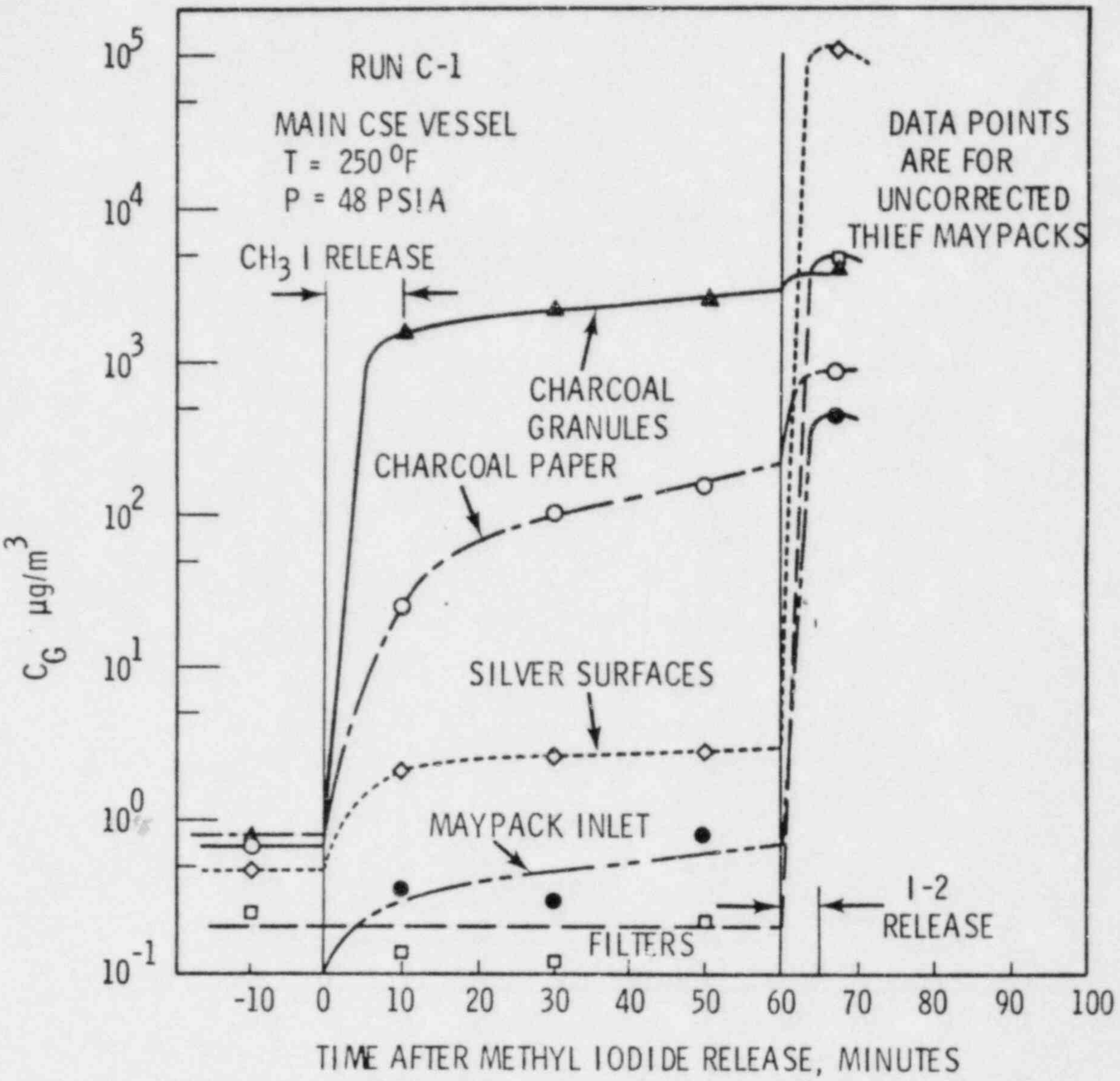


FIGURE 5. Response of Maypack Sampler to Sequential Release of Methyl Iodide and Elemental Iodine

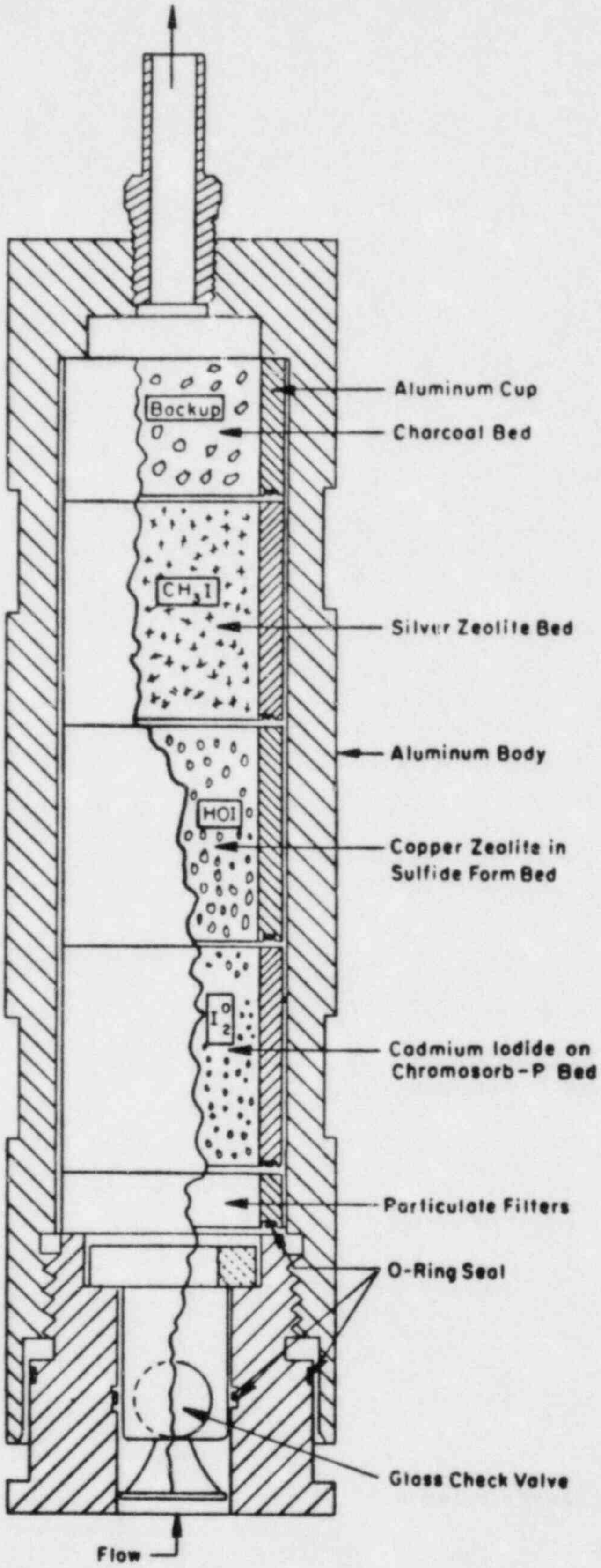


FIGURE 6. ANC Iodine Sampler Cartridge

All samples were counted with a 2 in. x 2 in. NaI (Tl) crystal detector and a multi-channel analyzer. The system was calibrated for four fixed counting geometries and was used for calibrating the ^{131}I tracer of each test.

Liquid samples were taken from the main vessel sump just downstream of the sampling heat exchanger. Liquid from the C.V. sump was continuously pumped through the sampling and sump mixing systems for the duration of the tests.

4.1.4 Spray Solution Makeup

After thoroughly flushing the storage tank and all lines with demineralized water, the 1500 ppm B-50 ppm N_2H_4 spray solution was prepared by dissolving 179 lb of granular boric acid in 2500 gallons of demineralized water. Then 880 ml of 64 percent hydrazine (Practical Grade) was added and after stirring for 2 hrs, samples were taken for hydrazine analysis. The 10 ppm excess of hydrazine, used to offset depletion from oxidation during storage, resulted in the desired 50 ppm of N_2H_4. The resistivity of the demineralized water was >0.25 megohm-cm and its pH was about 6.5.

The boric acid was "Special Quality Grade" granules obtained from the U.S. Borax Chemical Company, Los Angeles, California. Table 1 is a copy of the analysis provided by them.

TABLE 1. ANALYSIS OF GRANULAR BORIC ACID

CHEMICAL	
Boric Oxide (B_2O_3)	56.4%
Water (H_2O)	43.6
Boric Acid (H_3BO_3)	100.1

Impurities	Maximum	Typical
Sodium (Na)	0.001 %	0.000 %
Chloride (Cl)	0.00004	0.00002
Sulfate (SO_4)	0.00016	0.00009
Phosphate (PO_4)	0.001	0.000
Iron (Fe)	0.0002	0.00008
Heavy metals (as Pb)	0.0002	0.00010
Calcium (Ca)	0.005	0.000
Water-insoluble	0.005	0.000

4.1.5 Spray System

The spray system flow sheet is shown in Figure 7. About 100 ft of the piping was carbon steel with about 200 ft of 304 SS. The storage tank, vessel and all pumps, lines and nozzles were thoroughly flushed with demineralized water during shakedown tests and between each test. Just prior to iodine injection, the spray header was primed with solution to to provide a prompt starting time. The spray rate was controlled by maintaining a pressure differential of 40 ± 2 psi across the nozzles.

4.1.6 Pre-Test Preparations

Since the CSE vessel and all ancillary systems had been in a standby condition for three years it was necessary to "de-mothball" or reinstall some equipment and confirm instrument calibrations. The final test for all systems was a shakedown test at 280°F and 64 psia pressure during which the vessel leak rate was measured to verify that leakage would be an insignificant factor during the 8-hour test.

4.2 EXPERIMENTAL PROCEDURE

Before each experiment was begun, a comprehensive description of the proposed experiment was written. These "Run Plans," served primarily as a guide to the operations staff in conducting the experiment, but were also essential in detailed planning of the experiments.

The general procedure used in all the experiments is outlined as follows:

- Spray nozzles were tested for flow rate and coverage.
- The vessel was sealed and air recirculated through an absolute filter until the condensation nuclei concentration was $< 500\ \mathrm{cm}^{-3}$.
- The vessel was brought up to operating conditions by feeding 100 psig steam into the vessel near the bottom of the drywell. The vessel temperature and pressure was stabilized at the initial run conditions and the wet well pressure maintained at 3 psig differential above the main vessel pressure.

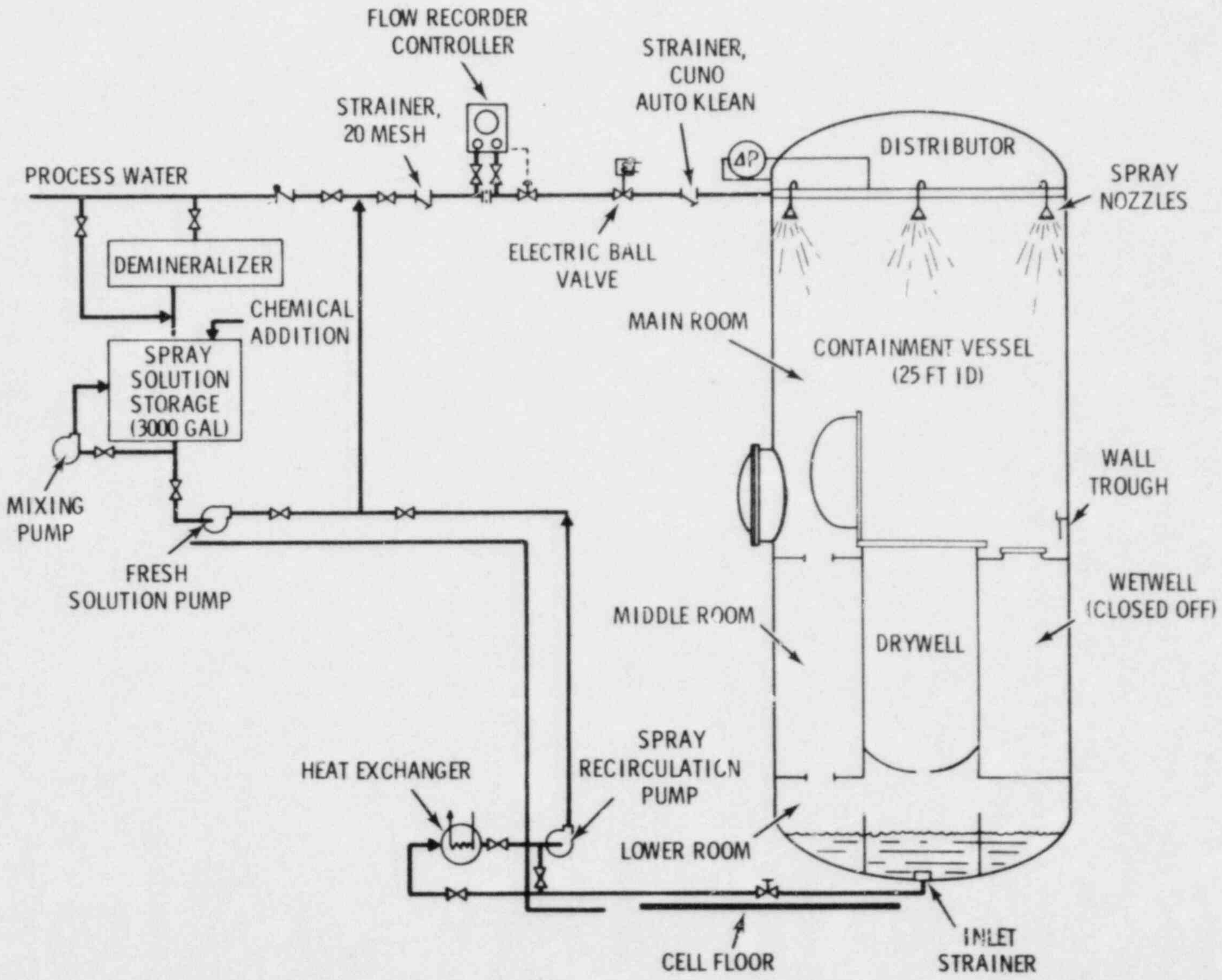


FIGURE 7. Flowsheet of CSE Spray System

- The sump liquid formed by steam condensation was mixed, sampled for activity, and discharged down to a heel of approximately 200 liters. The fresh spray pump was activated just long enough to fill the header. The iodine-discharge line was then heated to temperature, the 100 psig steam was cut off, and the injection steam jet operated to produce a vacuum of 5 in. of Hg.
- Just prior to injection, the liquid sampling and vessel pool mixing pumps were started.
- Iodine injection was started at $t = t_0$ and all operating data recorded (steam pressure, airflow, vacuum) as a function of time. At completion of iodine injection all delivery line valves were closed. Steam jet valves were closed and the 100 lb steam valve opened to maintain temperature and pressure conditions in the vessel.
- For all tests except T-4 atmospheric samples were taken prior to spraying to establish the natural deposition rate.
- Fresh spray was started 5 min after the last aerosol sampling period. During all spray periods, the primary spray flow rate control was the differential pressure across the spray nozzles. This pressure was held constant at 40 psid to maintain the desired drop size distribution. The steam feed was increased at the start of spraying to maintain near isothermal conditions in the vessel except for run T-4 where the temperature and pressure were allowed to decay throughout the test period. A set of gas samples was taken after iodine injection and immediately following each spray period for Runs 1-3. For Run 4, samples were taken during the initial spray period and then after each successive spray period.
- Liquid samples were taken from the sump at a frequency scheduled to produce the best evaluation of the liquid volume and iodine and hydrazine concentration. This time was generally 5 min before the end of the spray period.

