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EFFECT OF CONTINUOUS SPRAY OPERATION
ON THE REMOVAL OF AEROSOLS AND GASES
IN THE CONTAINMENT SYSTEMS EXPERIMENT

A. K. Postma and L. F. Coleman

December 1970

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Physics and Engineering Division

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ABSTRACT

Results of two large scale experiments on fission product removal by sprays are reported in detail. For these two Containment Systems Experiment (CSE) tests, spraying was begun prior to injection of fission product simulants into the gas phase. Spraying with recirculated liquid was continued for 24 hours at an average temperature of 250 °F. In one of the tests the spray additive was sodium hydroxide at pH 9.4 and in the other the hydroxide was augmented by 1 wt% sodium thiosulfate. These tests showed that aerosol particles and inorganic iodine are rapidly removed from the gas phase by spray, and that the degree of removal continued to increase over the 24 hour period of spray recirculation. The methyl iodide removal rate, which was slow for caustic spray, was increased an order of magnitude by the presence of the thiosulfate. The experimental results are in agreement with previously published data obtained in the Containment Systems Experiment.

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I. INTRODUCTION

This report presents the results of large scale experiments on the removal of fission products from containment atmospheres by sprays. Engineered safety systems for many water cooled power reactors include containment spray systems to remove fission products which become airborne in the containment vessel as a result of postulated accidents. The rapid removal of airborne fission products reduces the source term in calculations of potential radiation exposure to the public due to serious accidents. Analyses^(1,2) of potential radiation exposure are important in assessing the suitability of the site for a proposed reactor plant.

Iodine-131 is usually the critical fission product in calculations of radiological consequences of fission product release accidents; hence its rate of absorption by spray systems enters importantly into the site safety analysis. Because of the importance of iodine absorption by sprays, the USAEC Division of Reactor Development and Technology has sponsored an extensive program to develop experimentally verified mathematical methods for predicting the absorption rate under post-accident conditions. Work reported in this document is part of that program.

The Containment Systems Experiment (CSE) program provides a large scale model containment vessel in which the removal of airborne fission products by natural processes and by engineered safety systems has been studied. The CSE containment vessel has many features of an actual power reactor containment building. Its 30,000 ft³ volume has several

smaller compartments and has a painted shell. Both of these features can affect the transport of aerosols and gases. The size of the vessel permits spray experiments in which the most important parameters appearing in mathematical models are either at full scale or within a factor of four of full scale.

A previous report⁽³⁾ of results obtained in the CSE system presented the results of spray absorption of fission products when sprays were operated for relatively short time periods. Those tests were designed to demonstrate the effects of parameters shown to be important in models of spray absorption. The previously reported experiments confirmed the adequacy of simple mathematical models to describe the spray absorption rate for the initial period of spray operations.

Two experiments have recently been completed in the CSE facility in which spraying was started prior to the release of fission products into the containment vessel and continued for 24 hr. Absorption of aerosols and gases during continuous spray operation is of interest because continuous spray operation more nearly duplicates the circumstances postulated for reactor accidents, and because long term equilibria have a chance to become established.

II. SUMMARY AND CONCLUSIONS

Two spray tests were carried out in the CSE containment vessel in which spray system operation was initiated prior to injection of iodine and cesium. Cold, fresh spray at 50 gpm (0.1 gpm/ft^2) was continued for 40 minutes. The spray liquid was then recirculated for about 1 day. This operating sequence was designed to test spray absorption models under conditions which closely simulate those postulated for accidents.

Run A-10 used a spray solution which contained 2750 ppm B as boric acid, neutralized with excess NaOH to a pH of 9.4. Run A-12 was similar, but used a spray solution which contained 1% sodium thiosulfate in addition to the basic borate. In both runs the initial containment atmosphere temperature was 250 °F and steam was added to maintain steady temperature and pressure.

The results of the theoretical and experimental work reported in this document support the following conclusions.

- Elemental iodine and aerosol particles are rapidly scrubbed from containment atmospheres by basic water spray containing sodium borate. Results of the two continuous spray tests reported here are in good agreement with previous spray experiments with the following exception. Whereas in previous CSE spray experiments about 1% of the inorganic iodine was not effectively removed by fresh spray, a slightly higher percentage of the inorganic iodine was not rapidly removed by base-borate spray in Run A-10. Approximately 3% of the total mass of iodine injected into the vessel in Run A-10 became airborne as a chemical species which was neither I_2 nor CH_3I , and which was removed with a 220 minute half-life. It is conjectured that this material was hypoiodous acid (HOI).
- Fission products were not re-evolved from spray liquid which was recirculated for 20 hours at 250 °F. The

airborne iodine concentration decreases with continued recirculation showing that solution chemical reactions continued to destroy volatile iodine species present in solution.

- The accumulation of fine spray drops (less than 100 microns in diameter) in a containment atmosphere does not occur to a significant extent. The mass of spray liquid suspended as a leakable aerosol is predicted to be less than 0.1% of the liquid airborne as spray drops. Thus only a very small percent (less than 0.001%) of the fission products initially airborne could become airborne by spray atomization. The extremely low gas phase concentrations measured after many hours of recirculation confirmed this prediction.
- Addition of 1 wt% sodium thiosulfate to a basic borate solution enhanced the scavenging of iodine from the gas phase. The extent of elemental iodine removal by fresh sprays, and the ultimate removal after extended recirculation were better than for the same solution without thiosulfate. Methyl iodide was removed from the gas phase with an 80 minute half-time. This is nine times faster than for the base-borate solution. The persistent inorganic species formed in Run A-10 did not appear in Run A-12 where the thiosulfate was present in the spray solution.
- A simple spray washout model based on use of an overall partition coefficient for elemental iodine described the washout to an extent considered adequate for most purposes. Discrepancies between the predicted and measured concentrations are of minor significance in calculating 2 hour dose reduction factors following postulated accidents.
- A weak point in existing iodine washout models is the use of an overall partition coefficient to describe the dissolution process. More information on the rate and extent

of solution reactions of elemental iodine are needed before fully realistic models of iodine washout can be used. More realistic models are needed to explain the appearance of the persistent inorganic specie observed in CSE tests, and to explain the increase in overall partition coefficient with time. Although the refinements which could be gained from better understanding of iodine chemistry would likely have little influence on calculated short term spray removal rates in containment vessels, better understanding of iodine dissolution kinetics would provide a firm basis for spray washout models and would help explain observed discrepancies between predictions and experimental measurements.

- The effective drop size for spray absorption is smaller than the mass median diameter. For the reported spray runs the effective mean size was approximately 1000 microns as compared with a mass median diameter of 1200 microns. Thus calculations based on the mass median diameter will predict slower removal rates than would be predicted if the drop size distribution is properly accounted for.
- Cesium and uranium aerosol particles were effectively removed by sprays. The observed washout rate was faster than predicted using particle sizes obtained during the experiments with a cascade impactor. It is concluded that evaporation of water from particles occurred within the impactor sampler, causing the measured particle sizes to be appreciably smaller than the in-situ size.

III. THEORETICAL PREDICTION OF WASHOUT BY SPRAYS

A. GENERAL CONSIDERATIONS OF SPRAY ABSORPTION

1. Purpose of Theoretical Treatment Given in This Report

The purpose of the CSE fission product study has been to provide experimental information which will serve as a basis for assessing fission product behavior in postaccident containment atmospheres. The transport properties of radioactive materials depends on their physical and chemical forms, and on the mechanisms which cause their deposition. The magnitudes of the deposition rates depend greatly on the experimental system parameters. Hence, the use of experimental results obtained in CSE to predict behavior in postulated accidents must be on the basis of mathematical models which account for differences in physical parameters.

Time and economic limitations in the CSE tests have prevented extensive testing to show the influence of each variable singly. Thus, the experiments were designed to test mechanistic theoretical models. The models are described in this section of this report. Enough detail has been provided to show the reader the assumptions made in deriving models.

The experimental results are described in detail; hence if one wishes to test his own model he may ignore the theoretical discussion section of this report, and proceed to the description of experimental results. The theoretical discussions presented in this chapter serve as a framework for interpreting the experimental results. This theoretical framework has provided a means for describing the physical phenomena which are of controlling importance.

2. Material Balance Equations

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

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

in which

V = volume of main containment space,

C_g = gas phase concentration in main containment volume,

t = time

G = generation rate of component within the main containment volume,

C_{g2} = gas phase concentration in connected volumes,

B_{12} = exchange coefficient for interroom transport,

k_g = instantaneous surface average mass transfer coefficient,

C_{gi} = gas concentration of solute at a deposition surface,

A = surface area available for deposition,

R_G = rate of gas phase reaction of species in main containment volume.

The left member 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 member of Equation (1) represents deposition of a species 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.

Equation (1) is only one of the set of simultaneous material balance equations which are needed to describe the gas phase concentrations. Equations similar to Equation (1) need to be written for each of the connected volumes. A second set of equations are also needed to account for phase equilibria. Fortunately, for many cases of practical interest, the material balance equations may be greatly simplified. Specific cases of interest will be developed in the following discussion.

3. Mass Transfer from a Gas to a Liquid Surface

In gas absorption, solute gas diffuses from the bulk of the gas to the liquid surface. The rate of this transport is governed by the magnitudes of the concentration gradient and the diffusion coefficients (laminar and turbulent) which transport the solute to the absorbing surface. At the gas-liquid interface, the solute dissolves in the liquid. Interfacial dissolution is a very rapid process. For most physical situations, including those expected in post-accident containment atmospheres, surface saturation would exist. Mathematically, this is equivalent to

$$C_{li} = H C_{gi} \quad (2)$$

where H = equilibrium partition coefficient. This equation relates the interfacial gas and liquid phase compositions by means of a partition coefficient, H .

The gas phase mass transfer coefficient for a binary gas mixture is defined in terms of the rate of transfer and the concentration gradient as

$$\dot{N}_{Ao} = k_g (C_{gb} - C_{gi}) + x_{gi} (\dot{N}_{Ao} + \dot{N}_{Bo}) \quad (3)$$

where

- k_g = gas phase mass transfer coefficient,
- C_{gb} = concentration of species A in bulk of gas,
- C_{gi} = concentration of A in gas at interface,
- x_{gi} = mole fraction of A in gas at interface,
- $\dot{N}_{Ao}$ = flux of A at interface,
- $\dot{N}_{Bo}$ = flux of species B at interface.

As defined in Equation (3) the transfer coefficient, k_g , accounts for transport due to diffusional processes. The

bulk motion contribution to the transport is separately accounted for by the product of the total flux and the concentration, evaluated at the interface.

Similarly, the liquid phase mass transfer coefficient is defined by

$$\vec{N}_{Ao} = k_{\ell} (C_{\ell i} - C_{\ell b}) + X_{\ell i} (\vec{N}_{Ao} + \vec{N}_{Bo}) \quad (4)$$

where k_{ℓ} = liquid phase mass transfer coefficient,
 $C_{\ell i}$ = solute concentration in liquid at interface,
 $X_{\ell i}$ = mole fraction of solute in liquid at interface,
 $C_{\ell b}$ = solute concentration in bulk of liquid,
 $\vec{N}_{Ao} + \vec{N}_{Bo}$ = total flux of mass on liquid side of interface.

At a particular interfacial position the flux of solute is the same in both phases. The resistance to mass transfer in the gas and liquid phase may be related to the mass transfer coefficients and the equilibrium partition coefficient. For negligible bulk convective flow, the overall mass transfer resistance may be written as

$$\frac{1}{K_G} = \frac{1}{k_g} + \frac{1}{Hk_{\ell}} \quad (5)$$

where $\frac{1}{K_G}$ = overall transfer resistance,
 K_G = overall mass transfer coefficient,
 $\frac{1}{k_g}$ = gas phase transfer resistance,
 $\frac{1}{Hk_{\ell}}$ = liquid phase transfer resistance.