- Following the last aerosol sample period, spray water was recirculated through the heat exchanger to expediate cool down. The last liquid sample was collected about 24 hours after test termination.
- Between tests, the vessel was sprayed successively with the remainder of the fresh spray solution, tap water and deionized water prior to 8 hrs of air purging.

4.2.1 Test Conditions

The general test conditions were designed as follows:

Test No. 1 - Isothermal at 280°F-, 12-7G3 nozzles-Burst I_2 release - 48 gal/min spray flow
Test No. 2 - Isothermal at 150°F, 12-7G3 nozzles-Burst I_2 release - 48 gal/min spray flow
Test No. 3 - Isothermal at 150°F, 3-1713A nozzles-Burst I_2 release - 45 gal/min spray flow
Test No. 4 - Decaying Temperature and Pressure from 280°F - 3-1713A nozzles, 1 hr I_2 release during recirculated spray flow of 45 gal/min.

Two types of spray nozzles were used during this study. The 7G3 nozzles were used in two of the tests to obtain data comparable to previous CSE experiments. The 1713A nozzles are the type used in most existing reactor containment spray systems. The goal of test T-2 and T-3 (duplicate conditions except for the nozzles) was to delineate significant differences in the spray effectiveness of the two types of nozzles.

For Tests 1, 2, and 3, four gas samples were taken at 5-min intervals, 5 min after iodine injection. This was followed by a 10-min fresh spray period, a 30-min gas phase sampling period, a 30-min fresh spray period and a 20-min sampling period. This was followed by five recirculated spray periods of 1 hr duration with 20-min sampling periods after each spray.

For Test 4, fresh solution was sprayed into the vessel for 45 min and then three gas samples were taken. Iodine aerosol injection was started simultaneously with recirculation of the vessel sump. Iodine was to be injected at a linear rate for 1 hr and the continuous spray period lasted for 2 hrs. Gas phase sampling was at 15-min intervals for the first hour and at 30-min intervals for the second hour. During the first period of spraying, hydrazine was fed into the spray water line at a rate equivalent to 50 ppm N_2H_4 concentration. Sodium hydroxide was injected into the spray water during each spray period thereafter to increase the pH to 7.0-7.5. Four 1-hr spray periods interspersed with 20-min gas sampling periods completed the experiment.

Test conditions used in each experiment are reported in tabular form. Table 2 lists the physical dimensions common to all experiments. Table 3 describes the spray nozzles used and Table 4 lists the atmospheric conditions prevailing during the fresh solution spray periods. Figures 8 through 11 are plots of the temperature and pressure history for the four experiments. The arithmetic average temperature shown for the main room was obtained from five thermocouples positioned as shown in Figure 1. Other room and liquid temperatures were from single thermocouple measurements. The individual thermocouples in the main room differed by less than 5°F at any time.

TABLE 2. PHYSICAL CONDITIONS COMMON TO ALL SPRAY EXPERIMENTS

Volume above deck including drywell	21,005 ft^3	595 m^3
Surface area above deck including drywell	6,140 ft^2	569 m^2
Surface area/volume	0.293 ft^{-1}	0.958 m^{-1}
Cross section area, main vessel	490 ft^2	45.5 m^2
Cross section area, drywell	95 ft^2	8.8 m^2
Volume, middle room	2,089 ft^3	59 m^3
Surface area, middle room	1,363 ft^2	127 m^2
Volume, lower room	3,384 ft^3	96 m^3
Surface area, lower room	2,057 ft^2	191 m^2
Total volume of all rooms	26,477 ft^3	751 m^3
Total surface area, all rooms	9,560 ft^2	888 m^2
Drop fall height to deck	33.8 ft	10.3 m
Drop fall height to drywell bottom	50.5 ft	15.4 m
Surface coating	All interior surfaces coated with phenolic paint(a)	
Thermal insulation	All exterior surfaces covered with 1-in. fiberglass insulation(b)	

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a. Two coats Phenoline 302 over one coat Phenoline 300 primer. The Carboline Co., St. Louis, Missouri.

b. k = 0.027 Btu/(hr)(ft^2)(°F/ft) at 200°F, Type PF-615, Owens-Corning Fiberglas Corp.

TABLE 3. NOZZLES USED IN SPRAY EXPERIMENTS

Runs T-1, T-2

Nozzle Type:	Spraying Systems Co. 3/4 - 7G3
Nozzle Characteristics:	Fog Type, full cone

Number	12	
Layout	Square Grid	(Figure 1)
Spacing	6 ft apart	
Pressure	40 psid	
Rated Flow	4 gpm	
MMD	1210 μ	
σ_g	1.5	

Runs T-3, T-4

Nozzle Type:	Spraying Systems Co. 1713-A
Nozzle Characteristics:	Hollow cone

Number used	3	
Layout	Triangular Grid	(Figure 1)
Spacing	∿12 ft apart	
Pressure	40 psid	
Rated Flow	15 gpm	
MMD*	1100 μ	
σ_g**	1.5	

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*Mass median diameter as reported by nozzle manufacturer.

**Geometric Standard deviation as reported by nozzle manufacturer.

TABLE 4. SPRAY CONDITIONS - FRESH SOLUTION

	Run 1	Run 2	Run 3	Run 4
Initial Conditions				
Temp., °F	280	154	146	281
Pressure, psig	46	4	3.5	44.8
1st Spray - Fresh				
Starting Time, t_o + t min	30	30	40	0(a)
Vapor Temp. °F	280	151	157	281
Pressure psig	46	3.6	4.25	44.8
Stopping Time, t_o + t min	40	40	50	45
Vapor Temp. °F	270	150	150	213
Pressure psig	43	3.5	4.0	17.5
Duration, min.	10	10	10	45
Total Flow Rate gpm	46	40.9	50.3	50.6
Volume Sprayed gal.	460	409	503	2276
2nd Spray - Fresh				
Starting Time, min.	70	70	75	67(b)
Vapor Temp. °F	278	149	153	212
Pressure, psig	47	3.6	4.15	17.3
Stopping Time, min.	100	100	105	185
Vapor Temp. °F	255	137	136	175
Pressure, psig	39.5	3.2	3.0	10.75
Duration, min.	30	30	30	118
Total Flow Rate gpm	45.9	40	49.1	50.2
Volume Sprayed gal.	1377	1200	1473	5923(c)

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a. Fresh solution sprayed to vessel prior to iodine injection.

b. Iodine injected during first hour of recirculated spray.

c. Recirculated spray for 118 min.

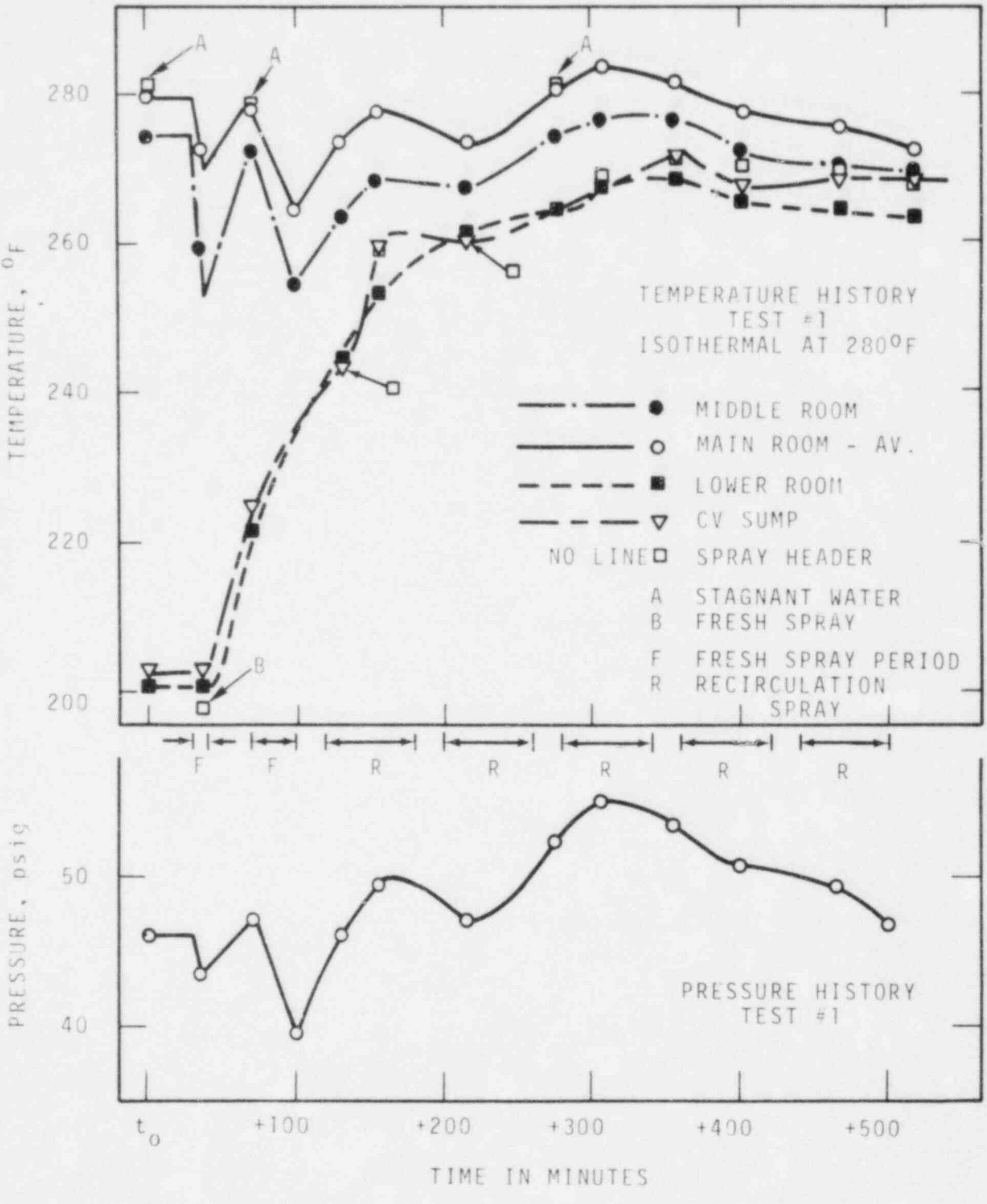

FIGURE 8. Temperature-Pressure History - Test T-1

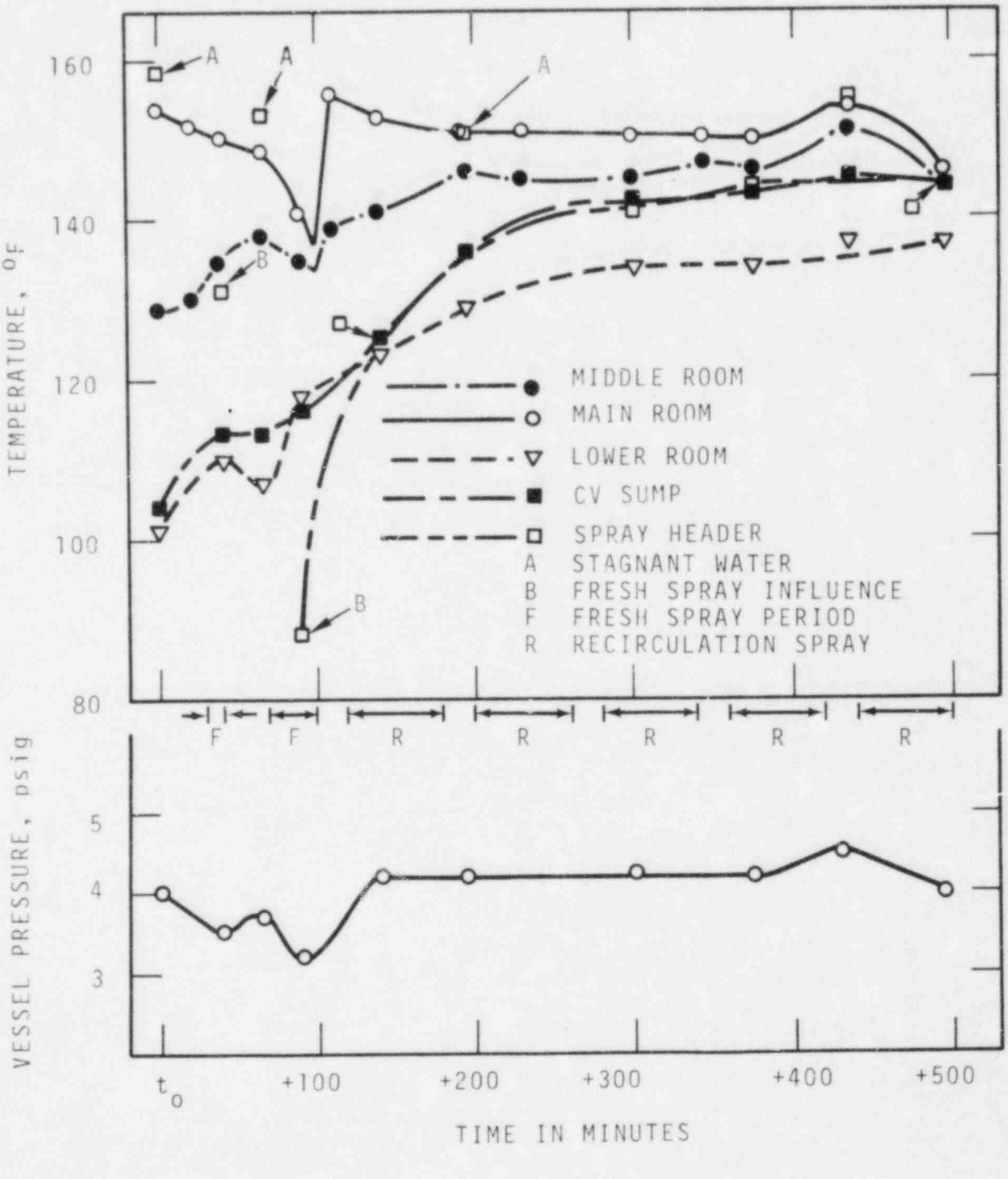

FIGURE 9. Temperature-Pressure History - Test T-2

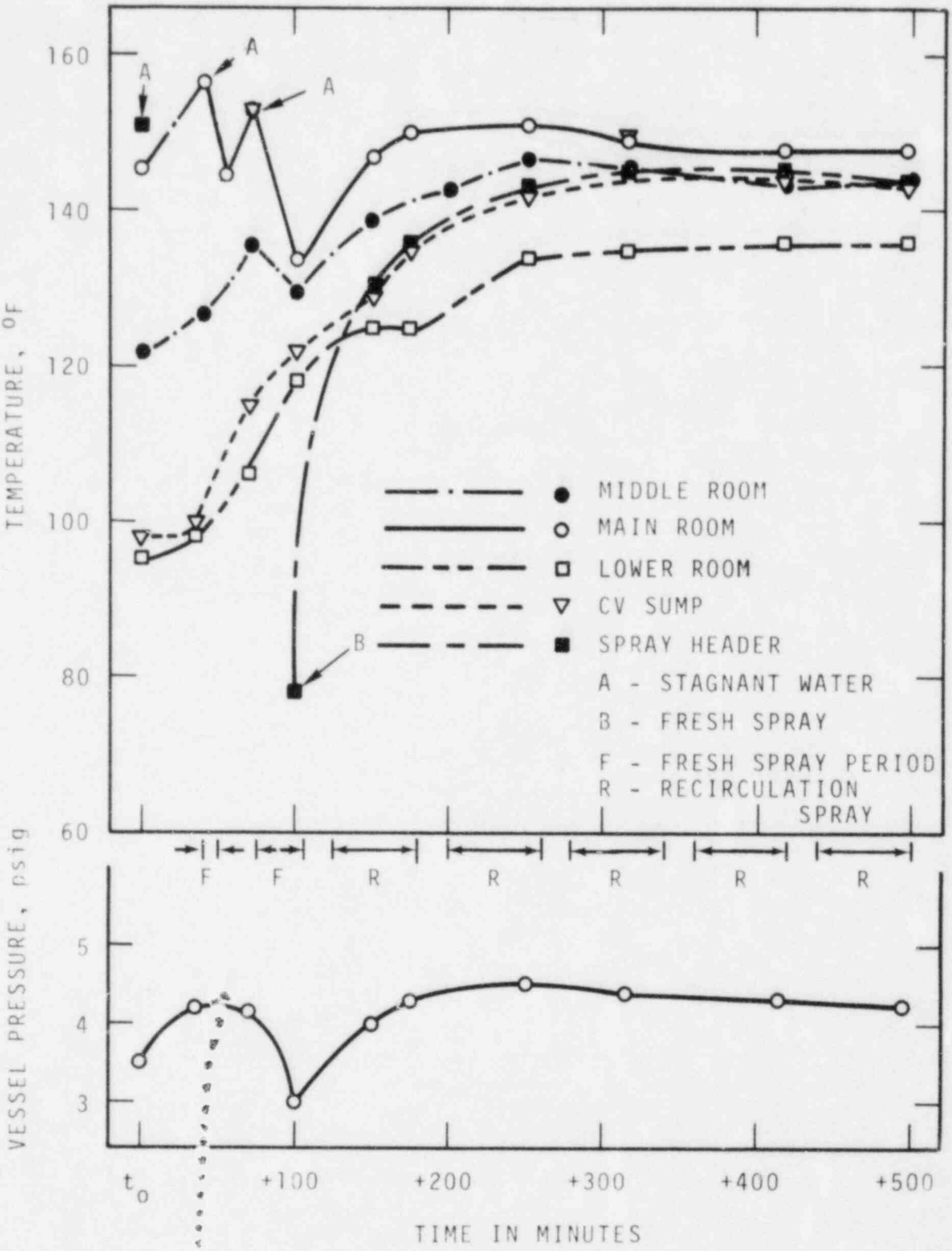

FIGURE 10. Temperature-Pressure History - Test T-3

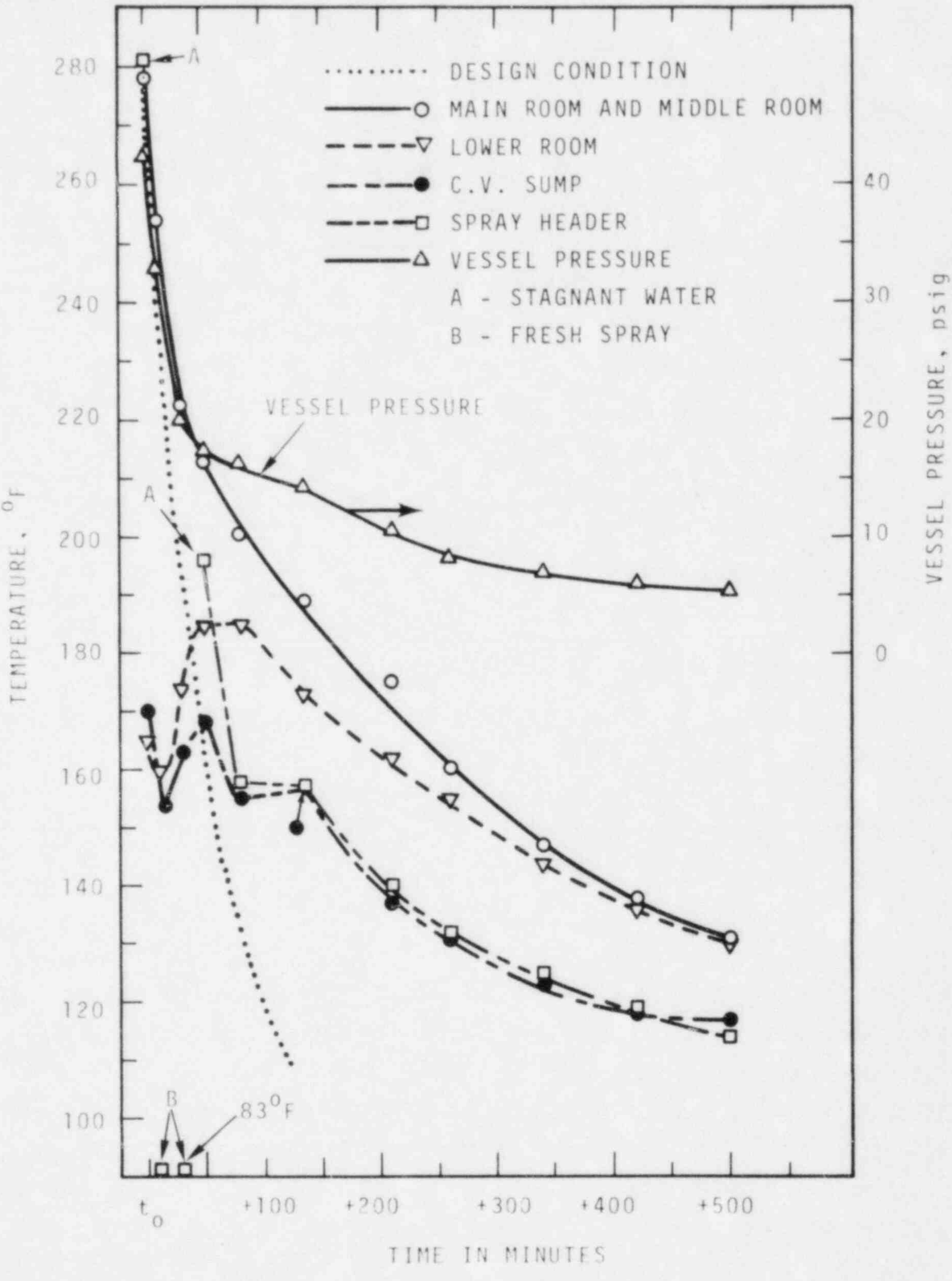

FIGURE 11. Temperature-Pressure History - Test T-4

5.0 EXPERIMENTAL RESULTS

5.1 GENERAL INFORMATION

5.1.1 Sampling

The airborne iodine concentrations for Tests 1-3 were measured prior to the first spray and between each successive spray period to obtain the aerosol depletion due to natural processes. Extrapolation of the resulting lines to the start and end of the spray periods provided concentration differences used to calculate washout half-lives.

For Test 4, aerosol injection during spraying, sampling was at 15 min intervals during the 67 min injection and then 30 min intervals to the end of the initial 120 min spray period. After that, samples were taken between each spray period. Thus, empirical data is available for comparison with theory on maximum I_2 concentration for prolonged release and the variation of partion coefficients as a function of time.

5.1.2 Treatment of Data

For conformity with previous experiments, only the Maypack samplers were used to obtain the average gas phase iodine concentration. The ANC samplers were used at selected times to obtain the HOI component. The data were plotted by principal components that tend to segregate the iodine species as follows: 1) "Total Iodine" is the sum of all Maypack components, 2) "Elemental Iodine" is the sum of the glass fiber filter and silver surfaces, since no particulates were injected, 3) "Inorganic Iodine" was defined as the total of the glass fiber and charcoal impregnated filter plus silver surfaces and 4) "Organic Iodine" (CH_3I), that retained by the KI impregnated activated charcoal. The iodine retained by the charcoal paper, plotted separately, may contain some I_2 and CH_3I as well as the HOI. The I_2 fraction retained by the charcoal paper would be insignificant with respect to other forms following the second spray period. The ANC copper sulfide bed plot was defined as HOI.

5.1.3 General Observations

The I^{131} activity on the silver screens downstream of the silver membranes was below detection after the final 10-min fresh spray and was significant only when the silver membranes were accidentally ruptured during pressurization of the sampling airlock. The majority of the failed filters ruptured during the higher pressure tests when the ball valves were difficult to move. When this occurred, segregation by species was precluded and only total iodine values were obtained.

5.1.4 Liquid Sampling

Pre-experiment tests with the recirculating spray pump (P-17) were conducted to obtain volume holdup as a function of spraying time. At a flow rate of 48 gpm at 40 psid, the holdup volume increased continuously up to about 100 min of spraying time after which the volume was constant. During periods of recirculation, the liquid samples were withdrawn about 5 min prior to pump shutdown in an effort to minimize the error in volume determination. The deck holdup volume plus the volume in the containment vessel sump generally over-estimated the contained volume. This was principally due to the uncertainty in the deck volume following the 20-min sampling periods between sprays. Erroneous volume values would effect only the material balance for iodine and not the partition coefficient $\left(\frac{C_l}{C_g}\right)$ after thorough mixing had occurred.

Generally, by the end of the second recirculated spray period (t_0 + 255 min) the originally highly distorted iodine concentration due to deck holdup had equalized and any reduction in concentration was a function of dilution from steam condensation or loss to the metal surfaces of the spray system. The iodine concentration in the liquid is shown in Appendix C.

5.2 RESULTS OF 280°F ISOTHERMAL TEST - TEST NO. T-1

(7G-3 Spray Nozzles)

The airborne iodine concentration was measured over an 8-hr period following release into the containment vessel. The average gas phase concentration of the iodine forms in the main room of the containment vessel are plotted against time in Figure 12 and tabulated in Appendix A. For clarity the statistical limits were shown for only a few of the data points at the concentration levels where they become a significant source of variance. These are the 95 percent confidence limits based on the sample countting rate and apply to all other points near the same concentration level.

The elemental iodine decreased with a half life of 1.4 min during the 10 min fresh spray period and 25.5 min during the following 30 min fresh spray. Other calculated half lives are shown in Table I, Appendix B. Elemental iodine slowly decreased during the first three recirculated spray periods and then remained approximately constant at a very low level to the end of the test. The HOI gas concentration decreased through the first recirculated spray period and then remained constant. Organic iodides appeared to decrease slowly with spray time. The apparent slight increase in organic iodides following the last spray period is not significant because the magnitude of the increase is within experimental error, and is at an extremely low concentration level.

5.3 RESULTS OF 150°F ISOTHERMAL TEST - TEST NO. T-2

(7G-3 Spray Nozzles)

The airborne iodine concentration was measured over an 8-hr period following release into the containment vessel. The average gas phase concentration of the iodine forms are plotted against time in Figure 13 and tabulated in Appendix A. As with Test 1, the limits shown are the 2σ limits based on the sample counting rate.

The elemental iodine decreased with a half life of 1 min during the first fresh spray period of 10 min. The half life during the 30 min fresh spray period was 32 min. Half lives calculated for other periods are listed in Table I, Appendix B. After the first 60 min recirculated spray period, the gas phase concentration of total iodine, inorganic iodine and HOI remained essentially constant. There was approximately an order of magnitude decrease in the HOI concentration during the fresh spray periods.