This equation applies if H is independent of concentration. For values of H which are larger than one thousand, gas phase resistance dominates. If H is of order of ten or less, liquid phase mass transfer resistance is a controlling factor.

The numerical value of H for elemental iodine is relatively large; hence its absorption under accident conditions will be controlled primarily by gas phase mass transfer resistance. Organic iodides such as methyl iodide have partition coefficients near unity, and hence their absorption will be controlled by liquid phase mass transfer resistance.

B. ABSORPTION LIMITED BY GAS PHASE MASS TRANSFER RESISTANCE

1. Initial Absorption with Negligible Back-Pressure

For gases which have large partition coefficients and for aerosol particles, the absorption rate will be limited by gas phase mass transfer resistance. In addition to negligible liquid resistance, the interfacial concentration of the solute in the gas phase will be very low, and may be neglected compared to the bulk gas concentration. Thus, the concentration driving force, $C_{gb} - C_{gi}$ is numerically well approximated by choosing $C_{gi} = 0$.

During the early stages of spray washout with negligible back pressure, the spray removal rate would typically be large compared to the rate of interroom transport. For this case, one may neglect the quantity $(C_{g2} - C_g) B_{12}$ in Equation (I).

For negligible back pressure and interroom transport, the washout equation obtained from simplification of Equation (1) is

$$V \frac{dC_g}{dt} = G - \sum_j (k_g C_g A)_j - R_G \quad (6)$$

Equation (6) is much more easily solved than Equation (1) because a number of parameters have been omitted. The form of the solution to Equation (6) depends on how the parameters

of Equation (6) vary with time and concentration. A special case of interest is the case where k_g , A , V , and G are constant, and R_G is zero. The solution of Equation (6) for this case is

$$C_g = \frac{G}{\sum_j (k_g A)_j} \left[1 - \exp - \left(\frac{\sum_j (k_g A)_j}{V} t \right) \right] \quad (7)$$

If the generation (addition) rate of solute gas is zero the solute concentration will decrease exponentially with a half-life of $t_{1/2} = \frac{0.693 V}{\sum_j (k_g A)_j}$. For a containment region, the value

of $\sum_i (k_g A)_j$ may be taken as the sum for drops, wall liquid films, and dry surfaces.

$$\sum_j (k_g A)_j = (k_g A)_{\text{drops}} + (k_g A)_{\text{wall film}} + (k_g A)_{\text{dry surfaces}} \quad (8)$$

For a sprayed containment volume, uptake of a gas for which H is large by dry surfaces will be negligible compared to that by the wetted wall surfaces and falling drops. Hence for elemental iodine, and other soluble gases, one may neglect uptake by dry surfaces.

$$\sum_j (k_g A)_j = (k_g A)_{\text{drop}} + (k_g A)_{\text{wall film}} \quad (9)$$

The mass transfer coefficient to the wetted wall film may be estimated from a heat-mass transfer analogy and the transfer rate to drops may be estimated on the basis of a correlation of mass transfer data.

For turbulent flow along a vertical wall, the mass transfer coefficient is predicted from a heat transfer analogy to be⁽⁴⁾

$$k_g = \frac{D}{L} (0.13) (GrSc)^{1/3} \quad (10)$$

where k_g = natural convection mass transfer coefficient to a vertical wall,
 D = gas phase diffusivity,
 L = length of vertical surface,
 Gr = Grashof number,
 Sc = Schmidt number.

Equation (10) would be expected to apply for smooth surfaces. Waves and steam condensation will enhance the transfer rate over that calculated from Equation (10).

For falling drops the transfer coefficient may be estimated from a correlation proposed by Frossling⁽⁵⁾ and modified by Ranz and Marshall⁽⁶⁾

$$k_g = \frac{D}{d} (2 + 0.6 Re^{0.5} Sc^{0.33}) \quad (11)$$

where d = drop diameter,
 Re = Reynolds number.

For fresh spray in large containment vessels, absorption by the wall film of soluble gases such as I_2 , will be small compared to absorption by drops for early time. This is because the mass transfer coefficient to drops is about two orders of magnitude greater than to the wetted walls. Although the exposed surface area of the wetted wall surfaces may be 5 to 10 times larger than that of falling drops, the product of surface area and transfer coefficient for drops is large compared to that for wetted walls.

(a) Simplified Model for Monosize, Terminal Velocity Drops

The surface area exposed by drops of diameter, d , is

$$A = \frac{6F t_e}{d} \quad (12)$$

where F = volumetric generation rate of drops,
 t_e = time drop remains airborne.

Combining the surface area shown in Equation (12) with the transfer coefficient shown in Equation (11) gives for drops,

$$(k_g A)_{\text{drops}} = \frac{6F t_e D (2 + 0.6 \text{Re}^{0.5} \text{Sc}^{0.33})}{d^2} \quad (13)$$

The drop exposure time and the relative velocity of the drop must be estimated before Equation (13) can be applied. The simplest model for calculating exposure time and relative velocity is one in which drops are considered to fall at terminal velocity over the entire fall height. Hence, the relative velocity is equal to the terminal settling velocity, and the exposure time is

$$t_e = \frac{h}{v_t} \quad (14)$$

where h = distance of fall,
 v_t = terminal settling velocity of drop.

(b) Effect of Changing Drop Velocity on Absorption

Theoretically, the absorption should be evaluated by summing the instantaneous absorption rate over the whole drop trajectory. Mathematically, this summation process may be written as

$$(k_g A)_{\text{drops}} = \frac{6FD}{d^2} \int_{t=0}^{t=t_e} (2 + 0.6 \text{Re}^{0.5} \text{Sc}^{0.33}) dt \quad (15)$$

Equation (15) may be evaluated if the initial velocity of the drop is known, and if one makes additional assumptions regarding the drop deceleration. In order to establish the relative importance of initial velocity on absorption in the CSE system,

Equation (15) was evaluated assuming an initial downward velocity of 1890 cm/sec, assuming a stagnant steam-air atmosphere, and assuming that the drop drag coefficient was equal to that of solid spheres. The velocity of 1890 cm/sec is equal to the nozzle flow rate divided by the cross-sectional area of the orifice. The results of this calculation are shown in Figure 1, where the absorption predicted for the initial velocity case is compared to absorption based on the terminal settling velocity model. The results shown in Figure 1 indicate that the decreased exposure time due to the initial downward velocity causes a reduction in the predicted absorption for a given drop. For fall heights greater than about 30 ft the predicted reduction in the amount absorbed is not of great importance. For example, for the CSE main room, a minimum fall height of 34 ft exists. For 1200 μ diameter drops, a reduction in efficiency of only 10% is predicted. This effect is small. Other errors in applying absorption theory are potentially of greater significance. From this brief study of the influence of initial velocity, it is concluded that for CSE and larger systems, the reduced drop exposure time due to an initial downward drop velocity is of little practical importance. Models based on terminal settling velocity will yield predictions which are entirely satisfactory from a practical standpoint.

(c) Effect of Drop Size Spectrum on Spray Absorption

The absorption equations developed in the preceding discussion apply for drops of a single size. Spray nozzles produce drops having a range of diameters; hence application of the theoretical predictions to a spray requires one to break the size distribution into narrow size range fractions and apply the theory incrementally, or to select a mean size to represent the distribution. The latter approach is commonly used because it requires less effort.

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FIGURE 1 Effect of Initial Downward Velocity on Drop Absorption

Calculations based on a mean drop size can be interpreted with assurance only when the correct mean size is known. The following discussion is intended to provide insight on the question of the correct mean drop size to represent absorption by a spray.

If one considers the drop size spectrum to consist of i intervals, with volume fraction Q_i associated with each size interval, the absorption capacity of the spray may be represented mathematically as

$$k_g A = 6FD \sum_i \frac{Q_i}{d_i^2} \int_{t=0}^{t=t_e} (2 + Re_i^{0.5} Sc^{0.33}) dt \quad (16)$$

where Q_i = volume fraction of spray in i^{th} size interval.

Equation (16) applies for a mathematical model which neglects solute back-pressure at the drop surface, but allows for an initial drop velocity different than the terminal velocity. The correct mean is by definition the one which gives the same calculated washout as obtained by summing over the whole drop size spectrum. Thus, from Equations (15) and (16), the correct mean diameter is

$$d_m^2 = \frac{\int_{t=0}^{t=t_e} (2 + 0.6 Re_m^{0.5} Sc^{0.33}) dt}{\sum_i \frac{Q_i}{d_i^2} \int_{t=0}^{t=t_e} (2 + 0.6 Re_i^{0.5} Sc^{0.33}) dt} \quad (17)$$

where d_m = correct mean drop diameter.

The mean drop diameter predicted by Equation (17) was evaluated for drop distributions produced by two nozzles used in CSE spray experiments. Two absorption models were used. In one, drops were assumed to enter with a downward velocity

of 1890 cm/sec. In the second, the drops were assumed to fall with terminal velocity for the entire fall height. Drop size spectra were taken from data supplied by the manufacturer of the nozzles. The results of this calculation are shown in Table I.

TABLE I. Mean Values of Spray Drop Diameters

Nozzle Type*	Operating Pressure Drop	Mass Median Diameter	Approx. Std. Deviation	Correct Average Diam(1)	Correct Average Diam(2)
7G3	40 psid	1210 μ	1.5	980 μ	1000 μ
A-20	40 psid	770 μ	1.5	650 μ	700 μ

* *Spraying Systems Co., Bellwood, Illinois.*

1. *Calculational model based on drops at terminal velocity for entire fall height.*
2. *Calculational model based on drops with initial downward velocity of 1890 cm/sec.*

The data in Table I show that the correct average diameters are smaller than the mass median diameters. Hence for the gas phase limited model with no back-pressure of solute gas, predictions based on the mass median diameter will be conservative in the sense that the predicted washout rate will be slower than would be predicted if a stepwise calculation were made accounting for the actual size distribution.

The value of the correct mean depends on the calculational model used to relate absorption to drop size, on the shape of the drop size spectrum, and on the physical input parameters which characterize a specific application. For this reason it is of interest to examine other cases. Parsly⁽⁷⁾ has made calculations of the influence of drop size spectra on absorption in the Nuclear Safety Pilot Plant, using a model which

neglects back pressure of solute at the drop surface, and which accounts for an initial drop velocity. The results of Parsly's⁽⁷⁾ calculations are shown in Table II.

TABLE II. Results of Parsly's⁽⁷⁾ Calculations on the Effect of Geometric Standard Deviation on Spray Performance in NSPP

Drop Number Median Diam	Temp, °C	σ_g	Drop Mass Median Diam, μ	Half-Life for I ₂ Removal, sec	Estimated Half-Life Based on MMD
100*	30	1.0	100	6.4	6.4
100	30	1.5	164	11.4	17
100	30	1.8	281	23.2	50
100	30	2.0	423	38.7	114
700**	120	1.0	700	32.3	32.3
700	120	1.2	774	36.8	39.4
700	120	1.4	984	49.9	63.7
700	120	1.6	1355	74.1	121
700	120	1.8	1963	115.2	254
700	120	2.0	2970	181.7	579

* Total flow of 0.25 gpm through 12 nozzles.

** Total flow of 9.5 gpm through 1 nozzle.

Two columns shown in Table II were not included in Parsly's report.⁽⁷⁾ These are the mass median diameter, and the estimated $t_{1/2}$ based on the mass median diameter. The $t_{1/2}$ based on the mass median diameter was calculated from Parsly's numbers by making the reasonable assumption that the washout rate varied inversely with the square of the drop diameter. The most important conclusion to be drawn from Table II is that the washout rate based on the mass median diameter will conservatively predict the absorption compared to calculations based on the actual drop size spectrum. The

broader the drop size spectrum (larger a_g , geometric standard deviation) the more conservative is the prediction.

The above conclusions regarding mean drop size apply to models in which gas phase resistance controls the absorption rate. At the opposite extreme is absorption controlled by mass transfer in the liquid phase. Postma⁽⁸⁾ considered the question of mean size in drop absorption controlled entirely by liquid phase mass transfer resistance. Using the assumption of terminal settling velocity, calculations were made for stagnant and well mixed drop models.

The results of Postma's⁽⁸⁾ calculations are summarized in Table III. These calculations show that the correct mean drop diameter, $\bar{d}$, is smaller than the mass median diameter, MMD. Since smaller drops are more effective than larger drops, the absorption rate predicted on the basis of the mass median diameter will be less than would be predicted by correctly accounting for the drop size spectrum.

These calculations for a number of special situations which bracket the conditions expected in spray chambers show that the correct mean size is smaller than the mass median diameter. Hence absorption rates based on the mass median diameter will be

TABLE III. Mean Drop Size Calculated by Postma⁽⁸⁾ for Mass Transfer Controlled by Liquid Phase Resistance*

Mass Median Drop Diameter, μ	First Order Reaction Velocity, sec^{-1}	$\left[\frac{\bar{d}}{\text{MMD}} \right]$ Stagnant	$\left[\frac{\bar{d}}{\text{MMD}} \right]$ Well Mixed
360	10	0.86	0.92
360	1	0.89	0.89
360	0.1	0.94	0.89

* Methyl iodide absorption at 100 °C by drops falling 9 ft.

lower than if the correct mean size is used. From a practical standpoint, the mass median diameter is easier to obtain from size data than the correct mean. Hence conservative calculation of washout rate can be made on the basis of the mass median diameter. If one wishes to more precisely predict the absorption rate, the calculation should be based on the actual drop size spectrum.

(d) Absorption by Wall Film Liquid

The gas phase transfer coefficient to wetted wall surfaces is less amenable to calculation than transfer to drops. The magnitude of the gas phase mass transfer coefficient for the wetted wall will depend on the flow condition and mixing within the gas phase boundary layer. During the spray period, flow along the wall will be induced by thermal gradients, by drag from the flowing liquid film, and by motion of the gas phase due to the falling drops. Prior to initiation of sprays, the wall is cooler than the bulk gas which causes a natural convection flow downward along the wall. If spray liquid is much cooler than the containment vessel, the gas phase will be rapidly cooled to a temperature below the wall temperature. This rapid cooling will cause a natural convection flow up the wall. Hence the wall flow regime existing prior to spray initiation will not persist after cold sprays are initiated.

The mass transfer coefficient to the wall surface is defined by

$$\vec{N}_{Ao} = k_g (C_{gb} - C_{gi}) + X_{gi} (\vec{N}_{Ao} + \vec{N}_{Bo}) \quad (3)$$

where k_g = mass transfer coefficient to wall by diffusional processes,
 C_{gb} = solute gas phase concentration in bulk of gas,

C_{gi} = solute gas phase concentration at liquid interface,

X_{gi} = mole fraction of solute in gas at interface

$(N_{Ao} + N_{Bo})$ = total mass flux at liquid interface.

For turbulent natural convection along a flat surface, the mass transfer coefficient may be obtained by analogy from the heat transfer coefficient. Substituting the Schmidt number for the Prandtl number gives

$$\frac{k_g L}{D} = 0.13 (GrSc)^{1/3} \quad (10)$$

where k_g = transfer coefficient in gas phase,
 L = length of vertical surface,
 D = diffusivity of solute in gas,
 Gr = Grashov number,
 Sc = Schmidt number.

This transfer coefficient applies for negligible bulk flow of material normal to the gas-liquid interface. In reactor containment systems, appreciable condensation of water vapor will occur on the walls of the containment vessel, and this will cause a bulk flow of gas toward the surface. Bulk flow enhances the mass transfer coefficient. For a laminar flowing stream, the effect of bulk motion on the transfer coefficient has been presented by Bird, Stewart, and Lightfoot.⁽⁹⁾

The magnitude of the calculated correction of mass transfer enhancement depends to a minor extent on the transport theory used. The magnitude of the correction factor is a function of the dimensionless ratio

$$\phi = \frac{N_{Ao} + N_{Bo}}{k_g} \quad (18)$$

where $N_{Ao} + N_{Bo}$ = net mass flux at interface for a binary gas mixture.

For the steam-air system, species B represents the steam-air mixture, and A the trace radioactive species present. The enhancement in the transfer rate is given in terms of the ratio of the mass transfer coefficient with transfer to that with negligible transfer

$$\theta = \frac{k_g^*}{k_g} \quad (19)$$

where k_g^* = mass transfer coefficient under high mass transfer conditions.

Evaluation of Equation (19) using measured steam fluxes ($0.03 \text{ lb hr}^{-1} \text{ ft}^{-2}$) and a mass transfer coefficient based on Equation (10), give $\phi \approx 0.02$. From Bird, Stewart and Lightfoot,⁽⁹⁾ θ is about 1.01 for $\phi = 0.02$. Since the predicted values of the transfer coefficients are no better than about $\pm 20\%$, making a correction for the bulk motion term is not justified. Numerical evaluations of Equation (10) for conditions expected following loss-of-coolant accidents in water-cooled reactors are given by Knudsen and Hilliard.⁽⁴⁾

The bulk flow contribution to mass transfer, $X_{gi} (\vec{N}_{Ao} + \vec{N}_{Bo})$, will vanish for all cases of mass transfer in which back'pressure of solute gas is considered to be negligible, i.e., $C_{gi} = 0$. Hence it appears that the transfer rate is best predicted by

$$N_A = 0.13 \frac{D}{L} (\text{Gr Sc})^{1/3} C_{gb}. \quad (20)$$

If forced convection were encountered, due perhaps to operation of recirculating air cleaning equipment, the transfer coefficient would be larger than predicted by Equation (10).

2. Effect of Drop Saturation on Spray Absorption Rate by Fresh Sprays

The washout models discussed in the previous section of this report were based on the assumption that back-pressure at the gas-liquid interface was negligible. While this assumption appears to be verified for initial absorption of elemental iodine in the CSE vessel, extension of spray washout results to full scale reactor containment systems requires assessment of drop saturation for fall heights of 100 ft or more.

For gases which have partition coefficient greater than about 1000, liquid phase mass transfer resistance is small compared to gas phase resistance [see Equation (5)]. For such gases, the degree of mixing in the liquid phase is relatively unimportant in determining the absorption rate. Hence a model based on a well mixed drop may be used to predict the effect of saturation on the drop absorption rate. For a well mixed drop, a material balance on the liquid phase leads to

$$k_g A (C_g - C_{gi}) = V \frac{dC_{la}}{dt} \quad (21)$$

where k_g = gas phase mass transfer coefficient
 A = drop surface area
 C_g = concentration of solute gas in bulk of gas,
 C_{gi} = concentration of solute gas at drop interface,
 V = volume of the drop,
 C_{la} = volumetric average drop concentration,
 t = exposure time.

Applying the well mixed criterion and assuming surface saturation, the surface condition is $C_{la} = H C_{gi}$. For k_g , A , V , and C_g constant during a drop transit time, Equation (21) may be integrated to

$$\frac{C_{la}}{C_g} = H \left(1 - \exp \left(- \frac{6 k_g t_e}{H d} \right) \right) \quad (22)$$

where C_ℓ = concentration in drop at end of fall time, t_e .

For small values of $\frac{6 k_g t_e}{H d}$, Equation (22) simplifies to

$$\frac{C_\ell}{C_g} = \frac{6 k_g t_e}{d} \quad (23)$$

The zero back-pressure model, Equation (23), is a good approximation only when $\frac{6 k_g t_e}{H d}$ is smaller than about 0.1. For larger values of this dimensionless parameter, drop saturation is appreciable, and the spray absorption rate is reduced from that predicted neglecting back-pressure.

As noted, the previous discussion of drop saturation was based on the assumption that the drops were perfectly mixed at all times. The maximum possible error which could be introduced by this assumption was evaluated by numerically solving the diffusion equation in a sphere, allowing for gas phase resistance to transfer as predicted from Equation (11). The infinite series representing this case was taken from the work of Danckwerts.⁽¹⁰⁾ Results of this calculation are shown in Figure 2, where absorption by stagnant and well mixed drops is compared.

For low values of H (H less than 100), drops become saturated for fall heights greater than about 50 ft, hence, mixing is of little influence for greater fall heights.

At the opposite end of the spectrum (H greater than 10^4), drop mixing is unimportant because liquid resistance to mass transfer is negligible. For fall heights encountered in containment systems, the maximum discrepancy caused by neglecting liquid phase transfer resistance occurs at an H value of about 1000. Thus, neglect of liquid phase resistance causes an error of less than 30% for CSE tests. From earlier CSE spray experiments,⁽³⁾ it was concluded that H was greater than 3000. The error introduced by assuming well mixed drops appears to be unimportant in assessing drop saturation, but isn't entirely negligible in predicting washout rates.

FIGURE 2. Comparison of Drop Absorption for Stagnant and Well Mixed Drops

3. Removal of Aerosol Particles by Sprays

The mechanisms which contribute to capture of aerosol particles in containment vessels include gravitational settling, inertial impaction, Brownian diffusion, thermophoresis, diffusiophoresis, electrical attraction, and the interception effect. Particle capture will occur at the surface of falling drops and at the walls and horizontal surfaces of the vessel. The purpose of this review is to show how the removal rate due to the several mechanisms can be related to the physical parameters of the spray system.

Particle capture by a spray may be evaluated by considering the spray to be an assemblage of noninteracting single drops. This is not precisely true, but appears to be a reasonable assumption for containment spray systems. Based on this assumption, the rate of washout may be easily related to the collection efficiency for a single drop.

A material balance on the gas phase of a well mixed containment vessel gives for the washout half-time

$$t_{1/2} = \frac{0.693 V}{\frac{3hEF}{2d} + v_G A_F + v_w A_w} \quad (24)$$

where

- V = volume of gas phase,
- h = fall height,
- d = drop diameter,
- E = total collection efficiency of a single drop,
- F = flow rate for drops,
- v_G = gravitational settling deposition velocity,
- v_w = wall deposition velocity of particles, surface average,
- A_F = floor area (horizontal projection),
- A_w = area of effective wall surface.

Equation (24) is for a single drop size and application to sprays which contain a wide spectrum of sizes should be done incrementally, accounting for the effect of drop size.

(a) Gravitational Settling

The major effect of gravitational settling will be to cause particles to deposit on horizontal surfaces. For a well mixed chamber, the gravitational settling deposition velocity may be taken as the terminal settling velocity of the particles:

$$v_G = \text{terminal velocity} = mgB \quad (25)$$

where m = particle mass,
 B = particle mobility,
 g = acceleration due to gravity,
 v_G = gravitational settling deposition velocity.