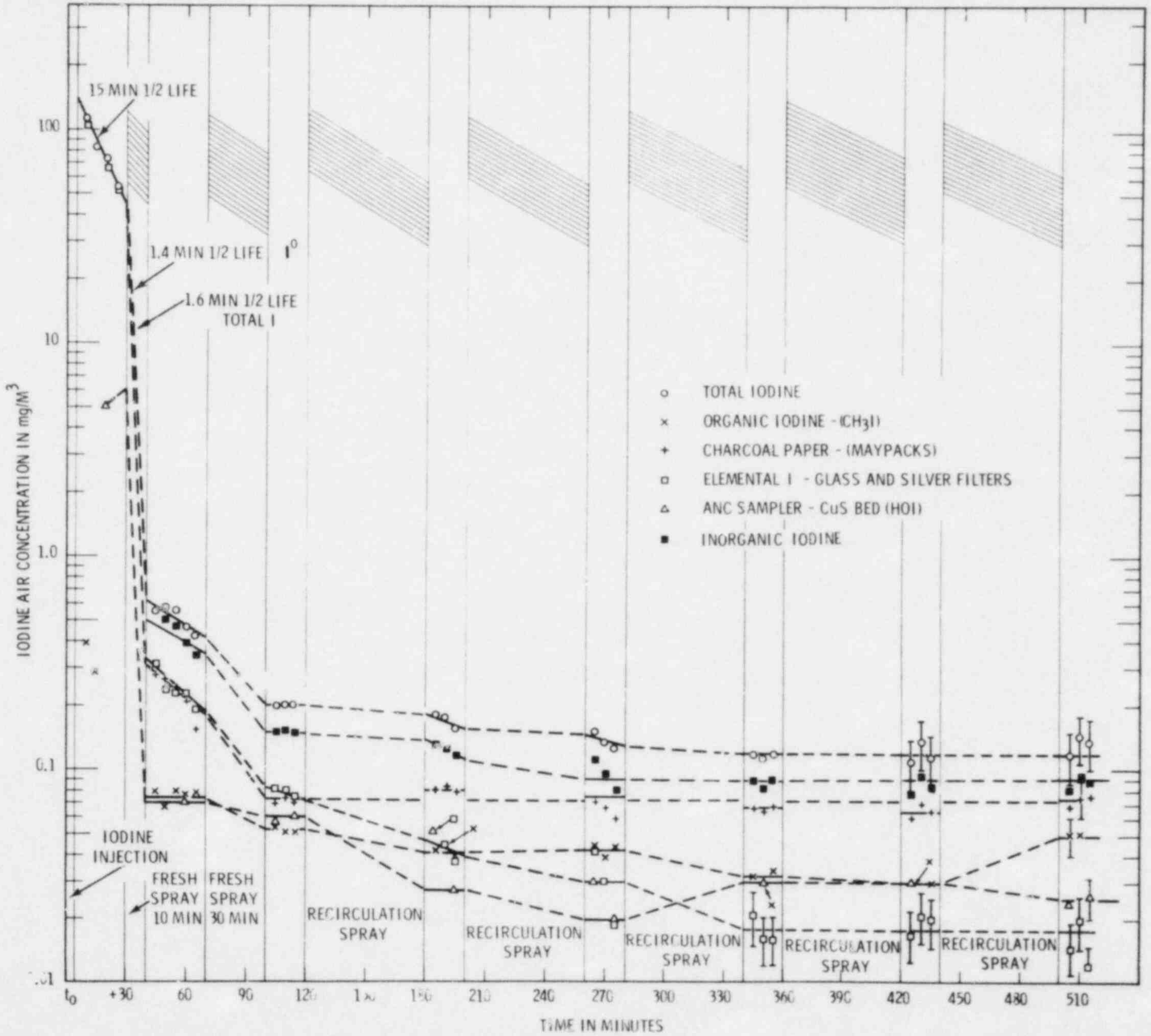

FIGURE 12. Gas Phase Iodine Concentration with Time - Test T-1

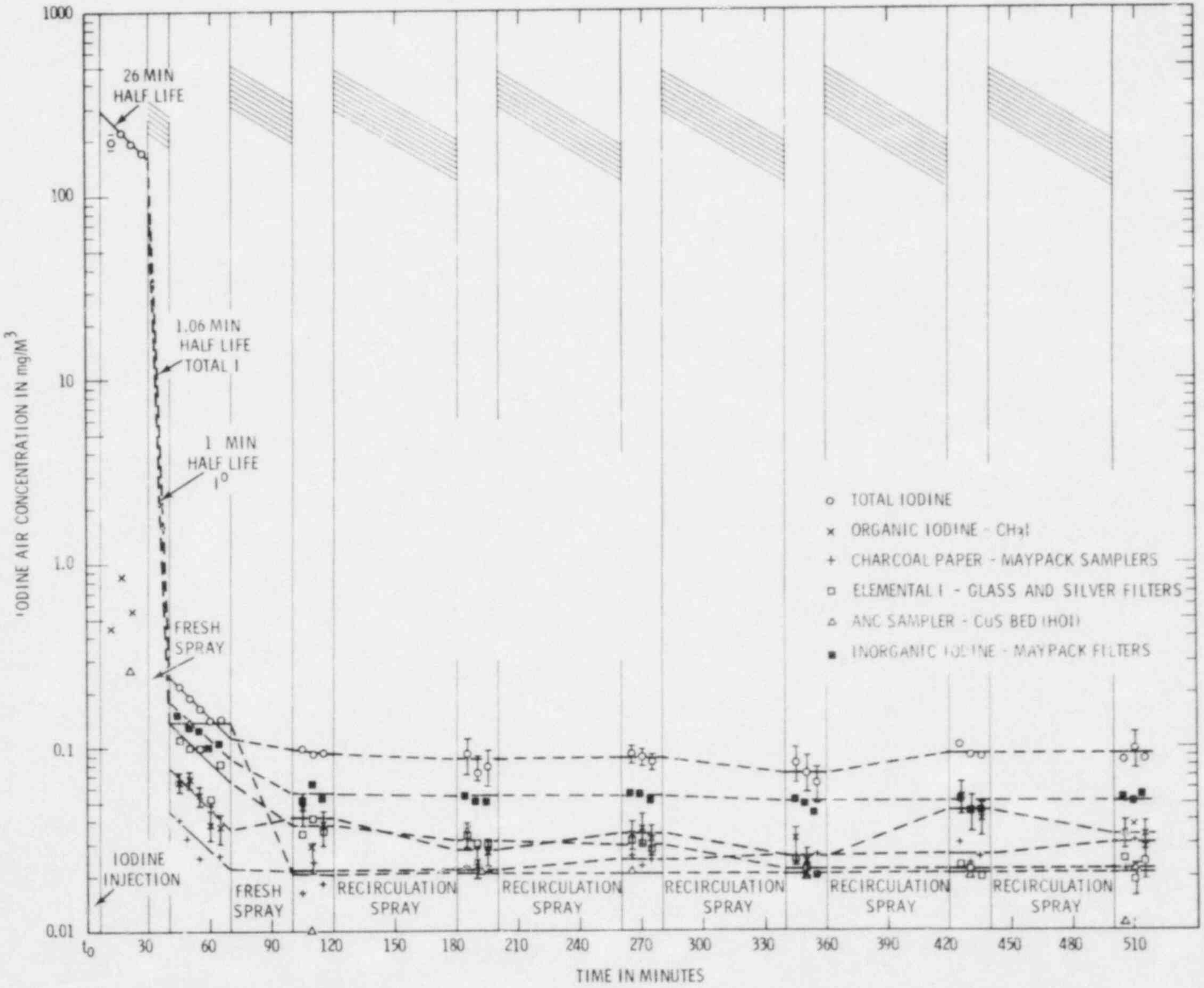

FIGURE 13. Gas Phase Iodine Concentration with Time - Test T-2

Elemental iodine decreased up to the end of the third recirculation period and then remained constant. Organic iodide concentration remained essentially constant following the second fresh spray period.

5.4 RESULTS OF 150°F IOSTHERMAL TEST - TEST NO. T-3
(1713A - Spray Nozzles)

Improper operation of a ball valve on the aerosol injection line occurred in this test. This resulted in a partial plugging of the severely reduced opening about 2 min into the injection period. Consequently, the injection period was extended and the weight injected was about 5 percent of that expected under normal conditions. While unplanned, this faulty valve operation provided a comparison of the spray washout rate with concentration for the three isothermal tests.

The gas phase iodine concentration was measured over an 8-hr period following the iodine injection into the vessel. The average gas phase concentrations of the iodine forms are plotted in Figure 14 and tabulated in Appendix A. Again limits shown are the 2σ limits based on counting rate of the samples.

The elemental iodine decreased with a half-life of 1.7 min during the first fresh spray period of 10 min. The half-life increased to 12.4 min during the 30 min fresh spray period. Half lives of other periods are tabulated in Table II, Appendix A. Elemental iodine and HOI gradually decreased after the first recirculated spray period while organic, inorganic and total iodine remained relatively constant at an extremely low level.

5.5 RESULTS OF THE SIMULATED EXTENDED I_2 RELEASE - TEST NO. T-4

The iodine injection period of 60 min during recirculation of fresh spray water depicted to a degree the conditions prevailing for a delayed release and an extended uniform source term. Sodium hydroxide was added to the recirculated spray water after the first 2-hr spray period to evaluate the effect on gas phase concentration of spray solution neutralization.

The gas phase concentration of iodine is plotted as a function of time in Figure 15 and tabulated in Appendix A. The total iodine concentration

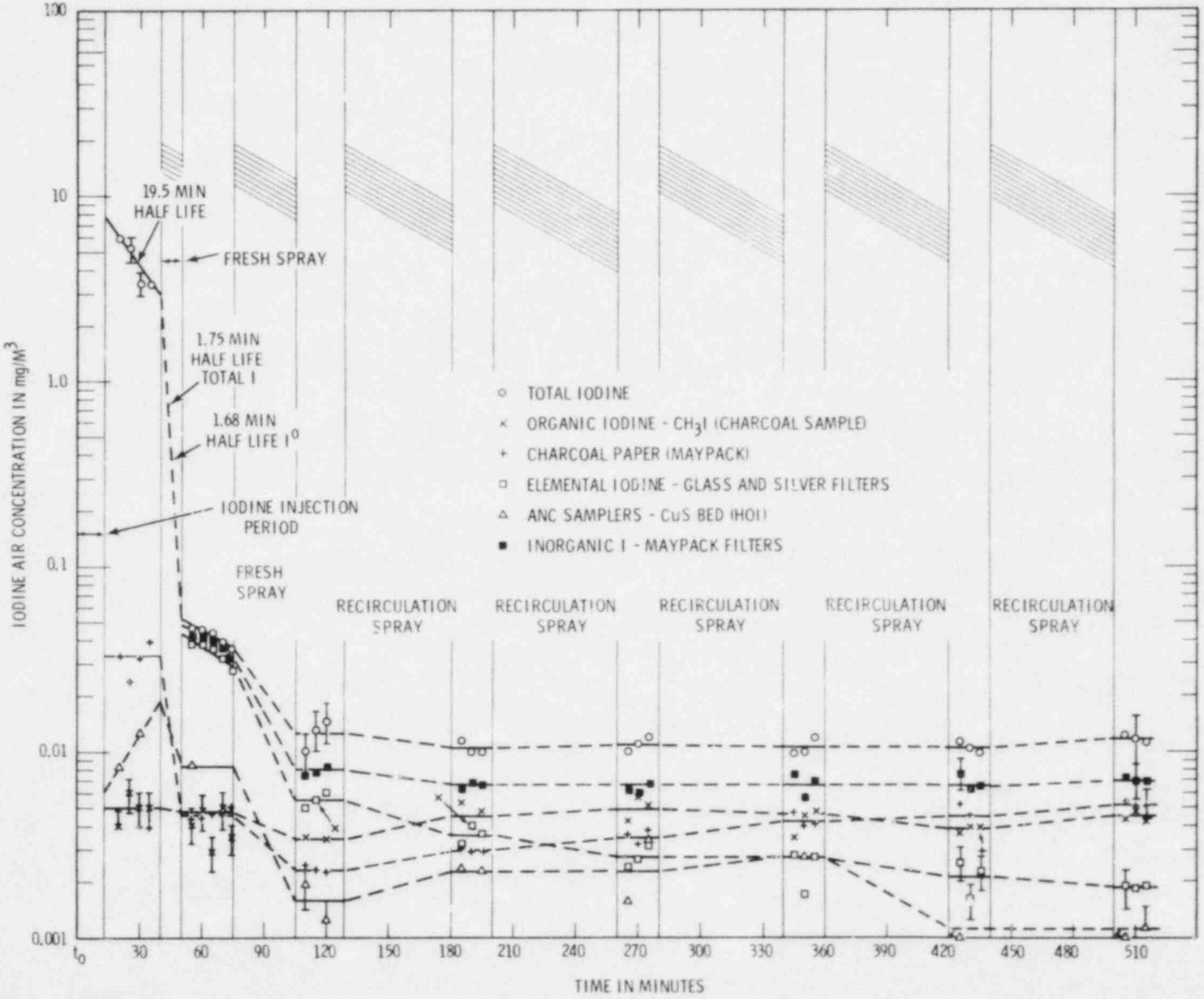

FIGURE 14. Gas Phase Iodine Concentration with Time - Test T-3

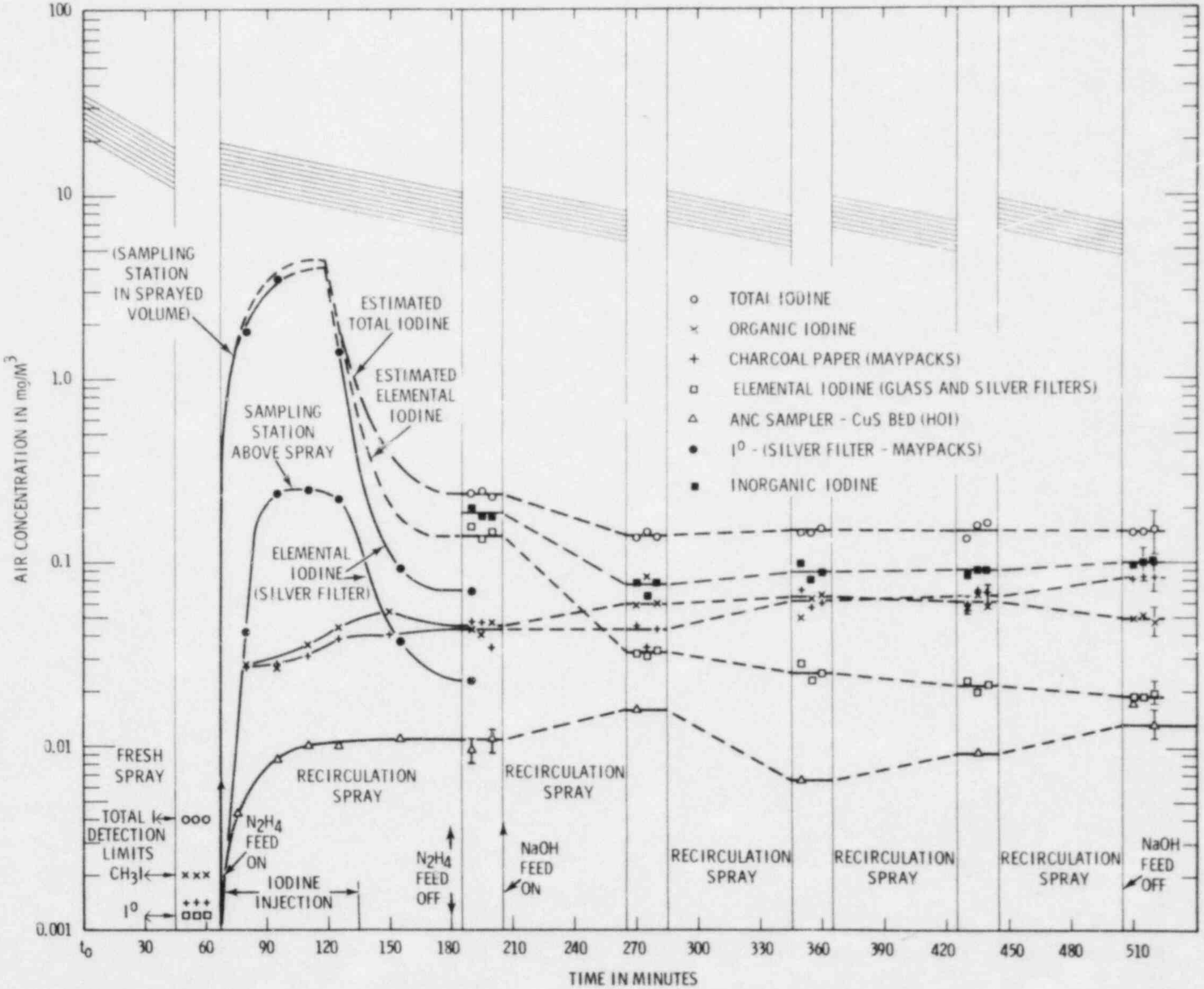

FIGURE 15. Gas Phase Iodine Concentration with Time - Test T-4

for the initial injection and spray period is uncertain due to contamination of the particulate filter with spray drops and mist. The minute discolored specs on some filters and the highly distorted ratios of particulate to silver filter activity were evidence of the problem. This necessitated the use of the silver membrane activity to estimate the gas phase concentration for total iodine. The ratio of iodine found on the particulate and silver membranes following the injection period of Test 1 was used to estimate the total and elemental iodine over the 2-hr period. Data for both Maypack sampling stations are shown because they were somewhat different. One was above the directly sprayed volume. This difference is explained by the injection of iodine directly into the sprayed volume. Under this condition and with the prevailing rapid removal rate, the gas escaping to the unsprayed region of the vessel would have a lower concentration than that deep in the sprayed region. This unequal gas phase distribution would disappear shortly after cessation of the first spray period. This behavior is confirmed by samples taken during that period of time. If the concentration difference is assumed to be real, a volume weighted average concentration for the two stations would be about 75 percent of that shown for the sprayed volume in Figure 15.

The second spray period produced a reduction in the gas concentration for total, inorganic and elemental forms, with what appears to be a slight increase in organic and HOI. However, the CH_3I and HOI concentrations were about equal at the end of the first spray period and at end of the test. After the third spray period all iodine forms except elemental and HOI remained constant. Elemental iodine concentration continued to decrease to the end of the test while HOI appeared to increase slightly with increasing pH. Based on the total iodine injected as measured by the liquid concentration, the fractions remaining airborne after the initial 2-hr spray periods and at the end of the test are shown in Table 5.