(b) Brownian Diffusion

Very small particles are capable of appreciable diffusional transfer as a result of Brownian motion. Thus they will behave as gases qualitatively, but with much lower diffusion coefficients. The particle diffusivity may be calculated from Einstein's⁽¹¹⁾ equation

$$D_p = k T B \quad (26)$$

where D_p = diffusion coefficient for particle,
 T = absolute temperature,
 B = particle mobility,
 k = Boltzmann's constant.

For drops moving through a gas at terminal velocity, the target efficiency predicted on the basis of Frössling's⁽⁵⁾ equation is

$$E_{BD} = \frac{4 D_p (2 + 0.6 Re^{0.5} Sc^{0.33})}{dv_t} \quad (27)$$

where E_{BD} = target efficiency for Brownian diffusion,
 v_t = drop terminal velocity,
 Sc = Schmidt number based on particle diffusivity,
 Re = Reynolds number for drop,
 d = drop diameter.

Use of the Frössling equation, Equation (11), for predicting aerosol deposition is not fully justified because the Schmidt numbers associated with aerosol particles are generally much larger than the Schmidt numbers for the experiments which verify Equation (11). There is no reasonable alternative, however, as needed experimental data are not available.

(c) Inertial Impaction

Inertial impaction occurs because particles are able to cross stream lines as a result of their inertia. For impaction on the forward part of a sphere or drop, the target efficiency is a function of the ratio of the particle stopping distance to the diameter of the sphere (Stokes No.).⁽¹²⁾ The target efficiency measured by Ranz and Wong⁽¹³⁾ appears to agree with the predictions based on potential flow. Very few data are available for particles below 2 μ in diameter which is the size of primary interest here. For Stokes numbers less than 0.0834, an impaction efficiency of zero is predicted.

(d) Interception

The interception effect requires no inertia. A particle will be intercepted by a collector if its trajectory passes within one particle radius. For potential flow around a sphere the interception target efficiency is⁽¹³⁾

$$E_{INT} = 3 \frac{d_p}{d} \quad (28)$$

where d_p = spherical particle diameter,
 d = drop diameter.

(e) Diffusiophoresis

Pressure suppression sprays may enter the containment vessel considerably cooler than the atmosphere temperature. Steam will condense on the cool droplets, giving rise to a vapor flux which will cause particle motion toward the drop. An estimate of the particle capture can be made by considering condensation on a stationary drop.

The diffusiophoretic velocity in the slip flow regime for spherical particles is(14)

$$\vec{V}_D = (1 + \sigma_{12} \gamma_2) \frac{D}{\gamma_2} \vec{\nabla} \gamma_{1\infty} \quad (29)$$

where $\vec{V}_D$ = diffusiophoretic velocity,

$$\sigma_{12} = \text{slip factor} = 0.95 \frac{m_1 - m_2}{m_1 + m_2} - 1.05 \frac{d_1 - d_2}{d_1 + d_2},$$

γ_2 = mole fraction of air,

$\gamma_{1\infty}$ = mole fraction of water vapor far from particle,

D = diffusivity of water in air,

m_1 = molecular mass of water,

m_2 = molecular mass of air,

d_1 = molecular diameter of water,

d_2 = molecular diameter of air.

The concentration gradient $\nabla \gamma_{1\infty}$ at the surface of a drop may be obtained in terms of the condensation rate. The time integrated velocity multiplied by the drop surface area gives the volume of the particle-containing gas swept to the surface. The effective target efficiency is found to be approximately

$$E_D = \frac{4 (1 + \sigma_{12} \gamma_2) \rho_l a C_{p\ell} \Delta T_\ell}{3 Ch \lambda_c} \quad (30)$$

where E_D = drop target efficiency due to diffusiophoresis,
 ΔT_ℓ = temperature rise of spray drops in chamber,
 ρ_ℓ = density of liquid spray,
 λ_c = latent heat of condensation of water per mole,
 $C_{p\ell}$ = heat capacity of spray liquid,
 C = total gas concentration in containment volume,
 a = drop radius,
 h = drop fall height.

(f) Thermophoresis

Thermal gradients associated with heat transfer will cause particle movement towards a surface on which vapor is condensing. However, for steam-air mixtures typical of containment atmospheres, thermophoresis will be negligible compared to diffusiophoresis.^(15,16) Hence, thermophoresis will be neglected. Thermophoresis is not always negligible compared to diffusiophoresis. For example, for water drops falling in unsaturated air, thermophoresis may be a dominant capture mechanism.

(g) Electrical Attraction

Electrical forces can be very effective in causing particle capture by falling drops. If the particle and drop charges are known, the target efficiency may be calculated.⁽¹⁷⁾ Experimental measurements by Kraemer and Johnstone⁽¹⁷⁾ verified the predictions. Some calculations for reactor containment sprays have been given.⁽¹⁸⁾ For the CSE experiments it has been concluded that existing electrical charges are too low to provide appreciable particle collection.⁽¹⁹⁾ This conclusion was based on measured particle electrical mobilities and estimates of the maximum drop charges.

(h) Growth and Evaporation of Particles in a Steam-Air Atmosphere

Particles suspended in a gas phase containing a condensable vapor may grow if the gas phase becomes more saturated due to temperature or pressure changes. Likewise, if the thermodynamic conditions are altered so as to decrease the degree of saturation, liquid already condensed on the particle may evaporate, reducing the size of the particle.

If an insoluble surface is present, drops of critical radius will form on this surface at a higher rate than they will self-nucleate. This is because they have less volume and require fewer molecules than for homogeneous nucleation; hence, the free energy increase is smaller. Fletcher⁽²⁰⁾ has derived an expression for this free energy increase as a function of the radius of the nucleating particle and of the contact angle, between the water/air interface and the water/particle interface.

$$\Delta G(R^*) = \frac{16 \pi \sigma^3}{3[n_\ell kT \ln S]^2} f(\cos \phi, \frac{R_0}{R^*}) \quad (31)$$

where $\Delta G(R^*)$ = the free energy associated with nucleation to a critical size R^* ,
 R_0 = initial radius of nucleating particle,
 σ = interfacial free energy per unit area between liquid and vapor,
 n_ℓ = number of molecules per unit volume of liquid,
 k = Boltzman Constant,
 S = saturation ratio = $\frac{p}{p_\infty}$,
 p_∞ = vapor pressure over a plane liquid surface at equilibrium,
 p = vapor pressure in gas phase,
 f = a complex algebraic function,
 ϕ = wetting angle between liquid and solid.

From this expression the saturation required to cause nucleation in 1 sec was calculated by Fletcher. This calculation shows that lower saturations are required to nucleate in the presence of particles. Hence, if insoluble particles are present, water will condense on them before self-nucleation occurs. However, supersaturation (compared to a vapor in equilibrium with a plane liquid surface) is required to cause condensation upon an insoluble particle. If the atmosphere is precisely at saturation, water condensed on insoluble particles will evaporate. Fuel materials such as uranium oxide would be characteristic of insoluble particles.

Direct application of this result to uranium oxide aerosols is not achievable because the wetting angle of water on the oxide particles is not known. However, the fact that super-saturation is required to induce nucleation indicates a difference in behavior as compared to cesium particles which nucleate from subsaturated atmospheres.

A soluble particle will nucleate a vapor at a partial pressure less than the saturation pressure. This is due to vapor pressure lowering caused by solutes according to Raoult's law behavior. Using the van't Hoff factor, i , to take into account the dissociation of inorganic salts, and using the Kelvin equation to account for the effect of surface curvature, the equilibrium saturation ratio S , over a solution droplet composed of liquid of gram molecular weight M_0 , and containing mass m , of a solute of gram molecular weight M , is given by

$$S = \left(\exp \frac{2\sigma'}{n_L kTa} \right) \left[1 + \frac{i m M_0}{M \left(\frac{4}{3} \pi a^3 \rho - m \right)} \right]^{-1} \quad (32)$$

where S = equilibrium vapor pressure/vapor pressure over a pure plane liquid surface,
 a = surface tension,
 n_L = number of molecules per cm^3 of liquid,
 k = Boltzmann's constant,
 T = absolute temperature,
 a = drop radius.

In Equation (32) the primes refer to the properties of the solution. A numerical evaluation of this equation is shown graphically in Figure 3. From Figure 3 it is apparent that soluble particles can act as nucleation sites without having to depend on chance agglomerations of water molecules to reach a critical size.

The size of soluble particles within a containment atmosphere depends on the relative humidity of the gas phase. Thus the size will change if the thermodynamic properties of the gas phase is altered. An example of the relative change in particle size which would occur as a result of changes in relative humidity is shown in Figure 3, where the equilibrium particle size is shown as a function of relative humidity. Figure 3 applies specifically to cesium present as cesium hydroxide. Similar behavior would be predicted for other soluble materials. An important result of this calculation is the comparatively large change in particle size which can occur as a result of small changes in relative humidity. This behavior is especially important in the design of particle sampling devices for measuring particle size. The measured particle size will accurately represent the in-situ size only if the sampling device operates under constant relative-humidity conditions.

(i) Comparison of Particle Capture Mechanisms for Falling Drops

The relative importance of the several particle capture mechanisms depends primarily on the particle size, drop size,

FIGURE 3. Equilibrium Size of Cesium Hydroxide Drops in Steam-Air Atmosphere

and ambient conditions. Particle capture for conditions typical of those in the CSE tests have been calculated, and displayed in Figure 4. Brownian diffusion is important for very small particles. For particles larger than about $2\ \mu$ inertial impaction is the predominant mechanism. For cold spray, diffusiophoretic capture is important for a wide range of particle sizes.

(j) Wall Capture of Aerosol Particles

The walls of the containment vessel represent a surface area considerably larger than that of the drops and thus represent a potential area for significant deposition. For large vessels, the boundary layer would be turbulent, providing a transport mechanism for particle deposition. Diffusiophoresis will also aid wall deposition. Theories and data relative to turbulent deposition are discussed by Sehmel. (21) During a spray period, the wall deposition of particles is expected to be small compared to capture by spray drops because of the higher transport coefficient to the falling drops. For this reason wall deposition of particles is not further considered in this report.

C. ABSORPTION CONTROLLED BY LIQUID PHASE MASS TRANSFER RESISTANCE

According to Equation (5) the liquid phase transfer resistance will dominate where the product Hk_ℓ is small compared to k_g . For the spray drops and wall films of interest in containment systems this will be true for materials which have partition coefficients smaller than 10. Of the materials identified in reactor containment systems, the organic iodides would be expected to be absorbed at a rate controlled by liquid phase resistance.

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FIGURE 4. Predicted Particle Collection Efficiency for Falling Drops

1. Absorption by Falling Drops

For a stagnant falling drop, the absorption in time t_e is given by Danckwerts⁽¹⁰⁾ as

$$B = 6 H \beta \sum_{n=1}^{\infty} \frac{\alpha + \left(\frac{\beta n^2 \pi^2}{\alpha + \beta n^2 \pi^2} \right) \left(1 - \exp - [\alpha + \beta n^2 \pi^2] \right)}{\alpha + \beta n^2 \pi^2} \quad (33)$$

where B = amount of solute absorbed/(unit volume) (Cg),
 $a = k t_e$,
 $\beta = D t_e / a^2$,
 t_e = drop exposure time,
 D = diffusivity of solute in liquid,
 a = drop radius,
 k = first order solution reaction rate constant,
 H = equilibrium partition coefficient.

This equation applies for a stagnant drop, with negligible concentration gradients in the gas phase. A slightly more complex equation which accounts for gas phase resistance is also given by Danckwerts.⁽¹⁰⁾ An upper limit to absorption may be estimated by assuming the drop to be perfectly mixed at all times. The absorption equation for a perfectly mixed drop is

$$B = H (\alpha + 1) \quad (34)$$

Unfortunately, available data do not permit the effect of mixing to be adequately assessed. Studies on larger drops^(8,23,24,25) have shown that circulation can occur, but that small amounts of surface active agents can effectively inhibit circulation. A comparison between absorption rates calculated from Equations (33) and (34) has been presented.⁽²⁶⁾

2. Absorption by Wall Films

For liquid phase controlled wall film absorption, transfer rates may be calculated from the penetration theory, or from laminar flow theory. The differential equation describing absorption into a smooth laminar film is

$$V_{\max} \left[1 - \left(\frac{x}{\delta} \right)^2 \right] \frac{\partial C}{\partial z} = D \frac{\partial^2 C}{\partial x^2} - k C \quad (35)$$

where $V_{\max}$ = velocity at the gas-liquid interface,
 x = distance from surface of film,
 δ = thickness of film,
 z = distance measured along film,
 k = first order reaction rate constant.

For short laminar films the solute does not have time to penetrate far into the film, and hence the absorption takes place as though the film were infinite in thickness. The differential equation for absorption in such films may be obtained from Equation (35) by setting $x = 0$. This is the penetration theory approximation and the mathematical solution is given by Dankwerts.⁽²⁷⁾ Most experimental data obtained for short wetted wall columns for laminar flow, agree reasonably with this penetration theory solution.

For the long films encountered in containment vessels, laminar flow calculations indicate that the solute would diffuse all the way through the film. A lower limit to absorption in thin films can be estimated by solving Equation (35) for $\frac{\partial C}{\partial z} = 0$. This gives, for a zero concentration gradient at the solid wall

$$\frac{dq}{dt} = C_{li} \sqrt{kD} \tanh (\sqrt{k/D} \delta) \quad (36)$$

where $\frac{dq}{dt}$ = absorption rate per unit area.

The film thickness, δ , used in Equation (36) may be estimated from laminar flow theory and experimental measurements of the wall flow rate.

Turbulence, waves, and rivulet formation will cause mixing in actual films. An upper limit to film absorption may be estimated by considering the film to be perfectly mixed. For this case the total film absorption rate for the whole vessel would be

$$\text{Absorption Rate} = k C_{li} V_{WF} + C_{li} L_F \quad (37)$$

where V_{WF} = volume of liquid held up on walls as film,
 L_F = flow rate of liquid film.

In this analysis of wall film absorption, we have neglected reaction and dissolution of methyl iodide by the paint or surface of the wall. If appreciable transfer occurs into the solid wall, film absorption would be enhanced. Considerable effort has been devoted to developing paint additives capable of reacting with methyl iodide,⁽²⁸⁾ and if these were incorporated, the rate of transfer from the liquid film to the wall would have to be taken into account. An extensive review of absorption and fluid dynamics of thin films has been presented by Fulford.⁽²⁹⁾

In addition to vertical wall surfaces, liquid pools in the bottom of containment vessels represent a region where additional absorption will occur. Absorption in this volume may be significant if a chemical reaction destroys the dissolved gas. Realistic calculation of the absorption rate into the pool surface is possible only if surface renewal rates are known. Again, upper and lower limits may be computed based on a stagnant or a well mixed pool.

3. Formation of Volatile Species by Reaction in Liquid Phase

Dissolution of iodine chemical species such as I_2 and CH_3I may lead to subsequent generation of new chemical species which could then transfer to the gas phase. For example, the dissolution of I_2 in water leads to the following chemical reactions.

These reactions, discussed by Eggleton,⁽³⁰⁾ are not necessarily all that occur. Any chemical species formed in solution which has an appreciable volatility would enter the gas phase. For the reaction noted above, HOI is the chemical species most likely to enter the gas phase. Thus an additional equation

needs to be written to describe the overall iodine equilibrium. If HOI does contribute to the airborne concentration of iodine, other reactions which could lead to its formation and disappearance, such as

and

need to be considered.

Based on the equilibrium constants for reactions (39) through (42), the fraction of dissolved iodine present as the various species has been calculated. For the total iodine concentrations ($\sim 10^{-2}$ g/l) and pH values (1.9.5) used in most CSE tests, virtually all iodine in solution is predicted to be present as I^- and HOI.

At present, doubt exists relative to the existence of appreciable concentrations of HOI in the gas phase. The classical view has been that HOI exists only in solution, and that it is unstable in the gas phase. However, an unidentified airborne specie of iodine which does not behave as elemental iodine has been noted.⁽³¹⁾ This could be HOI. Russian workers have performed a series of experiments⁽³²⁾ in which iodine-containing water solutions were sparged, and evolution of gaseous iodine compounds was measured. They explained their results in terms of volatility of HOI. Recent studies^(33,34) have led workers at Idaho Nuclear Corp. to conclude that HOI is indeed volatile and represents an important airborne species of iodine, especially at low concentrations. Unfortunately, absolute techniques for isolation and detection of HOI have not yet been developed. In summation, it appears that volatile forms of iodine exist which are not I_2 or CH_3I . Quantitative calculation of the airborne concentration is not feasible at present. For the CSE experiments, the presence of a volatile species of I_2 which is not I_2 or CH_3I was considered as a potential factor of importance.

D. EFFECT OF RECIRCULATION

1. Approach to Equilibrium

In many reactor containment systems, the spray liquid introduced to cool the postaccident atmosphere and to trap

fission products will be cooled by heat exchange and recirculated through the spray nozzles. Thus, after an initial period of fresh spray, the liquid will enter the chamber with a nonzero solute concentration which will decrease the concentration driving force and slow the rate of absorption. Theoretically, recirculation of spray containing high concentrations of iodine could raise the iodine concentration in the containment vessel. The precise rate of decrease in gas phase concentration depends on the way in which the liquid is mixed within the chamber, and on the rate and extent of chemical reactions which occur within the chamber.

One case which is amenable to simple calculation is based on the following assumptions:

- 1) Henry's Law applies,
- 2) no liquid is held up within the chamber except in the sump,
- 3) The liquid in the sump is well mixed,
- 4) drop and atmosphere concentrations do not change appreciably during the drop fall time.

For this case, simultaneous material balances on the gas and liquid phases give

$$\frac{C_g}{C_{g0}} = \frac{V}{V + LH} + \frac{LH}{V + LH} \exp \left[- \left(\frac{K_g A}{V} \right) \left(\frac{V + LH}{LH} \right) t \right] \quad (46)$$

where K_g = overall transport coefficient,

L = liquid hold-up in sump,

A = interfacial area for transport,

H = equilibrium partition coefficient.

This equation predicts a rapid initial washout, and then a levelling of the gas phase concentration with time. This is a reasonable first approximation for washout of elemental iodine. The effect of recirculation on elemental iodine concentration is further described in this report in the chapter entitled "Comparison of Observed Washout with Theory."

For a slightly soluble species such as methyl iodide the effect of recirculation depends on the solution reaction rate. If the reaction rate is negligible, then the liquid will approach saturation during one pass through the chamber. The washout will follow Equation (46) with $K_g A$ being replaced by LH . If the liquid phase reaction rate is too small to enhance absorption during a single pass but fast enough to destroy the dissolved gas within the sump, the net effect will be to make the spray "fresh". For this case the gas phase washout would follow

$$\frac{C_g}{C_{g0}} = \exp \left(- \frac{FH}{V} \right) t \quad (47)$$

where F = liquid flow rate,

H = partition coefficient for unreacted species.

For still faster reactions, appreciable absorption enhancement per pass would occur, and an equation similar to Equation (47) would apply, with an effective H being calculated to account for the influence of the chemical reaction.

2. Potential Buildup of Fine Drops

Formation of spray drops from nozzles is attended by formation of fine drops. If these fine drops were able to accumulate, it is conceivable that they could represent a leakable aerosol. In this section we will examine the formation and removal of fine drops by sprays. A material balance on fine drops of size d may be used to relate the airborne drop concentration to time

$$G_d = R_d + \frac{d}{dt} (M_d) \quad (48)$$

where G_d = mass generation rate of fine drops,

R_d = rate of removal of fine drops,

M_d = total airborne mass of drops of diameter d ,

t = time.

The drop generation rate, G_d is equal to the production rate at the nozzles.

$$G_d = \rho F Q_d \quad (49)$$

where Q_d = fraction of liquid sprayed as drops of diameter d ,

ρ = liquid density

F = spray flow rate.

The removal rate may be taken as that due to gravity settling and capture by larger drops:

$$R_d = \frac{3}{2} \frac{C_d E h F_D}{D} + C_d U_t A \quad (50)$$

where C_d = concentration of fine drops,

E = collection efficiency of fine drops by large drops,

h = fall height of large drops,

F_D = flow rate of large drops,

D = diameter of larger drops,

C_d = concentration of suspended fine drops,

U_t = settling velocity of fine drops,

A = horizontal cross-sectional area of chamber.

Combining equations (48) through (50) leads to

$$\rho F Q_d = \frac{3}{2} \frac{C_d E h F_D}{D} + C_d U_t A + V \frac{d}{dt} (C_d) \quad (51)$$

The maximum concentration will occur at long times when $d/dt (C_d) = 0$. Therefore

$$\frac{\rho F Q_d}{\frac{3}{2} \frac{E h F_D}{D} + U_t A} = (C_d)_{\max} \quad (52)$$

In order to better understand the magnitude of the small drop concentration predicted by Equation (52), the

"fine" concentration is compared to the airborne concentration of large drops which results from spray operation. This concentration may be estimated by the relation,

$$C_{DM} = \frac{F}{A U_{tM}} \quad (53)$$

where C_{DM} = the concentration of large drops,

F = flow rate of drops,

U_{tM} = settling velocity of mean size.

Dividing $(C_d)_{max}$ by C_{DM} gives

$$\frac{(C_d)_{max}}{C_{DM}} = \frac{Q_d}{\frac{3}{2} \frac{EhF}{D_M A U_{tM}} - \frac{U_t}{U_{tM}}} \quad (54)$$

The fine drop concentration predicted by Equation (54) was evaluated using drop size data obtained by the manufacturer of the nozzles used in the CSE experiments. For small drop sizes, the existing curves were extrapolated, assuming log-normal behavior. The airborne concentrations of fine drops was calculated for three drop size ranges. The largest size range covered drops having diameters of 100 to 400 microns. An impaction efficiency, E , of unity, and a value of U_t for 100 micron drops were used for this size range. U_{tM} was chosen as the value for the mass median diameter, 1200 microns. These assumptions will cause an over-prediction compared to the value which would be predicted for a step-wise summation over all drop size increments. For the 100-400 micron range, airborne drops were estimated to represent a volume about 5% of that for the larger spray drops. An intermediate size range, 50 to 100 microns, was also treated using an E of 1.0 and U_t corresponding to a 50 micron drop. For this size range $(C_d)_{max}/C_{DM}$ was only 6×10^{-6} , showing that a negligible fraction of the spray would remain airborne as drops in this

size range. A small drop size range, 0-50 micron diameters, was treated using $E = 4 \times 10^{-4}$, the smallest E which can occur. This E is based on diffusion and interception, and neglects other deposition mechanisms such as diffusio-phoresis and thermophoresis; it is no doubt smaller than would actually occur. The value of $(C_d)_{\max}/C_{DM}$ for the small size range was 1.3×10^{-4} . These calculations demonstrate that the buildup of fine drops due to continued spraying would not be expected to be a factor in spray operation. For a containment spray system, less than 0.1% of the spray liquid would be airborne at any instant. Of this, less than $1.3 \times 10^{-2}\%$ would consist of drops smaller than 50 microns. Hence the presence of fine drops generated by spraying is expected to be of no practical consequence. These results are summarized in Table IV.