TABLE 5. AIRBORNE FRACTION OF IODINE SPECIES - TEST T-4
(fraction of injected iodine)

Iodine Forms	End of First[(A)] Spray Period	End of Test Period
Total	7×10^{-4}	5.1×10^{-4}
Elemental	4.3×10^{-4}	6.6×10^{-5}
Inorganic	6×10^{-4}	3.5×10^{-4}
Organic	1.3×10^{-4}	1.6×10^{-4}
HOI	4×10^{-5}	4.7×10^{-5}

A. One hour of spray during injection plus one hour following injection--two hours of continuous spraying

These results demonstrate the effectiveness of iodine removal by hydrazine-containing sprays. Less than 5.1×10^{-4} of the total iodine injected was airborne at the end of the 8-hr test. This is lower by a factor of 80 than would be calculated from AEC Regulatory Guides(2) by adding the organic iodide fraction (4 percent) to the spray cut-off limit for elemental iodine (0.1 percent).

5.6 COMPARISON OF SPRAY WASHOUT RATES, λ_s

The spray washout rates for elemental iodine for Tests 1, 2, and 3 were calculated for the 10-min fresh spray period using the equation

$$\frac{C_g}{C_{go}} = e^{-\lambda_s t} \qquad (30)$$

where

C_{go} = gas concentration of iodine at start of spray

C_g = gas concentration of iodine at end of spray

t = length of spray period in minutes.

To compensate for natural depletion processes during spray, λ_s was adjusted by the equation

$$\lambda_{obs} = \lambda_s + \lambda_{NT} \tag{31}$$

where

λ_s = corrected washout rate

λ_{obs} = observed rate for spray period

$$\lambda_{NT} = \frac{\lambda_i + \lambda_f}{2} \tag{32}$$

where

λ_i = observed depletion rate before spray

λ_f = observed depletion rate after spray

The rate constants, λ_s, measured in the present study are compared with those obtained from previous CSE tests using caustic and boric acid sprays in Table 6. The PWR washout rate constants shown in Table 6 were calculated from the observed rate constants using the PWR spray parameters of 3000 gpm flowrate and 2×10^6 ft^3 volume (F and V respectively) in Equation 5. These latter values should be conservative due to greater drop fall height of PWR vessels and for Tests 1 and 2 due to the larger drop size (1210) of the 7G-3 nozzles used in Tests T-1 and T-2.

The hydrazine traced sprays have comparable removal rates for PWR spray parameters to that predicted by Postma(1) from equilibrium studies (0.38 min^{-1}). For CSE parameters hydrazine sprays were equal to or better than sodium hydroxide sprays and were significantly better than boric acid with an unknown impurity (Test C-1).(5)

The washout spray rates shown are values for the first 10-min spray period. Because of the very fast washout rates, the airborne iodine concentration decreased by factors of the order of 2^{10}, and this great reduction factor leads to a slowing in the observed removal rate. Therefore, the

10-min average removal rate which was measured, was likely somewhat slower than the initial rate of removal. The 10-min period was chosen because many earlier CSE tests used 10-min spray periods.

TABLE 6. COMPARISON OF SPRAY WASHOUT RATES FOR ELEMENTAL IODINE

Run No.	Spray Flow GPM	Temp. °F	Conc. C_{go}* mg/M^3	Drop MMD μ	Washout λ min^{-1}	PWR λ-min^{-1}
			1500 ppm B as H_3BO_3 + 50 ppm N_2H_4			
1	46	280	44	1210	0.46	0.314
2	40	150	150	1210	0.682	0.54
3	50	150	3	1100	0.394	0.3
			3000 ppm B as H_3BO_3 + NaOH, pH 9.5			
A-4	49	77	38	1210	0.495	
A-6	49	250	21	1210	0.33	
			3000 ppm B as H_3BO_3			
C-1	160	249	75	1100	0.21	
A-7	49	249	25	1210	0.347	

---

*Iodine concentration in gas phase at start of spray.

5.7 COMPARISON OF SPRAY WASHOUT RATES WITH GAS PHASE IODINE CONCENTRATION

The spray washout constants observed suggested a concentration dependence overriding the other influencing differences between the test conditions of temperature, pressure and drop size. This led to a plot of the gas phase concentration at spray initiation against the spray washout rate observed as shown in Figure 16. In preparing this plot, differences in drop sizes and temperatures were not accounted for. From chemical considerations, the washout rate would not increase beyond an iodine concentration where the reaction would be limited by hydrazine availability.

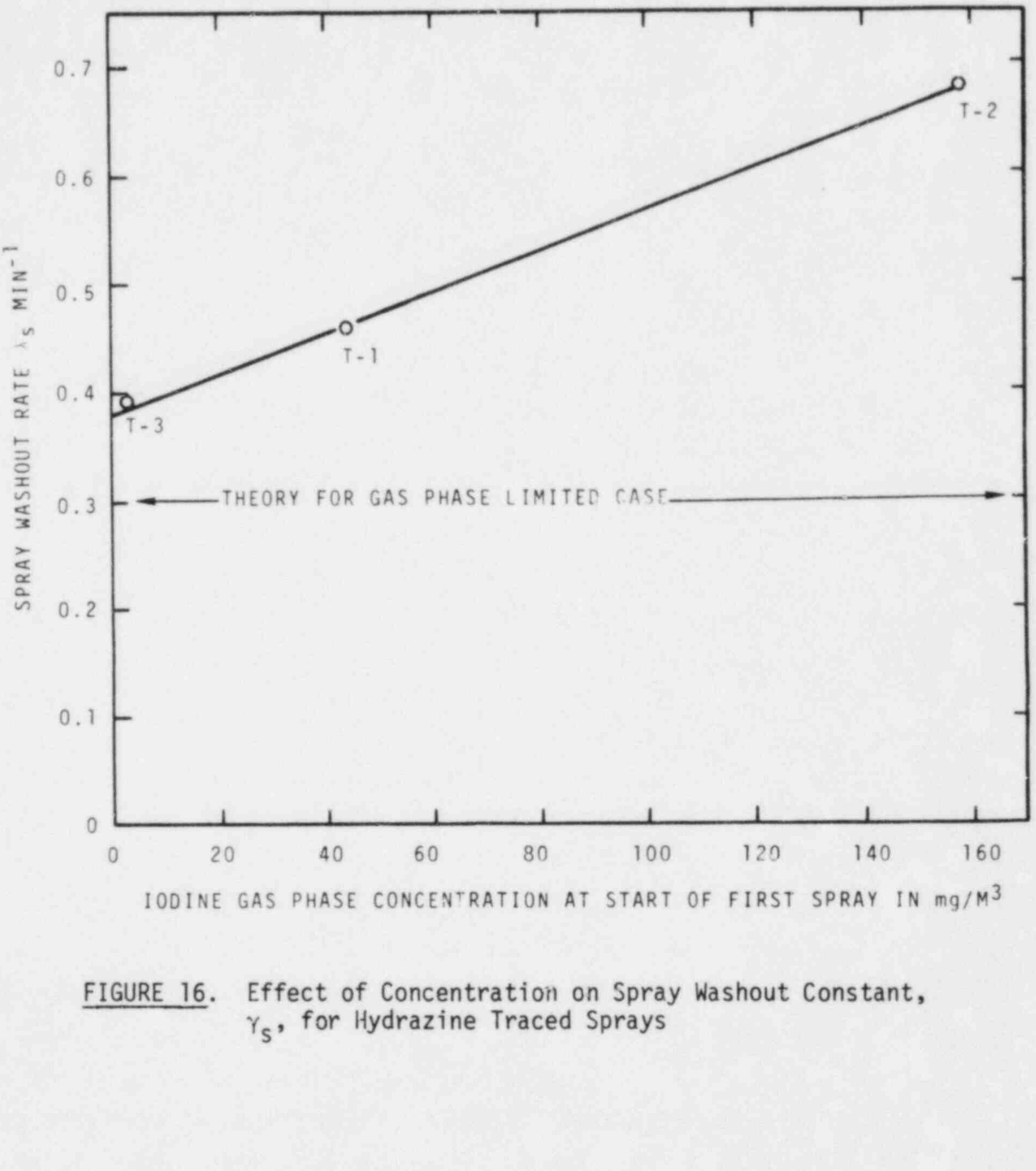

FIGURE 16. Effect of Concentration on Spray Washout Constant, γ_s, for Hydrazine Traced Sprays

The iodine concentration for a PWR under LOCA conditions has been conservatively estimated at 90 mg/M^3. Then from Figure 16 the spray washout rate for 90 mg/M^3 of 0.555 can be related to the spray parameters for the standard PWR. This calculation produced a λ_s = 0.358 and a 2 hr DRF based on 10 percent cutoff of 8.3--comparable to the predicted 8.4 based on Postma's(1) equilibration studies or a 2 Hr DRF of 16 based on 4 percent cutoff. This spray washout rate calculated for a PWR would be highly conservative since only the spray parameters F and V were taken into consideration and not the drop fall height which is about a factor of 3 greater than that of CSE.

5.8 FORMATION AND DEPLETION OF ORGANIC IODIDES AND HYPOIODUS ACID

Previous studies as well as theory have shown that organic iodides (CH_3I) and Hypoiodus acid (HOI) would be removed from the gas phase at a much slower rate than other iodine species generated during a LOCA; CH_3I due to the limiting liquid mass transfer coefficient and HOI due to its volatility. In caustic sprays HOI would be the major iodine specie in solution and consequently its volatility could be important where the high pH is used to increase the partition coefficient. The mechanisms of reaction between hydrazine and iodine, studied by Sen Gupta and Sen Gupta(8), showed that the reacting species was HOI. Thus the degree of HOI volatility for hydrazine sprays is of no concern even with complete degradation of the hydrazine with time since the reaction has been shown to be irreversible. To support this evidence and relate it to LOCA conditions, ANC samplers, which were shown by Keller et al.(10) to be more specific for HOI separation, were used at selected times.

The fractions of injected iodine which appeared as HOI in the ANC samplers are listed in Table 7. Generally, the HOI fractions are less than 0.1 percent, a very low level. Washout of HOI by hydrazine spray was apparent in Test T-1, T-2, and T-3. The initial concentration of HOI in Test T-1 was singularly high compared to the other test results. The hydrazine spray effectively removed the HOI, and by the end of the first spray, the airborne HOI concentration was only 0.044 percent of the injected iodine. The first spray apparently reduced the HOI concentration by a factor of 84. Therefore, when HOI is present in appreciable levels, it is rapidly removed by the hydrazine spray. It is possible that sodium hydroxide sprays would also have removed the HOI component. This is supported from the fact that no slowly removed species (except injected CH_3I) equivalent to 3.7 percent of injected iodide were found in any of the earlier CSE tests.

TABLE 7. ORGANIC IODINE AND HYPOIODUS ACID IN THE GAS PHASE (in percent of total iodine injected)

Sampling Time	Test Number							
	T-1		T-2		T-3		T-4	
	CH_3I	HOI	CH_3I	HOI	CH_3I	HOI	CH_3I	HOI
Before first spray	0.25	3.7	0.22	0.1	0.05	0.19		
Maximum during first spray							0.02	0.004
After first spray	0.05	0.044	0.025	0.045	0.047	0.085		
After third spray							0.023	0.0023
End of test	0.03	0.015	0.021	0.007	0.047	0.012	0.017	0.0047

In Test T-4 the HOI increased during the 1-hr injection period to about 0.004 percent and remained constant to the end of the 2-hr spray period. The subsequent fluctuations in the concentrations are not significant since all fall within the error limits and the final concentration is about equal to the initial maximum value.

It should be pointed out that the results obtained for HOI cannot be considered unequivocal. First, there are still questions remaining regarding the existence of HOI and its behavior in samplers. Second, the 3.7 percent concentration was indicated by only a single sample. Therefore, the interpretation of the data in terms of washout rate is questionable. The only firm conclusion which is borne out by the present data (and all past CSE spray results) is that if HOI is formed in appreciable quantities, then it is rapidly removed by sprays.

The fractions of CH_3I calculated for this series of tests are listed in Table 7. The values shown are based on the total iodine injected into the vessel and the measured gas concentration of CH_3I at the designated sampling times. In Test T-1 the measured CH_3I concentration appeared to decrease with time from about 0.25 to 0.03 percent during the test period with the major reduction occurring during the fresh solution spray periods. A similar behavior was observed for Test T-2. The CH_3I concentration remained essentially constant throughout Test T-3 and T-4 at about 0.05 and 0.02 percent. Obviously, the major CH_3I concentration changes coincided with those of total iodine in the gas phase, but only for the two tests having significantly higher initial iodine concentration. This, coupled with the known lack of complete discrimination of iodine species by the samplers and probable minimal formation of CH_3I in the vessel led to the anticipated conclusion that hydrazine traced sprays have little, if any, affinity for organic iodides.

At the end of the 8-hr tests, the total iodine remaining in the gas phase is less than 0.1 percent of the total iodine injected. Therefore, if one were to use a mathematical model to apply the results to larger containment vessels, the cut-off concentration should be equal to or less than 0.1 percent of the release concentration (grams released/total gas volume).

5.9 COMPARISON OF SPRAY EFFECTIVENESS

5.9.1 Initial Fresh Spray Periods

Initially, elemental iodine was the major component in the gas phase. For a given spray drop, it's iodine enrichment at the end of the fall height compared to the gas phase concentration is a measure of its removal effectiveness. This ratio of liquid to gas concentration was calculated from the spray flowrate and the observed time averaged washout rate, using

$$\frac{C_\ell}{C_g} = \frac{V}{F} \lambda_s \qquad (34)$$

where

λ_s = measured spray washout coefficient for spray only

V = gas volume

F = spray flowrate

The drop enrichment calculated from Equation 34 is compared to absorption theory in Figure 17 for the fresh spray periods of the three burst release tests.

Two of the three tests showed the effectiveness of the spray drops exceeded the perfect sink models. In the other test, the measured rate was 85 percent of the perfect sink theory, which is within the expected errors for the empirical data and the theoretical prediction. The measured values of $\frac{\lambda_s V}{F}$ are ordered by concentration.