TABLE IV. Predicted Maximum Concentration of Fine Drops in CSE Spray

<u>Drop Size Range</u>	$\frac{(C_d)_{\max}^*}{C_{DM}^{**}}$
100-400 microns	0.05
50-100 microns	6×10^{-6}
0-50 microns	1.3×10^{-4}

* $(C_d)_{\max}$ = maximum mass concentration of fine drops in gas phase.

** C_{DM} = mass concentration calculated for 1200 μ drops.

E. EFFECT OF STEAM CONDENSATION ON SPRAY ABSORPTION

For some reactor systems, the spray solutions pass through heat exchangers to cool the water during recirculation. For such a system, condensation of water onto drops will occur as long as steam is being generated. For the CSE experiments heat exchangers were not used in the spray circuit, and recirculation caused the temperature of the

spray solution to quickly approach that of the vessel atmosphere. Condensation on drops was minimal during recirculation. The CSE spray system thus differs from reactor systems using heat exchangers. The potential influence of condensation on absorption will be briefly discussed.

1. Increase in Drop Diameter by Condensation

The maximum amount of water which can condense on a drop is determined by the temperature difference between the entering drops and the containment atmosphere. For a containment atmosphere temperature of 250 °F and for water entering at 70 °F, the temperature rise is equal to or less than 180 °F. A heat balance on the drop gives

$$\text{heat of condensation} = \text{sensible heat increase} \quad (55a)$$

$$\lambda_c M_c = \frac{\pi}{6} d^3 \rho C_p (180) \quad (55b)$$

$$M_c = \frac{30 \pi d^3 \rho C_p}{\lambda_c} \quad (55c)$$

Hence the final mass is

$$M = \frac{\pi}{6} d^3 \rho + \frac{30 \pi d^3 \rho C_p}{\lambda_c} \quad (55d)$$

and the final size is

$$d_f = d \left(1 + \frac{180 C_p}{\lambda_c} \right)^{1/3} \quad (56)$$

For water, taking $C_p = 1 \text{ Btu/}^\circ\text{F lb}$ and $\lambda_c = 1000 \text{ Btu/lb}$, d_f is about 6% greater than the initial size. This is probably the maximum increase in size as in practice the temperature difference could well be less than 180 °F, and not all heat is transferred by means of water condensation. This 6% change in drop size is relatively unimportant. It would cause differences in absorption of 10-15%, which is of negligible importance for most cases of practical interest.

2. Effect of Build-Up of a Pure Water Layer

Chemical reactions play an important role in absorption of I_2 and CH_3I . Hence the build-up of pure water on the surface of a drop by condensation could influence the absorption rate. From the preceding calculation, it was concluded that drops would increase in diameter by about 6%. Thus for a 1000 micron diameter drop, a pure water layer having a thickness of 30 microns might form at the surface. A conservative analysis of the effect of this layer may be based on the assumption that convective mixing within the drop is negligible. Molecular diffusivities in water are about $4 \times 10^{-5} \text{ cm}^2/\text{sec}$ at 70 °F and increase with temperature. Diffusion calculations indicate that the surface concentration of a reactive reagent would reach 50% of the bulk concentration in a time of about 0.1 second. Since drop residence times are of the order of seconds, the condensate layer could not greatly influence the overall absorption. For a 3 second fall time one would predict that the transfer rate would be reduced by about 3%. The model used in arriving at this estimate will yield an overestimate of the effect, because drop mixing was neglected, and because the absorption rate was assumed to be linearly related to the concentration of a dissolved reactive solute.

3. Increased Transfer Due to Sweep Effect

The gas phase transfer coefficient will be enhanced because of bulk motion toward the surface caused by the steam flux. This effect would obviously be negligible for organic iodides such as CH_3I because their transfer rate is controlled by liquid phase resistance. The degree of enhancement of gas phase transfer, for an airborne species which exhibited zero back pressure at the surface, was estimated from theory. The drop was assumed to fall at terminal velocity. The water condensation rate was calculated from Equation (11) in

conjunction with a heat transfer model based on a well mixed drop. The enhancement in the transfer coefficient was calculated using data presented by Bird, et al.⁽⁹⁾ The results of this calculation are presented in Table V.

TABLE V. Predicted Enhancement of Gas Phase Mass Transfer Due to Water Condensation

<u>Drop Diameter</u>	<u>Percent Enhancement*</u>
500	0.5%
1000	2.5%
2000	10%

* *Initial drop temperature 70 °F and atmosphere temperature 250 °F.*

The data of Bird, et al.⁽⁹⁾ used to obtain the predictions shown in Table V were calculated from the penetration theory. Models based on film theory and boundary layer theory give comparable results. Although these models would not be expected to apply precisely to drops, large discrepancies would not be expected. Thus one would not expect water condensation to greatly enhance the absorption of iodine vapor in a containment vessel.

4. Effect of Condensation on Aerosol Particle Capture

Water vapor condensation adds a diffusiophoretic mechanism for aerosol capture. For a broad range of particle sizes (0.1 to 2 μ) the diffusiophoretic effect can be the dominant capture mechanism. Hot spray would not be expected to remove aerosol particles as well as cold spray. This effect is shown in Figure 4. A spray system which included a heat exchanger to cool sprays during the recirculation period would be more efficient in removing aerosol particles than one which did not. The CSE system would thus be typical of the latter.

IV. EXPERIMENTAL MEASUREMENTS

A. DESCRIPTION OF CSE SYSTEM

The CSE experimental equipment comprises a model containment vessel with provision for generating fission product simulants and measuring their behavior under accident conditions. The components of this system are described in more detail by Hilliard⁽³⁾ and by Linderoth.⁽³⁵⁾ The experimental equipment used in recirculating spray tests is shown schematically in Figure 5.

The containment vessel is composed of three interconnected vessels. An outer vessel, called the main containment vessel, 30,680 ft³; an inner vessel, called the drywell, 2286 ft³; and the vessel composing two-thirds of the annular space between the drywell and the main containment vessel, called the wetwell, 4207 ft³. The main containment vessel is 25 ft diameter, 66.7 ft overall height. All 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. For the spray experiments discussed here the lid of the 11-ft diameter drywell was raised so that its volume was common to the main room. The combined volume of this "main room" is 21,005 ft³. One third of the annular space between the drywell and main containment vessel is a small access area called the "middle room", 2089 ft³ in volume. Below the middle room, drywell, and wetwell is a third space called the "lower room", 3380 ft³ in volume. The wetwell volumes were sealed off and not exposed to steam or fission product simulants in these

* *Manufactured by the Carboline Co., St. Louis, Missouri.*

FIGURE 5. Schematic Diagram of Containment Arrangement
Used in CSE Spray Tests

experiments. 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 accumulate in three locations: the drywell pool, the main vessel pool located in the lower room, and on the flat deck of the main room. The first two are stirred, sampled frequently, and the liquid volume monitored. The liquid on the deck is not monitored. It drains into the main pool and together with the main room wall trough is the source of the main vessel pool.

A line from the plant steam boiler, terminated near the bottom of the drywell, provides steam input to heat the vessel and its atmosphere.

B. GENERATION OF AEROSOLS AND GASES

Aerosols and gases were used in the CSE tests to simulate airborne fission products expected to be present following a fuel overheating accident. The simulant materials included elemental iodine and methyl iodide to represent halogens, cesium oxide to represent volatile solids, and uranium oxide to represent non-volatile solids. For analytical purposes the species were tagged with I-131 and Cs-137. Uranium was assayed by counting the alpha particles emitted from normal uranium. The activity levels were trace compared to the level of activity expected in post-accident containment atmospheres. A full description of the methods of generation of the simulants has been given by Coleman.⁽³⁶⁾ The generating methods are briefly described as follows.

1. Elemental Iodine

One hundred grams of stable elemental iodine was equilibrated with about 1 curie of I-131 by mixing I crystals (reagent grade) with carrier-free I-131 present chemically as NaI.

The molten mixture was maintained in a sealed quartz vessel at 130 °C for two hours to assure complete exchange of iodine isotopes. The exchange half-life is about 10 minutes under these conditions. (36)

The iodine was released by passing air over the iodine in a quartz vessel which was heated electrically. The iodine was released at a rate of about 10 g/minute. The airborne iodine was mixed with the cesium aerosol, and then passed over molten UO_2 to permit interaction between the hot fuel and iodine. A twenty foot long stainless steel pipe heated electrically, delivered the airborne iodine, cesium, and uranium to the containment vessel. A steam jet located inside the containment vessel provided the pressure drop required to deliver the simulants from the point of generation into the containment vessel. The iodine vapor formed in this way was characterized by means of a CSE Maypack. (37) More than 99% of the airborne iodine was captured by silver components. Between 0.2% and 0.5% was trapped on the filter, and less than 0.1% reached the charcoal paper. Very small amounts of iodine (<0.05%) reached the charcoal bed of the Maypack sampler.

2. Methyl Iodide

Traced methyl iodide was prepared by isotopic exchange of NaI^{131} with CH_3I in a solution of methanol and water. Analysis of the volatile fraction showed that the exchange was largely complete after 2 hours at room temperature. (36) Equilibrium was carried out in glass apparatus. The solution was transferred to a stainless steel U-tube which was connected to the methyl iodide delivery line. The methyl iodide was released by warming and passing an air stream through the U-tube. The methyl iodide was not contacted with hot UO_2 , but entered the containment vessel through a separate injection line. This separate injection line was necessary to prevent thermal decomposition of CH_3I . Collection of the generated CH_3I in

Maypack samplers showed that greater than 95% of the activity reached the charcoal bed of the Maypack. Most of the remaining 5% was retained on the charcoal filter preceding the charcoal bed.

3. Cesium Aerosol

Cesium aerosol was generated by heating tagged cesium carbonate to a temperature high enough to cause volatilization. Based on equilibrium partial pressures, it is expected that the most predominant chemical species airborne was Cs_2O . $\text{Cs}(\text{OH})$ and Cs are also expected to exist in the gas phase. The Cs_2CO_3 was heated to about 1200 °C in a nickel boat, causing an optically dense aerosol to be generated within the air stream. This aerosol is mixed with the iodine vapor and then passed through the UO_2 furnace. Intimate mixing of the I and Cs within the UO_2 furnace and in the aerosol delivery line provides opportunity for reaction to form CsI . About 6 grams of Cs are volatilized compared to the 100 grams of I. Thus if chemical interaction were complete, 10% of the I would enter the containment vessel as CsI .

4. Uranium Oxide Aerosol

Fuel aerosol was produced by inductively heating zircaloy or stainless steel clad UO_2 rods packed to 95% theoretical density. Rods were 1/2" diameter by 3" long, containing approximately 80 g of UO_2 . The fuel element was supported on a 200 g bed of granular UO_2 . The quartz tube containing the UO_2 was surrounded by a cooling jacket to inhibit reaction and rupture of the quartz furnace tube. The UO_2 fuel pieces were molten and held at a temperature of about 2200 °C. The aerosol particles generated were agglomerates with mass median aerodynamic diameters near one micron. The primary particles making up the agglomerate particles ranged in size from 0.01 to 0.5 microns. Aerosol was produced at a rate of

about 200 milligrams per minute for a time period of 20 minutes. The uranium oxide was heated to the melting point 10 minutes before I and Cs generation was begun. Generation was terminated 10 minutes after the initiation of iodine release.

C. CHARACTERIZATION OF THE CONTAINMENT ATMOSPHERE

The concentration of fission products in the CSE vessel was measured by air samples taken at 14 positions within the containment vessel. At each sampling position a cluster of 12 individual samplers permits sampling at 11 times, leaving one sample for measuring the background level of contamination. The spatial positions of the samplers are shown in a cross-sectional view of the CSE vessel in Figure 6. The spatial positions of the sampling points are further described in Table VI.

TABLE VI. Locations of Maypack Clusters Used in CSE Spray Experiments

<u>Maypack Cluster Number</u>	<u>Elevation,^(a) (ft)</u>	<u>Radius, (ft)</u>	<u>Azimuth^(b) (degrees)</u>	
M 02	+12	0	0	0 of Main Room
M 05	+33	0	0	Top dome
M 12	-6	4.5	135	Drywell, near top
M 13	-18	4.5	135	Drywell, near bottom
M 14	-12	10	260	Middle room
M 15	-24	10	260	Bottom room
M 16	+24	11	45	
M 18	0	11	45	
M 19	0	11	135	
M 21	+24	0	0	
M 22	+12	6	270	
M 23	0	11	270	
M 24	+12	11	45	
M 25	+24	11	270	

a. Main deck is at -5.5 ft.

b. Zero degrees is at center of 8' equipment access entry.

FIGURE 6. Location of Maypack Clusters in CSE

Individual samplers consist of a number of adsorbents in series. A sketch of the CSE Maypack sampler is shown in Figure 7.

The adsorbent characteristics of this sampling train have been reported by McCormack.⁽³⁷⁾ The interpretation of the sampler is briefly as follows: (1) Particulate materials are captured by the inlet filter, (2) Elemental iodine is captured by the silver screen and the silver membrane filter, (3) Elemental iodine and volatile forms of inorganic iodine which penetrate the filter and screen components are trapped by the charcoal paper component, (4) Organic iodides, including methyl iodide, are trapped within the charcoal bed.

One of the samplers within each cluster is used to measure the background contamination of the sampler components caused by "breathing", leaks, diffusion through the inlet section, contamination during handling, etc. The background level is not important for correcting samples withdrawn early in the run, but is important for samples withdrawn at long times when the airborne concentration is very low.

In addition to the cluster Maypack samples, "thief" samples were withdrawn by inserting Maypack samplers through an airlock. These samples give data with very low background count levels since they were not exposed to the higher gas concentrations. All samples were withdrawn at a rate of 0.5 cfm (of air at atmosphere pressure) for 3 minutes duration.

D. LIQUID PHASE SAMPLING

The liquid phase was extensively sampled to aid in establishing the disposition of the fission product materials. Samples were periodically obtained from four spray drop samplers, from the wall run-off trough, from the drywell sump, and from the main sump. These samples were analyzed for iodine and cesium. Specific samples were analyzed for pH, boron content,

1	Inlet	6	Six Silver Plated Screens	11	Screen
2	Teflon Ball	7	Silver Membrane Filter	12	Spring
3	Nose Cone	8	Charcoal Loaded Filter	13	Body
4	Teflon Gasket	9	Stop Ring	14	End Cap
5	Two Particle Filters	10	Charcoal Bed	15	Outlet

FIGURE 7 Schematic Diagram of a CSE Maypack Showing Filter and Adsorber Arrangement

and sodium thiosulfate concentration. Iodine forms in the liquid phase were studied by filtration and benzene extraction of selected samples.

For the fresh spray periods of Runs A-10 and A-12, spray drop samples were collected in a stainless steel boat and withdrawn through the thief sampling port. This permitted collection of falling spray drops with a minimum of error due to holdup time or surface contamination.

E. EXPERIMENTAL CONDITIONS AND PROCEDURES FOR CONTINUOUS SPRAY TESTS

1. Test Procedure Sequence

The sequence of experimental steps used in Runs A-10 and A-12 is briefly listed below.

- 1) Install samplers and perform operational tests.
- 2) Pressurize vessel with air for leakage rate test.
- 3) Vent air pressure to ambient and recirculate air through high efficiency filter until condensation nuclei concentration is less than 300 nuclei per cm^3 .
- 4) Add steam until desired, steady state, operating conditions are reached (250 °F, 49 psia).
- 5) Drain liquid pools created by steam condensation during warm up.
- 6) Melt UO_2 to initiate $\text{UO}_2\text{-ZrO}_2$ aerosol production.
- 7) Initiate fresh spray, 50 gpm, 1210 μ mass median drop diameter.
- 8) Inject I_2 and cesium over molten UO_2 and into the containment atmosphere. 'Maintain the generation rate approximately linear over the release duration of about 10 minutes. Time zero for run is to be defined as when cesium-iodine release is initiated.
- 9) Sampling of gas phase, liquid pools and spray droplet liquid commenced. Temperature, pressure, liquid volumes, steam feed and anemometer reading taken throughout test.

- 10) Stop fresh spray at 40 minutes after time zero.
- 11) Start recirculating sprays at 50 minutes after time zero. Continue spraying for about 24 hours.
- 12) Turn off sprays at test termination, drain vessel pools and allow system to cool to about 100 °F.
- 13) Purge air from the vessel through charcoal beds and enter the vessel to retrieve the Maypack gas phase sampling clusters.
- 14) Disassemble gas phase samplers, package and label individual components for gamma energy analysis.
- 15) Initiate radiochemical analyses within one day following the test and continue for about 2 weeks until the 1500-2500 individual samples are processed.

2. Summary of Physical and Operational Conditions

CSE physical parameters important relative to spray absorption are listed in Table VII. Temperature and flow conditions specific to Runs A-10 and A-12 are presented in Table VIII. The amounts of simulant aerosol released to the containment atmosphere in Runs A-10 and A-12 are listed in Table IX. As noted in Table VIII, sprays were initiated before injection of iodine and cesium was begun. In Run A-10, methyl iodide was injected simultaneously with injection of elemental iodine. In Run A-12, methyl iodide was injected some 20 hours prior to initiation of I_2 release.

The temperatures and pressures within the containment vessel are shown in Figures 8 and 9 for Runs A-10 and A-12 respectively. In both of these runs, the fresh spray period caused a rapid decrease in the temperature and pressure within the vessel. Continued steam feed permitted the initial temperature to be reached as the spray was recirculated. In Run A-10, the rupture disc used to seal the wetwell volume from the containment space failed. The wetwells were pressurized with air, and hence the partial pressure of air in the containment vessel underwent a step increase.

TABLE VII. Numerical Values of Physical Parameters in CSE Spray Tests

<u>Parameter</u>	<u>Units</u>	<u>Numerical Value</u>
volume above deck including drywell	M ³ , (ft ³)	596, (21,005)
surface area above deck, including drywell	M ² , (ft ²)	569, (6140)
surface area/volume	M ⁻¹ , (ft ⁻¹)	0.958, (0.293)
horizontal cross-sectional area	M ² , (ft ²)	45.3, (487)
volume of middle room	M ³ , (ft ³)	59, (2089)
surface area of middle room	M ² , (ft ²)	127, (1363)
volume of lower room	M ³ , (ft ³)	96, (3384)
surface area of lower room	M ² , (ft ²)	191, (2057)
drop fall height to deck	M, (ft)	10.3, (33.8)
drop fall height to drywell sump	M, (ft)	15.4, (50.5)

TABLE VIII. Thermal and Flow Conditions for CSE Runs A-10 and A-12

<u>Parameter</u>	<u>Units</u>	<u>Value for Run A-10</u>	<u>Value for Run A-12</u>
spray flow rate	gpm	49	50
spray pressure drop	psi	40	40
number of spray nozzles	3/4-7G3*	12	12
drop mass median diameter	microns	1210*	1210*
geometric standard deviation of drop distribution	none	1.5*	1.5*
estimated fraction of upper volume sprayed	none	0.8	0.8
time of fresh spray period	minutes	(t ₀ - 2) → (t ₀ + 40)**	(t ₀ - 4) → (t ₀ + 40)
time of recirculating spray period	minutes	(t ₀ + 50) → (t ₀ + 1140)	(t ₀ + 50) → (t ₀ + 1320)
initial temperature	°F	249	253
initial vessel pressure	psia	49	47
initial condensation nuclei conc.	particles/cm ³	<300	<300
spray solution composition		a	b

* Drop size distribution data supplied by Spraying Systems Co., Bellwood, Ill.

** t₀ defined as beginning of I₂ release

a. 2750 ppm B as H₃BO₃ in NaOH, pH 9.4

b. 2750 ppm B as H₃BO₃ in NaOH, pH 9.2, 1 wt% Na₂S₂O₃

TABLE IX. Fission Product Simulants in CSE
Recirculating Spray Tests.

<u>Simulant Release Parameter</u>	<u>Units</u>	<u>Run A-10</u>	<u>Run A-12</u>
I ₂ release duration	min	10	10
Cs release duration	min	10	10
UO ₂ release duration	min	20	20
CH ₃ I release duration	min	10	10
I ₂ release mass conc*	mg/M ³	160	160
CH ₃ release mass conc*	mg/M ³	1.6	5
Cs release conc*	mg/M ³	12	7.9
UO ₂ - ZrO ₂ release conc*	mg/M ³	~3	~3

* release mass conc = total mass injected/596 M³

FIGURE 8. Temperature and Pressure for Run A-10

FIGURE 9. Temperature and Pressure for Run A-12

F. SUMMARY AND DISCUSSION OF EXPERIMENTAL RESULTS FOR RUNS
A-10 AND A-12

The source term in accident dose calculations is the product of leakage rate and gas phase concentration. Hence the magnitude of predicted doses varies linearly with the airborne concentration of fission products. The airborne concentration levels depend on how much fission product is released to the containment gas volume, on its rate of release, and on how fast the fission product is removed from the gas phase. The two CSE tests described in this report were designed to provide information on the rate of washout of fission products by sprays. The washout rate depends on system parameters such as spray flow rate, contained gas volume, and temperature. Hence the CSE data apply to specific values of these important parameters and washout rates for other systems must be calculated from mathematical models. The CSE results are interpreted in terms of theoretical models in the chapter of this report entitled, "Comparison of Observed Washout with Theory."

1. Time-Concentration Histories for Fission Products in the
Containment Gas Phase

The airborne concentrations of iodine species for Run A-10 are shown in Figures 10 through 14. The total iodine concentration, shown in Figure 10, attains a maximum concentration of about 10% of the value calculated by dividing the injected mass by the main room gas volume. After generation was terminated, the main room gas phase concentration rapidly decreased to a value which is some 30% of the maximum concentration (3% of the release concentration). Washout at times longer than 20 minutes occurred more slowly, even for fresh spray solution. The concentrations within the other two connected containment volumes increased with time until the main room concentration was reached. During recirculation the concentrations were equal in all compartments.

FIGURE 10. Total Airborne Iodine Concentration in Run A-10

FIGURE 11. Particulate Iodine Concentration in Run A-10

FIGURE 12. Elemental Iodine Concentration in Run A-10

FIGURE 13. Iodine Trapped by Charcoal Paper in Run A-10

FIGURE 14. Airborne Methyl Iodide Concentration in Run A-10

In Figure 11, the airborne concentration of particulate-associated iodine is shown as a function of time. During the iodine release period the iodine captured by the glass-fibre filter accounts for some 10% of the total iodine. After injection this fraction rapidly decreases, and for times longer than 12 minutes, the fraction of airborne iodine associated with particles is negligible. The data presented in Figure 11 for particulate-associated iodine are based on direct analysis of the filters. No corrections have been applied to account for potential adsorption of elemental iodine on the filter, which could account for as much as 20% of the total radioiodine found on the filter. (37)

The airborne concentration of iodine trapped by the silver components of the Maypack are shown in Figure 12. This fraction of the total has been called elemental iodine, because of the known deposition characteristics of elemental iodine on silver. It is possible that other forms of iodine, such as HOI , could account for a part of the material deposited on the silver screens. The concentration of elemental iodine increased rapidly during the injection period. Washout was rapid for about 10 minutes following the termination of injection. At longer times, removal from the gas phase was slow, even for fresh spray. This slow rate of removal by fresh spray is not expected to occur for elemental iodine; hence it is concluded that the silver screen activity is in part a chemical form of iodine less absorbable in water spray than is elemental iodine.