5.9.2 Recirculated Spray Periods - At Equilibrium

For longer periods of time, when a pseudo equilibrium exists between the liquid and gas phases, the ratio of the concentration of the solute in the two phases is a measure of overall spray effectiveness for recirculated spray periods. The relatively short duration of these tests, coupled with the length of time for all liquid in the vessel (floor hold-up plus sump) to become well mixed, limited the time span for comparison with other experiments. The partition coefficients for elemental iodine were calculated using the equation

$$H_e = \frac{C_{\ell e}}{C_{ge}} \tag{35}$$

where

H_e = partition coefficient at "equilibrium"

$C_{\ell e}$ = total iodine in liquid at "equilibrium"

C_{ge} = elemental iodine in gas phase at "equilibrium"

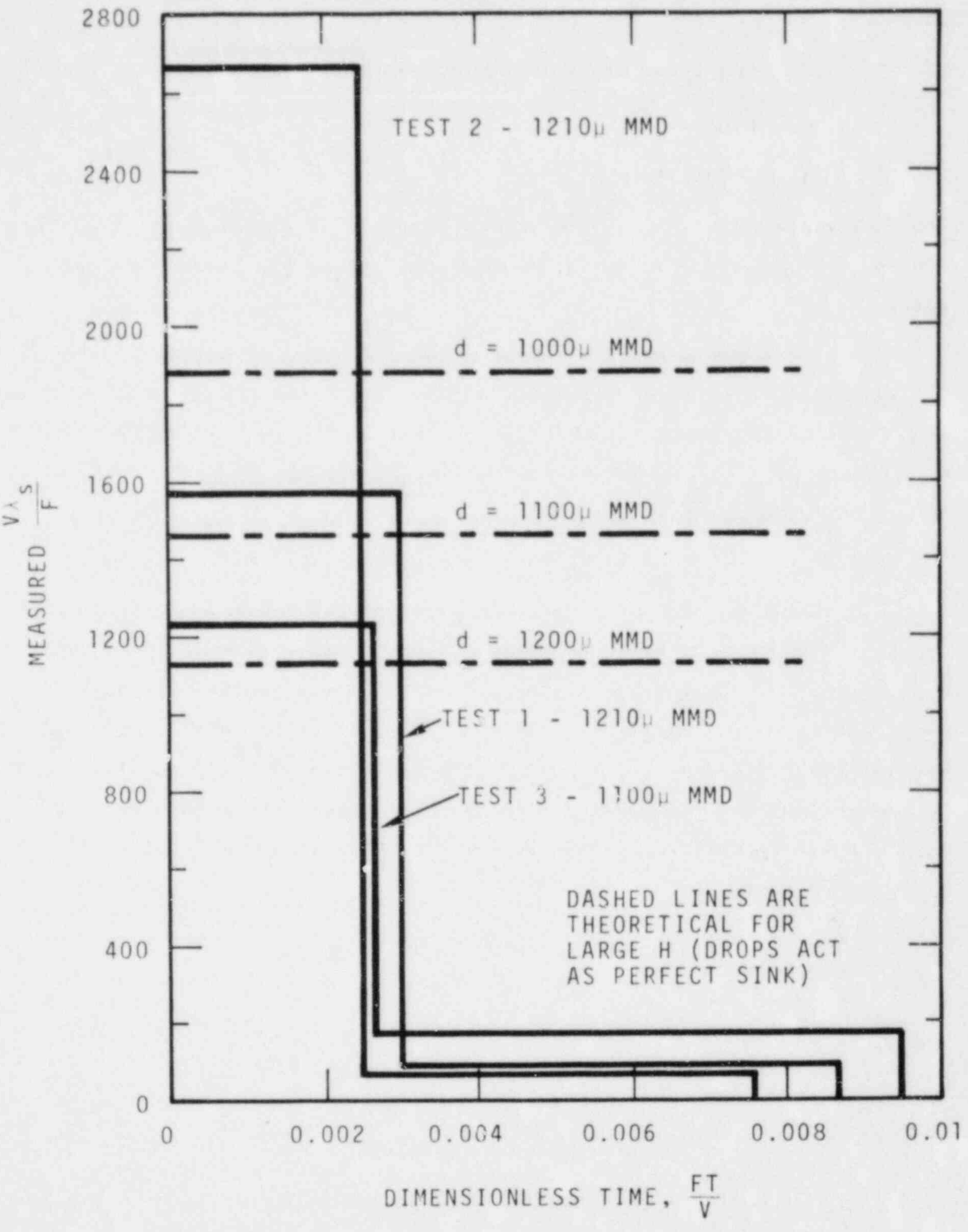

FIGURE 17. Spray Drop Effectiveness for Tests 1-3 1500 ppm B as H_3BO_3 + 50 ppm N_2H_4

and are compared with those for boric acid and caustic sprays of previously reported(5,15) CSE runs (C-1 and A-10) in Figure 18. Elemental iodine was used for comparison with the caustic and boric acid spray solutions.

The observed very high partition coefficients, greater than 100,000, illuminates the advantage of hydrazine traced sprays. The apparent influence of concentration is again illustrated by the long term pseudo equilibrium with the pseudo equilibrium coefficient being higher for higher iodine concentrations. The term pseudo equilibrium arises from the timewise formation of the ionic species which progressively removes the iodine in the liquid from equilibrium with the gas phase.

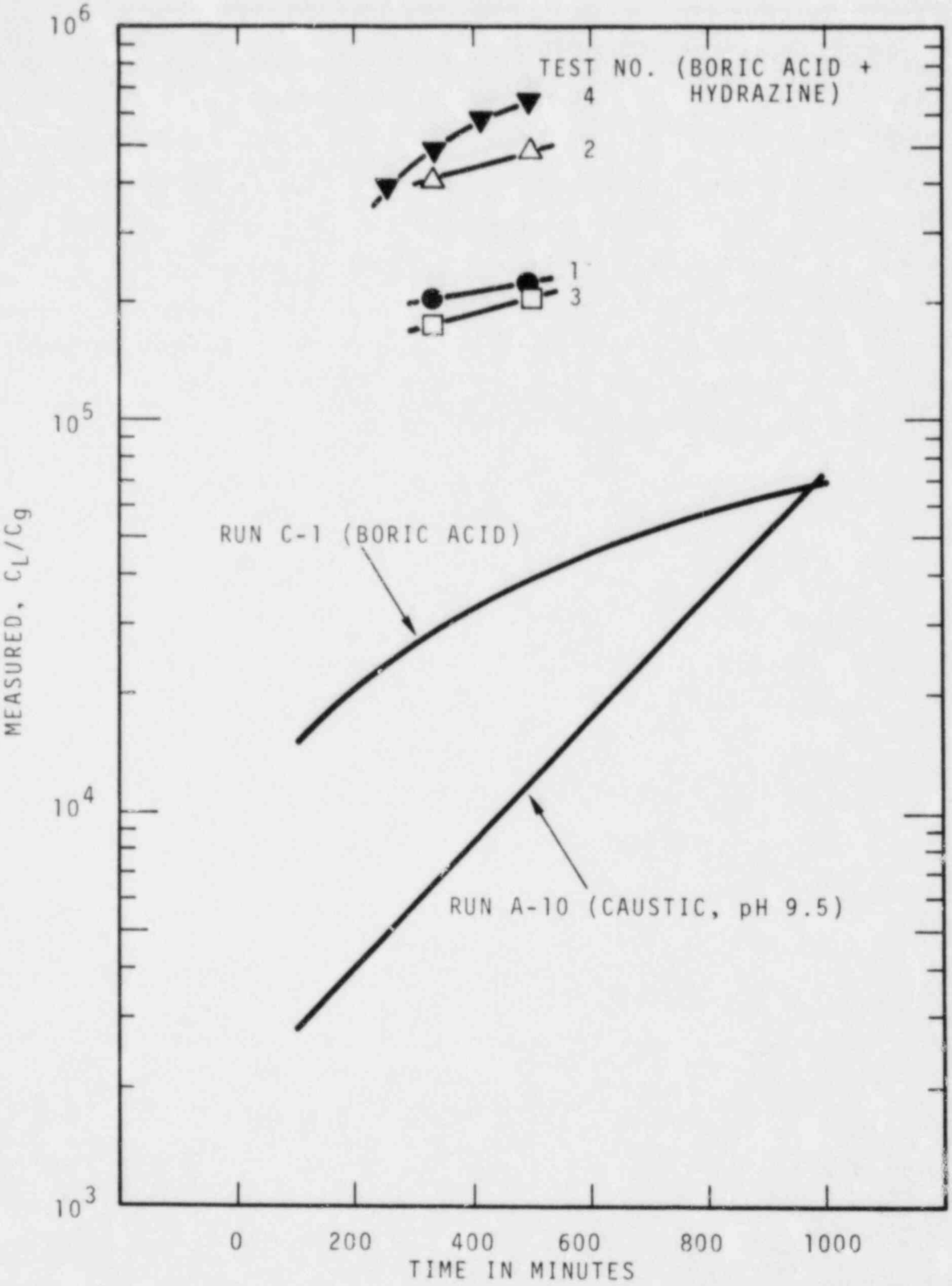

FIGURE 18. Partitioning of Elemental Iodine by Recirculated Sprays

6.0 COMPARISON OF HYDRAZINE TRACED SPRAYS WITH THEORY

6.1 OBSERVED SPRAY WASHOUT COEFFICIENTS WITH THEORY - TESTS T-1, T-2, and T-3

The spray washout rates observed for tests T-1, T-2 and T-3 can be compared with theory using the following equations:

for stagnant film model$^{(17)}$

$$E_{\text{Stag Film}} = 1 - \exp - \left[\frac{6\ k_g\ t_e}{d\ (H_o + \frac{k_g}{k_L})}\right] \qquad (36)$$

for well mixed model

$$E_{WM} = 1 - \exp - \left[\frac{6\ k_g\ t_e}{d\ H_o}\right] \qquad (37)$$

where

k_g = gas phase mass transfer coefficient,

k_L = liquid phase mass transfer coefficient = $\frac{2\Pi^2 D_L}{3d}$,

where

D_L = Diffusivity of iodine in the liquid,

d = drop diameter

t_e = drop exposure time,

H_o = partition coefficient,

E = drop absorption efficiency.

Drop adsorption efficiency is related to the spray washout rate λ_s by

$$\lambda_s = \frac{F\ H_o E}{V} \qquad (5)$$

where

F = spray flowrate, volume

V = gas phase volume

Equations (36) and (37) account for back pressure where saturation of the drop occurs.

For large partition coefficients (H of 10^4) the stagnant film model and the well mixed model yield similar predictions. The spray washout rates calculated by Equation (37) for Tests T-1, T-2 and T-3 conditions are compared with the observed rates in Table 8.

TABLE 8. COMPARISON OF OBSERVED SPRAY WASHOUT RATES WITH THEORETICAL PREDICTIONS - TESTS T-1, T-2, T-3

		Theory Prediction $H = 10^4$		
Test	Observed λ_s	Well Mixed Model λ_{WM}	Drop Size MMD	Spray Flow-GPM
T-1	0.46	0.30	1210μ	46
T-2	0.68	0.360	1210μ	40
T-3	0.40	0.45	1100μ	50

The observed washout rates are higher than theoretical except for Test T-3, where observed and theory agree within expected error bounds. The ratio of λ_{WM} for test experimental conditions $\frac{T\text{-}2}{T\text{-}1}$ and $\frac{T\text{-}3}{T\text{-}2}$ is a measure of the difference that would be expected from differing experimental parameters between the observed spray washout rates for the same tests. Since the observed ratios are significantly different from theory some other phenomenon which is related to gas phase concentration significantly altered the rate constants.

Previous CSE experiments as well as theory show that the spray washout rate is not a function of concentration for the range considered here. Since theoretical limiting washout rates were exceeded in two of the three tests, the possibility of two reaction mechanisms existing e.g., liquid phase and gas phase reactions is suggested. If some hydrazine under the test conditions is available for a gas phase reaction and reactant particles are formed, then two mechanisms would contribute to the spray washout rate since the washout rate of particles can also be large. Unlike liquid-gas phase mass transfer the particle washout rate is a function of iodine concentration because formation rate and size of particles would depend on airborne iodine concentration. Consequently the higher the gas phase concentration the higher the overall washout rate constant. The actual occurrence of the formation of particulates is illustrated by the fraction of iodine found on the particulate filters. Past CSE experience has shown that in the absence of particulates, about 10 percent of the gas-phase elemental iodine was retained by the glass fiber particulate filters. In the hydrazine spray tests the ratio of iodine on the particulate to silver membrane filters increased from 10 percent prior to spray to 50 percent following the first spray and then decreased with each successive spray to about 10 percent. The argument for two reaction mechanisms is also supported by the observed increase in λ_s with increasing concentration.

Since the concentration dependency appears to involve a second washout mechanism, application of the results to larger systems using a drop absorption model will be conservative in that one potentially important mechanism will have been neglected.

6.2 COMPARISON OF ELEMENTAL IODINE WASHOUT WITH THEORETICAL PREDICTIONS FOR RUN 4

The gas phase concentrations of elemental iodine observed in Run 4 are compared with those produced by simple models of spray washout in Figure 19. The run is divided into two time periods, each of which require a separate expression developed from a common differential equation which is subjected to different boundary conditions in each time period.

In the first time period the iodine is simultaneously released and scrubbed by a spray containing free hydrazine. For this time period the gas phase concentration of elemental iodine may be represented by the equation

$$C_g = \frac{W_o}{Vt_r}\left[tf_{nr} + \frac{f_{I_2}\left(1-e^{-\lambda t}\right)}{\lambda}\right] \tag{38}$$

where

W_o = mass of iodine released,
V = volume of gas space,
t_r = time of continuous release,
t = time from beginning of release,
f_{nr} = fraction of iodine present as a non-removable species,
f_{I_2} = fraction of iodine present as elemental iodine,
λ = removal rate constant for elemental iodine.

After iodine release has stopped, elemental iodine will be removed exponentially. Mathematically, this is described by

$$C_g = \frac{W_o}{V} \left[f_{nr} + \frac{f_{I_2}}{\lambda t} \left(1 - e^{-\lambda t_r} \right) e^{-\lambda C^{(t-t_r)}} \right] \quad (39)$$

These expressions were evaluated for Run T-4 using the following input parameters.

Wo = 200 grams
$V = 751\ M^3$
t_r = 60 minutes
$f_{nr} = 0.001$
$\lambda = 0.37\ \text{min}^{-1}$
$f_{I_2} = 0.999$

Results of the calculations are compared with experimental data in Figure 19. The good agreement between the measured gas concentration and those predicted by the well-mixed drop model confirms that hydrazine spray works as effectively for a prolonged source term during the recirculation mode as for a puff iodine release. The cut-off concentration level of $0.001C_R$ appears conservative by an order of magnitude.

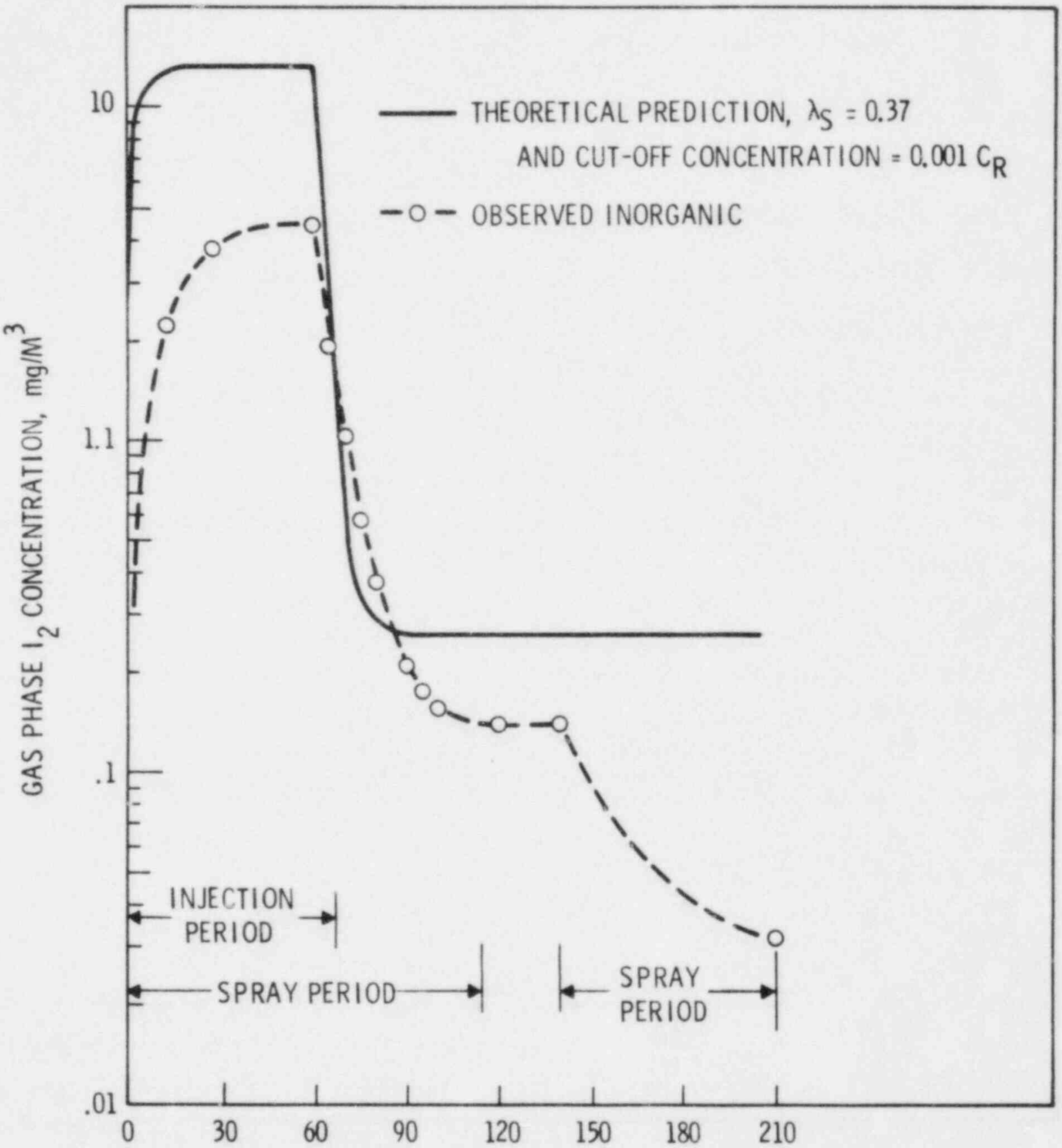

FIGURE 19. Comparison of Observed and Theoretical Spray Washout for Test T-4

The iodine generation rate and spray liquid concentration as a function of time is shown in Figure 20. The liquid concentration early in the spray period is biased to the low side due to dilution in the C.V. sump and hold up of the undiluted spray water on the deck of the main room as discussed previously.

Actually the value of H_o is obtained from the observation that the above equations predict a lower limit of removal of elemental iodine for $t \gg t_r$ of

$$C_g \underset{\text{lower limit}}{=} \frac{W_o}{V}\left(\frac{V/_{LH_o}}{1 + V/_{LH_o}}\right) \tag{40}$$

This assumes that the gas and liquid volumes come to equilibrium within the vessel (i.e. the gas phase iodine and the reacted iodine in the liquid) and no iodine is subsequently removed from the liquid by absorption on the metal. If we assume this lower limit is 0.1 mg/M^3, one obtains a value of $H_o = 2.1 \times 10^5$.

The calculated iodine concentration during the first period, using the values of the parameters listed above, is about twice that which was measured and the build up to a near-constant concentration level is more rapid than was observed. The explanation for this apparent discrepancy in the model is believed to be that the iodine is introduced into the containment vessel as a very concentrated gas stream from the generating station. Although mixing is relatively rapid within the vessel, the time-constant for mixing is probably longer than the time-constant for removal. Thus, the removal rate in the vicinity of the iodine release is much more rapid than it would be if the iodine were instantly mixed throughout the vessel. Consequently, the iodine concentration that is reached in the vicinity of the sample stations is considerably less than would be predicted by the simple model. Conversely, after the iodine release is terminated, mixing is still going on in the vessel and the decay rate (again in the vicinity of the samplers) is slower than predicted by the simple model because of continuing transport of iodine to the sample location by the mixing process.

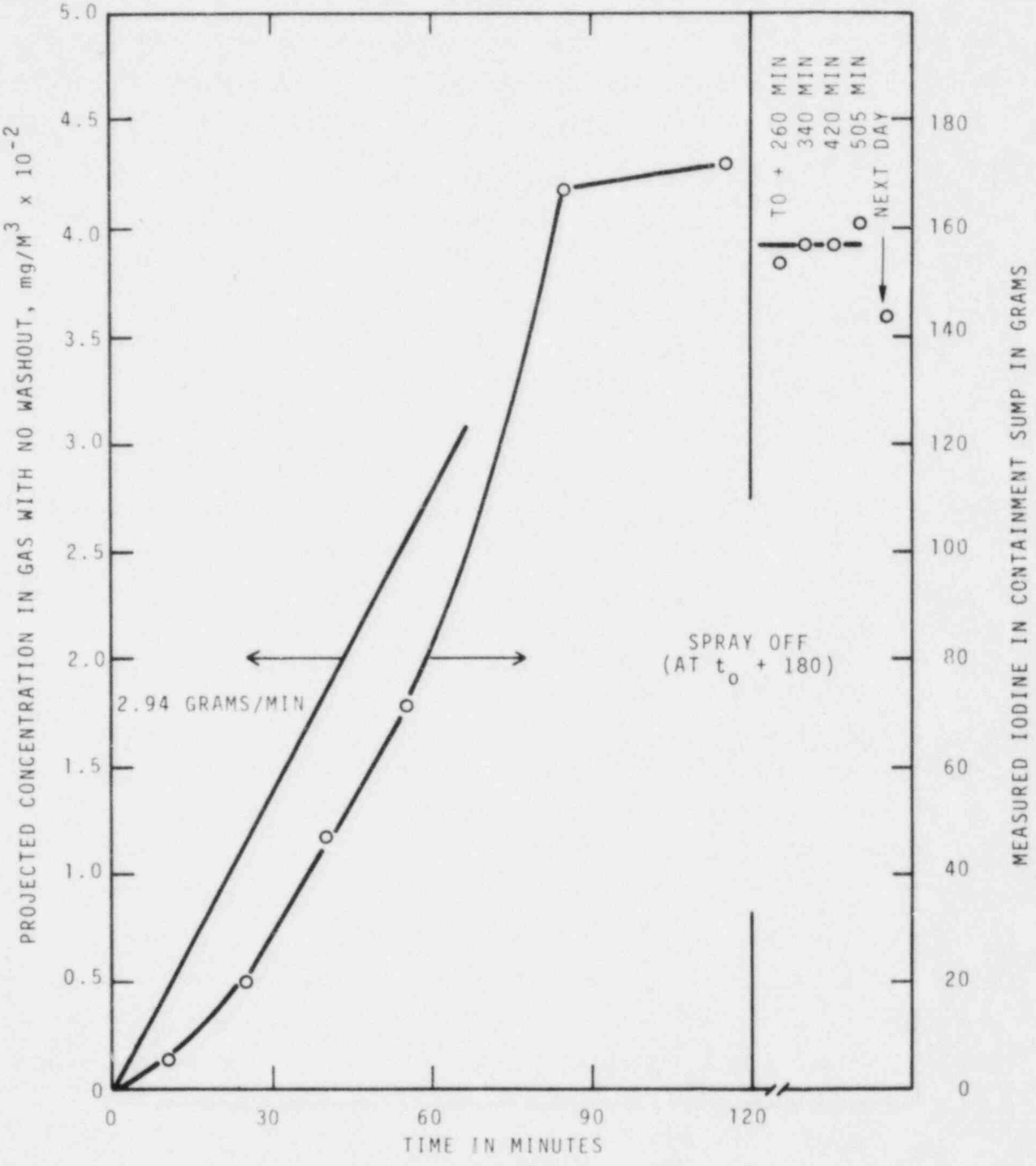

FIGURE 20. Test 4 - Iodine Injection and Liquid Concentration

One can conclude, however, that the calculated integrated dose reduction factor using the simple models would be conservative. Also that the performance of the hydrazine spray for the delayed and prolonged source term case was fully as good as that anticipated by the previous equilibrium measurements(1) and that observed for the puff release tests under isothermal conditions.

7.0 TWO-HOUR DRF IN A PWR BASED ON SPRAY SOLUTIONS CONTAINING HYDRAZINE

In the design basis accident iodine will be present in the form of particulates, elemental iodine, hypoiodous acid and methyl iodide with 4 percent as non-removable species. In these experiments where elemental iodine was introduced into a particle free atmosphere, the fractions present as particulates, hypoiodous acid and methyl iodide were insignificant with respect to the total iodine at start time of the first fresh spray period. Previous CSE experiments have shown that spray washout of particles was similar to elemental iodine. Thus a 2 hr dose reduction factor based on elemental iodine concentration in the gas phase prior to and after the first 10 min spray wash is a fair comparison for the standard PWR system under LOCA conditions. Since there was an apparent overriding gas concentration influence on the spray washout coefficient the 2 hr DRF's were calculated for all three applicable tests. Assuming a 4 percent cutoff, the spray washout equation for a puff release of iodine at spray time is:

$$C = C_o\ (0.96\ e^{-\lambda_s t} + 0.04) \tag{41}$$

where

C = Concentration of iodine at time t - gas phase

C_o = Concentration of iodine at time t_o - gas phase

λ_s = Spray washout constant for elemental iodine

t = Time from start of spray following puff release

The dose reduction factor is defined as:

$$DRF = \frac{\int_o^t C_o dt}{\int_o^t C\ dt} \tag{42}$$

The dose reduction factor may be written in terms of the spray washout, λ_s by substituting Equation (41) into equation (42) and performing the integration.

This gives

$$\mathrm{DRF} = \frac{\lambda_s t}{0.96\ (1-e^{-\lambda_s t}) + 0.04\lambda st} \tag{43}$$

for a 2 hr DRF, $(1-e^{-\lambda_s t}) \cong 1$ and the equation can be simplified to

$$\mathrm{DRF} = \frac{\lambda_s t}{0.96 + 0.04\lambda st} \tag{44}$$

Application of the spray washout constant of this test series to the assumed PWR containment vessel with 3000 gal/min spray flow rate and 2×10^6 ft^3 volume gave the 2 hr DRF's shown in Table 9 for 4 percent and 10 percent cutoff. These values would be conservative values due to the improved iodine absorption from the greater fall heights in the PWR and neglect of wall deposition. The "2 hr DRF Measured" values (Table 9) were calculated from Equation 44 using the measured fraction of total iodine remaining after 2 hours of spray time (200 min elapsed time) and the PWR λ_s values shown in the second column of the table. From Figures 12, 13 and 14 it should be noted that in 2 hours of spray time the airborne total iodine had essentially reached a steady state condition.

TABLE 9. TWO-HOUR DRF BASED ON STANDARD PWR PARAMETERS

Test No.	PWR λ_s	2 hr DRF 4% Cutoff	2 hr DRF 10% Cutoff	2 hr DRF Measured
1	0.314	15	8	33
2	0.54	18	8.8	62
3	0.3	15	8	30

Obviously, these values compare favorably with the 8.6 2-hr DRF predicted for caustic sprays with 10 percent methyl iodide and is considerably greater than the target value of 4. Postma calculated a 2-hr DRF (10 percent CH_3I) of 8.4 from the equilibration studies with boric acid-hydrazine sprays--in excellent agreement with the large scale tests.

8.0 HYDRAZINE DEGRADATION IN SPRAY LIQUID

Since hydrazine is destroyed by reaction with oxygen, reaction with iodine and by thermal degradation under LOCA conditions, it was essential to prove its effectiveness during the brief residence time as the fresh spray drop falls through the containment atmosphere. Also of concern was the ability of the additive to prevent evolution of iodine during recirculation periods. To follow the hydrazine concentration in the vessel sump, special liquid samples were collected periodically throughout the test periods, and the samples analyzed by a sensitive spectrophotometric method. The hydrazine concentration in the vessel sump liquid versus time is shown in Figure 21 for the four tests. Early samples (unplotted) are not truly representative of the hydrazine concentration due to the significant hold up on the deck and the resultant high dilution factor in the vessel sump. Relatively uniform concentrations occurred after about 2 hrs of spray time. Table 10 is a compilation of all the measured concentrations and the pH of vessel sump liquid.

8.1 TEST T-1 (280°F)

The maximum concentration of the fresh spray which should have occurred just after the second fresh spray (30 min period) was not obtained due to other more pertinent assignments requiring attention. Near the end of the first recirculated spray period only about 2 ppm of hydrazine was present in the spray liquid. The hydrazine iodine reaction would account for about a 20 percent reduction of the hydrazine concentration. Subsequent spray periods gradually reduced its concentration to 0.08 ppm at the end of the test. This extremely low concentration produced no deleterious effects with respect to evolution of iodine from the liquid or no discernible effect on the fresh spray washout rate. Comparison of T-1 with T-2 and T-3 concentrations for recirculated sprays, t_0 + 175 min and beyond, shows the effect of oxidation and temperature on hydrazine destruction.

8.2 TESTS T-2 AND T-3

The only significant difference between these two tests with respect to hydrazine behavior was the iodine concentration which was about 30 times

TABLE 10. HYDRAZINE CONCENTRATION AND p^H In Spray Solution Containing 1500 ppm Boric Acid

Sample Ident.	Test 1			Test 2			Test 3			Test 4			
	Time $t_o \pm$	N_2H_4 ppm	p^H	Time	N_2H_4	p^H	Time	N_2H_4	p^H	Sample No.	Time	N_2H_4	p^H
Fresh Spray Solution	-30	50	6.0	-60	50	6.0	-60	51.2	6.0		-10	79	6.8
C.V. Sump	-10	---	6.1	-20	---		-30	---	6.5	C.V. Sump	-10	---	5.5
1	+60	.06	6.1	+65	3.63	5.2	+70	32.7	6.0	1	+50	31.2	5.4
2	+175	1.84	6.1	+115	30.14	5.2	+120	43.12	5.7	2	+78	33.2	5.3
3	+255	0.34	5.9	+185	36.76	5.3	175	40.84	5.7	3	+93	30[a]	5.4
4	+335	0.17	6.0	+255	31.46	5.25	255	35.42	5.7	4	+110	31.2	5.3
5	+435	0.08	6.1	+340	28.16	5.2	335	30.8	5.7	5	+125	33.8	5.3
6	+495	0.08	6.3	+415	23.32	5.2	415	27.5	5.65	6	+155	45.6	5.4
7	N.S.			+495	14.96	5.3	495	25.3	5.8	7	+180	68.0	5.6
8	N.S.			N.S.	N.S.		N.S.			8	+260	64.5	6.0[b]
9	Next Day	0.06	6.0	Next Day	11.88	5.3	Foll	17.16	5.7	9	+340	52	6.4
										10	+420	44.4	6.8
										11	+500	37.2	7.2

(a) Hydrazine feed pump malfunction from t_o + 80-t_o + 100 min.

(b) NaOH feed on at t_o + 200 min.

higher initially for Test T-2. At the earliest sample period for a valid comparison, t_0 + 185, the N_2H_4 concentrations are comparable and about 70 and 80 percent of the original 50 ppm concentration for T-2 and T-3. The iodine-hydrazine reaction would account for about 30 percent and 2 percent of the reduction for tests T-2 and T-3. The significantly larger early reduction for Test T-3 is thought to be a function of hydrazine volatility and a larger unsprayed volume for this test and not increased degradation by oxidation and temperature. The concentration gradually decreased with recirculating time to about 30 percent and 50 percent at the end of the tests. Thus for LOCA conditions creating vessel atmosphere temperatures near 150°F the degradation reactions other than iodine are slow enough to preclude deleterious effects.

8.3 TEST T-4 (DECAYING TEMPERATURE FROM 280°F)

This test was designed to determine if hydrazine fed to hot recirculated spray water would be destroyed prior to reaching the spray header. Initially, the fresh spray water was injected into the containment via the spray nozzles prior to iodine release. During the first recirculation period of 2 hr, hydrazine was fed continuously to the recirculation line near the vessel outlet downstream of the liquid sample line. Iodine was injected during the first hour of this spray period and sodium hydroxide was injected during all subsequent spray periods to raise the pH to 7-8.

The fresh solution sprayed to the vessel prior to injection showed an apparent reduction in the hydrazine from 79 to 31 ppm. Dilution in the vessel sump and deck holdup would distort the true concentration to the low side. During recirculated spray periods the hydrazine concentration in the sump increased continuously except for the 20 min period when the injection pump was inoperative. The final concentration attained was approximately 70 percent of that expected from the measured feed quantity if no degradation had occurred. This 30 percent reduction was about equal to that of the hydrazine-iodine reaction. The intended feed rate of hydrazine of 50 ppm was not attained. Apparently the rushed repair of the pump did not restore the desired feed rate and only about 50 percent of the total feed for the 2 hr period was injected--an average rate of approximately 25 ppm. After the hydrazine feed had been stopped (t_0 + 180 min) hydrazine continually decreased to about one-half of the maximum value. The vessel gas phase temperature varied from about 220°F at the start of the N_2H_4 feed period down to 175°F at the end. The liquid spray temperature decreased from about 160°F to 140°F for the same period as shown in Figure 11.

8.4 CONCLUSIONS

From these tests it is self-evident that at even the maximum temperature of 280°F any 10 min fresh spray period containing 50 ppm of hydrazine following a puff release of iodine would be sufficient to reduce the airborne elemental iodine activity to less than 1.0 percent of the initial concentration. The fresh spray duration for a PWR is typically 60 min. Iodine from a LOCA would be released to the containment vessel before or within the first few minutes after initiation of the spray. Since the first 10 min of washout produced the primary influence on the 2-hr dose reduction factor, the residence time of hydrazine beyond that period is not important as long as the reactant products are nonvolatile and the reaction irreversible as shown by these tests.

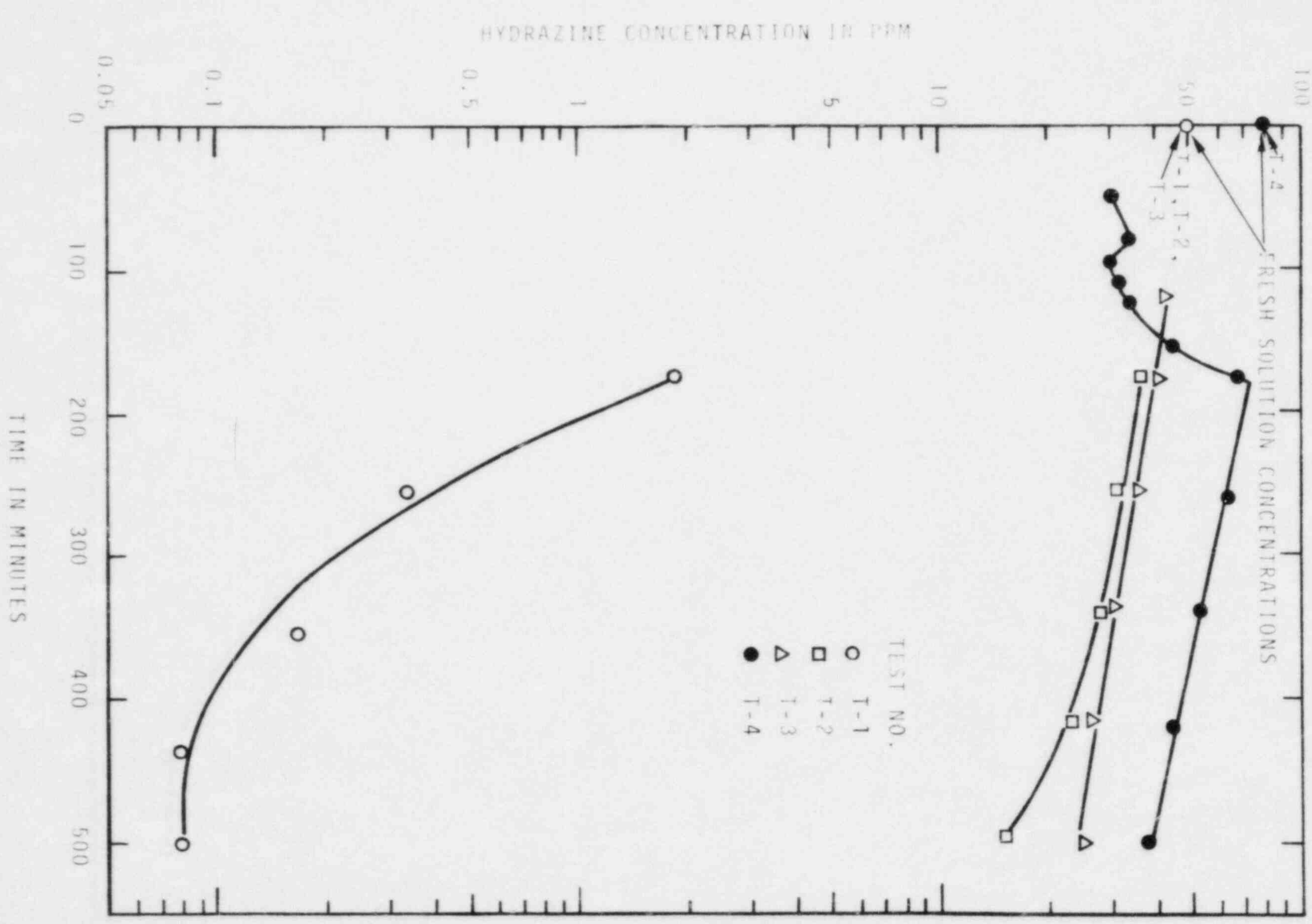

FIGURE 21. Hydrazine Concentration in C.V. Sump Liquid

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APPENDIX A

Test 1

Isothermal at 280 F

7G3 - Nozzles

1500 ppm B as H_3BO_3 + 50 ppm N_2H_4

Average Gas Phase Concentration

In mg/M3

Sample Time	Total Iodine	Elemental[(1)] Iodine	Inorganic[(2)] Iodine	Organic[(3)] Iodine x 10^2	Charcoal Paper x 10^2	HOI[(4)] x 10^2
10	111.25	107				
15	82	81.5		(Ruptured filters precluded segregation by species)		50
20	73.8	70.1				
25	54.5	53				
45	0.55	-	-	8	28.4	
50	0.572	0.234	0.5	6.8	27	7
55	0.55	0.233	0.47	8.1	24	
60	0.46	0.18	0.39	7.6	20.7	
65	0.422	0.19	0.34	7.8	15.2	
105	0.2	0.08	0.149	5.5	6.9	6
110	0.2	0.079	0.153	5.1	7.4	
115	0.195	0.074	0.147	5.1	7.3	
185	0.174	0.051	0.131	4.2	8.0	5
190	0.174	0.044	0.127	4.0	8.3	
195	0.155	0.037	0.115	3.5	7.8	27
265	0.148	0.043	0.113	4.2	7.0	3
270	0.134	0.029	0.095	3.95	6.6	
275	0.117	0.019	0.076	4.3	5.7	2
345	0.119	0.021	0.087	3.2	6.6	
350	0.115	0.016	0.081	3.0	6.5	3.1
355	0.119	0.016	0.084	3.5	6.8	
450	0.113	0.017	0.077	3.0	6.0	2.95
455	0.139	0.022	0.092	-	7.0	
460	0.115	0.02	0.085	3.0	6.5	
505	0.12	0.015	0.081	4.7	6.6	2.35
510	0.147	0.02	0.095	5.1	7.5	
515	0.139	0.011	0.089	-	7.7	2.57

1. Particulate filter + silver surfaces
2. Particulate filter + silver surfaces + charcoal paper
3. Charcoal bed
4. ANC - CuS bed

Test 2

Isothermal at 150 F
7G3 - Nozzles
1500 ppm B as H_3BO_3 + 50 ppm N_2H_4
Average Gas Phase Concentration
In mg/M^3

Sample Time t_o + Min	Total Iodine	Elemental[(1)] Iodine	Inorganic[(2)] Iodine	Organic[(3)] Iodine x 10^2	Charcoal Paper x 10^2	HOI[(4)] x 10^2
12	197	196.35		45		
17	226.5	225.5		85		
22	194	191.53		56		26.3
27	175	173.2				
45	0.213	0.11	0.15	6.5	4	5.4
50	0.187	0.099	0.131	6.7	3.2	
55	0.161	0.099	0.124	5.5	2.5	
60	0.139	0.051	0.101	3.7	5.0	
65	0.143	0.08	0.106	3.7	2.6	
105	0.098	0.034	0.05	4.8	1.6	
110	0.091	0.038	0.062	2.9	2.4	
115	0.093	0.035	0.053	3.8	1.8	0.98
185	0.092	0.033	0.055	3.6	2.2	
190	0.072	0.03	0.052	2.4	2.2	
195	0.078	0.03	0.051	2.7	2.1	2.2
265	0.092	0.031	0.057	3.4	2.6	2.1
270	0.088	0.03	0.056	3.7	2.3	
275	0.083	0.027	0.052	3.2	2.5	
345	0.082	0.025	0.051	3.1	2.6	
350	0.072	0.023	0.049	2.3	2.6	2.0
355	0.063	0.02	0.043	2.0	2.26	
425	0.107	0.023	0.053	5.4	3.0	
430	0.091	0.022	0.045	4.5	2.3	
435	0.088	0.02	0.045	4.2	2.5	
505	0.085	0.025	0.052	3.4	2.7	1.1
510	0.099	0.019	0.050	3.9	3.1	
515	0.088	0.024	0.054	3.4	3.0	2.2

---

1. Particulate filter + silver surfaces
2. Particulate filter + silver surfaces + charcoal paper
3. Charcoal bed
4. ANC - CuS bed

Test 3

Isothermal at 150 F

1713 A Nozzles

1500 ppm B as H_3BO_3 + 50 ppm N_2H_4

Average Gas Phase Concentration

In mg/M^3

Sample Time t_o + Min	Total Iodine x 10^2	Elemental[(1)] Iodine x 10^2	Inorganic[(2)] Iodine x 10^2	Organic[(3)] Iodine x 10^3	Charcoal Paper x 10^3	HOI[(4)] x 10^3
20	595	591		4	33	8.3
25	524	521		6	24	
30	340	336		5	32	12.5
35	337	333		5	39.5	
50	4.65	3.8	4.24	4.1	4.35	
55	4.55	3.8	4.24	4.8	4.35	8.5
60	4.35	3.6	4.07	2.9	4.65	
65	3.9	3.21	3.67	5	4.6	4.14
70	3.6	2.75	3.25	3.5	5	
110	1	0.5	0.745	3.5	2.45	1.87
115	1.3	0.55	0.78	5.5	2.3	
120	1.47	0.6	0.825	3.4	2.25	1.23
185	1.15	0.32	0.62	5.3	3	2.36
190	1	0.4	0.69	4	2.9	
195	1.07	0.36	0.65	4.8	2.9	2.26
265	1.04	0.24	0.6	4.3	3.6	1.56
270	1.17	0.265	0.59	5.8	3.25	
275	1.25	0.316	0.696	5.2	3.8	3.3
345	1	0.28	0.75	3.5	4.7	
350	1	0.17	0.57	4.6	4	2.76
355	1.2	0.275	0.685	4.8	4.1	
425	1.15	0.255	0.785	3.7	5.3	
430	1.05	0.162	0.622	4	4.6	0.3
435	1	0.23	0.63	3	4	
505	1.25	0.19	0.74	4.4	5.5	0.4
510	1.2	0.185	0.705	4.9	5.2	
515	1.15	0.188	0.708	3.3	5.2	1.2

---

1. Particulate filter + silver surfaces
2. Particulate filter + silver surfaces + charcoal paper
3. Charcoal bed
4. ANC - CuS bed

Test 4

Decaying Temperatures and Pressure with Spraying

1500 ppm B as H_3BO_3 + 50 ppm N_2H_4

Iodine Injection During Spraying - 1713A Nozzles

Average Gas Phase Concentration in mg/M^3

Sample Time	Total Iodine	Elemental Iodine	Inorganic[(2)] Iodine	Organic[(3)] Iodine	Charcoal Paper I	HOI[(4)]
t_o + 50	ND	ND	ND	ND	ND	ND
55	ND	ND	ND	ND	ND	
60	ND	ND	ND	ND	ND	
		A B				
90		1.33 0.042		0.0275	0.027	0.0043
95		3.52 0.24		0.0262	0.033	0.0085
110		--- 0.25		0.0357	0.031	0.01
125		1.323 0.224		0.044	0.038	0.01
155		0.091 0.037		0.054	0.041	0.011
190	0.244	0.157(1)	0.205	0.043	0.048	0.0095
195	0.24	0.133	0.180	0.04	0.047	
200	0.229	0.146	0.181	0.0475	0.035	0.011
270	0.136	0.033	0.078	0.0585	0.045	0.016
275	0.147	0.031	0.0655	0.083	0.0345	
280	0.139	0.033	0.077	0.06	0.043	
350	0.142	0.028	0.098	0.05	0.07	0.0067
355	0.143	0.023	0.08	0.0635	0.057	
360	0.151	0.025	0.085	0.067	0.06	
430	0.136	0.023	0.083	0.058	0.06	0.0094
435	0.16	0.02	0.091	0.068	0.071	
440	o.14	0.022	0.091	0.058	0.069	
510	0.149	0.019	0.10	0.05	0.082	0.0176
515	0.155	0.019	0.103	0.0525	0.084	
520	0.157	0.02	0.106	0.0485	0.086	0.0133

ND = Non Detectable
A - In sprayed volume - silver surfaces only
B - Above sprayed volume - silver surfaces only

1. Particulate filter + silver surfaces
2. Particulate filter + silver surfaces + charcoal paper
3. Charcoal bed
4. ANC - CuS bed

APPENDIX B

TABLE 1. OBSERVED PERIODIC HALF LIVES FOR ELEMENTAL IODINE

Period	Test Numbers T-1	 T-2	 T-3
		(In Minutes)	
First natural	15	26	20
First spray (fresh)	1.4	1	1.65
Second natural	34	30	42.6
Second spray (fresh)	25.5	32	12.4
Third natural	96	--	--
Third spray (recirculated)	103	464	98
Fourth spray (recirculated)	158	422	148
Fifth spray (recirculated)	82	150	184

APPENDIX C

Iodine Liquid Concentration

Vessel Sump

Test #1		Test #2		Test #3		Test #4	
Sample Time t_o + Min	I Conc. In g/M^3	Sample Time t_o + Min	I Conc. In g/M^3	Sample Time t_o + Min	I Conc. In g/M^3	Sample Time t_o + Min	I Conc. In g/M^3
60	13.6	65	19.19	70	1.33	50	0
175	5.722	115	18.39	120	0.52	78	0.512
255	4.14	180	11.5	175	0.55	93	1.77
335	3.7	255	11.7	255	0.464	108	3.82
435	3.6	340	10.8	335	0.482	123	5.67
495	3.4	415	10.75	415	0.463	153	12.87
		495	10.5	495	0.455	183	13.13
						260	12.83
						337	12.87
						417	12.73
						497	12.57

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