The concentration of iodine deposited on the charcoal paper, is shown in Figure 13. This component increases in concentration to a maximum at the end of the injection period. Its concentration remains essentially constant during the fresh spray period, showing that it is either removed very slowly or is generated at a rate equal to the removal rate. At the end of the fresh spray period, this component accounts for about

6% of the total airborne activity. After some 1100 minutes of spraying, 13% of the total airborne activity deposits on the charcoal paper. Since only two to three percent of methyl iodide drawn through the sampler would be expected to be trapped on the charcoal paper,⁽³⁷⁾ it is concluded that most of the material collected on the charcoal paper consists of higher organic iodide or other inorganic iodides which are not reactive with silver.

The airborne concentration of methyl iodide is shown in Figure 14 for Run A-10. Methyl iodide reaches its maximum concentration at the end of the release period and then is removed slowly by sprays. A removal half-time of some 12 hours was observed for the 1000 minute recirculating spray period. All of the radioiodine deposited in the granular charcoal bed was assumed to represent methyl iodide. Actually, the charcoal bed would also sorb chemical forms of iodine which penetrated the other Maypack components. The charcoal bed activity could thus include other penetrating chemical species.

Cesium and uranium particle concentrations for Run A-10 are shown in Figures 15 and 16. As expected, maximum concentrations develop at the end of the release period. The initial washout rate corresponds to a removal half-time of about 16 minutes. Cesium and uranium are washed out at the same rates after the release period. During the recirculation period, cesium is washed out at a rate corresponding to a half-time of 135 minutes. The similar behavior of cesium and uranium following the aerosol injection period is consistent with the postulation that the aerosol particles are agglomerates which contain both cesium and uranium. Particulate iodine was removed at about the same rate as cesium and uranium during the recirculation period. Hence, at least part of the iodine may be attached to the cesium and uranium aerosol particles. Particulate iodine, however, was removed much faster during

FIGURE 15. Airborne Cesium Concentration in Run A-10

FIGURE 16. Airborne Uranium Concentration in Run A-10

the early part of the fresh spray period than Cs and I_2 . This difference in washout behavior is consistent with two possibilities; (1) the particulate iodine may be associated with fog drops larger than 3 microns, or (2) a reversibility in iodine attachment to particles (including fog drops) may have depleted the iodine associated with particles.

In Run A-12, the operating sequence and thermal conditions were similar to Run A-10. However, the spray solution contained 1.0 wt% sodium thiosulfate.

The airborne concentration of methyl iodide, and of elemental plus particulate forms for Run A-12 are shown in Figure 17. The elemental forms and particulate forms are shown as a single data point. This numerical combination of filter and silver component activity appeared to be necessary because of capture of elemental iodine by the glass filter paper which was wet by fine drops of thiosulfate spray. The initial half-life for removal of these forms is about 2 minutes, which is numerically equal to the value expected for elemental iodine. After 5 minutes of spraying, the removal rate slows. During recirculation, the elemental and particulate forms are washed out at a rate which parallels that of methyl iodide.

Methyl iodide is removed during the fresh spray period with a half-life of about 150 minutes. The duration of the fresh spray period is short compared to the removal half-time. This prevents accurate determination of the slope of the concentration-time history. After steady-state temperature is reached during recirculation, methyl iodide is removed with an 80 minute half-life.

The fact that the elemental plus particulate concentration parallels that of methyl iodide is consistent with the postulation that the filter and screens were able to absorb 5-10% of the methyl iodide. However, we have been unable to postulate a

FIGURE 17. Airborne Iodine Concentration in Run A-12

reasonable mechanism for such high absorption of methyl iodide by the filter and silver screens. It is possible that the similarity in shape is coincidental.

The total airborne concentration of iodine, and the concentration of the charcoal paper fraction are displayed in Figure 18. Initially, the total iodine behaves as the elemental and particulate forms, because these two species form the major part of the airborne mass. After 20 minutes of spraying, methyl iodide is the dominant species, and the total iodine concentration is substantially the same as the methyl iodide concentration. The activity associated with the charcoal paper appears to be constant in concentration during the fresh spray period. The concentration falls during the recirculation period with a half-life of 80 minutes, the same as that for methyl iodide. It is likely that the charcoal paper activity is methyl iodide.

The total iodine in the gas phase reached a maximum concentration of about $7 \times 10^3 \mu\text{g}/\text{M}^3$. This is 4.5% of the concentration level which would have been attained if no absorption had occurred within the containment vessel.

The concentration of cesium and uranium aerosols are shown in Figure 19. The cesium concentration reached a maximum of approximately $700 \mu\text{g}/\text{M}^3$ at the end of the release period of 10 minutes. This concentration is about 7% of the concentration which would have been attained if no washout had occurred; washout of cesium particles continued during the fresh spray period at a rate equivalent to a half-life of 23 minutes. During recirculation, washout proceeded more slowly. The half-time for washout increased from 58 minutes to 90 minutes at 500 minutes after time zero.

Uranium particle data are incomplete due to analytical problems. It appeared that for the recirculating spray period appreciable wetting of the fiberglass filter occurred which caused particle migration into the filter. This prevented

FIGURE 18. Airborne Iodine Concentration in Run A-12

FIGURE 19. Airborne Particle Concentration in Run A-12

accurate analysis by alpha particle detection because an appreciable fraction of the alpha emissions were absorbed by the filter. The data obtained for uranium indicate washout at a rate similar to that for cesium particles. Similar behavior was observed in Run A-10, and this reinforces the postulation that an appreciable fraction of the uranium and cesium particles exist as co-agglomerates.

Methyl iodide was injected into the vessel 1162 minutes prior to release of other fission product simulants in Run A-12. The purpose of this early injection was to demonstrate the retention of methyl iodide on adsorbents within the Maypack sampler. The vessel atmosphere was at room temperature and atmospheric pressure at the time of injection. The concentration-time history shows a maximum about 100 minutes after injection. Following this maximum, the concentration decreases to 35% of the maximum over a period of 400 minutes, and then remains constant. The apparent change in concentration is attributed to three factors. These are (1) imperfect mixing in the gas phase prior to steam injection, hydrolysis of methyl iodide in the steam condensate, and an initial adsorption of methyl iodide in the paint covering the vessel shell. Virtually all of the methyl iodide was retained by the charcoal components of the sampler. For room temperature conditions, up to 30% of the methyl iodide was retained by the charcoal paper. For steam-air mixtures at 250 °F, the charcoal paper retained about 2% of the methyl iodide. These observations demonstrate that methyl iodide does not deposit on the inlet filter or on silver components of the Maypack sampler. For saturated steam-air mixtures at 250 °F, a few percent of the methyl iodide would deposit on the charcoal paper.

FIGURE 20. Behavior of Methyl Iodide in Containment Prior to Injection of Elemental Iodine

2. Concentration of Fission Products in Spray Liquid

The liquid in the drywell sump, the main vessel sump, the falling drops, and wall trough was sampled at regular time intervals. These samples do not provide an accounting for all fission products in the liquid because an appreciable volume of liquid is held up on the floor of the main room. This liquid is not sampled, hence its concentration is not well known during the early part of the run.

The concentration of iodine and cesium in the sumps of the drywell and the main vessel are shown in Figure 21 for Run A-10. The concentration of fission products in the drywell increases very rapidly following the start of fission product injection into the containment atmosphere. The concentration of fission products in liquid accumulated in the main sump does not increase immediately at time zero, but shows a 5-10 minute lag. This is caused primarily by holdup of spray liquid on the vessel deck. After the fresh spray period, the valving is changed to permit continuous draining of the drywell sump into the containment vessel sump, and recirculation of the liquid from the containment vessel sump through the spray nozzles. The concentration of cesium and iodine decreases slowly during the recirculation period as a result of dilution by steam condensate.

Comparison of the cesium concentration in the drywell versus that in the containment vessel with the curves for iodine implies that a greater fraction of the cesium is absorbed within the drywell than would be expected from a well mixed gas phase.

Spray liquid was sampled in four funnels located at two different distances from the nozzles. Results of the liquid concentration measurements are shown in Figure 22 for Run A-10.

FIGURE 21. Fission Product Concentration in Spray Liquid in Run A-10

FIGURE 22. Fission Product Concentration in Drop Liquid in Run A-10

Also shown in Figure 22 are the liquid concentrations measured by means of a "thief" sampler inserted through a Maypack port. These analyses show that iodine was absorbed rapidly for the first 10-15 minutes. After about 15 minutes, the drop absorption becomes approximately constant with time showing that the rapidly removed species is depleted.

For the first 10 minutes of spray operation, the concentration indicated by the thief sampler is appreciably less than indicated by the funnel samples. This may be due to non-uniform gas phase concentration during iodine release, or due to absorption at the surface of the funnel. The collection funnel located nearest to the nozzle header indicated the lowest iodine concentration, as expected. Drop concentrations indicated by the funnel collectors cannot be considered definitive because of absorption at the wetted surface and because of holdup and mixing in the tubing which delivers the liquid to the sampling station.

The liquid which intercepted the wall of the vessel was collected in a trough which attached to the outer wall. The wall liquid was piped to a measuring station where it was sampled, and the flow rate measured. The concentration of iodine and cesium in the wall liquid is displayed in Figure 23. The concentration peaks at about 7 minutes after the beginning of iodine injection, which is very nearly the same as was observed for the falling drops. The wall trough concentration does not decrease as rapidly as the falling drops following the maximum. This may reflect a relatively greater absorption efficiency of the wall film for the persistent activity species. For iodine, the wall film concentration builds to a value less than that indicated by the funnel drop collectors. However, at the end of 40 minutes of spraying, the wall concentration is about ten times higher than that of the drops.

FIGURE 23. Fission Product Concentration in Wall Liquid in Run A-10

The amounts of fission product iodine in the liquid sumps is shown in Figure 24 for Run A-10. This curve was obtained by multiplying the liquid concentration in the sumps by the volume of liquid indicated by a manometer depth gage. Iodine in solution in liquid retained on the main room floor was not accounted for during the fresh spray period. For the recirculation spray period, the iodine held up in liquid on the floor was estimated by multiplying the equilibrium volume of the floor pool (2750 ℓ) by the concentration in the spray liquid. The results show that some 85% of the iodine injected into the vessel can be accounted for in the liquid within about 30 minutes after injection was begun. Since only a small part of the remaining 15% appears in the gas, it is concluded that the bulk of the remaining 15% was plated on wall surfaces.

The amount of cesium in the liquid within the containment vessel for Run A-10 is shown in Figure 25. The data show that after about 30 minutes, 5.3 grams of cesium (76% of that injected) appears in the liquid. Continued spraying does not appreciably change the amount of cesium in the aqueous phase. Approximately 1.8 grams of cesium are unaccounted for (25%) and presumed to be plated on solid surfaces within the vessel. One data point (at 200 min) indicates an appreciably higher mass of cesium. This is most likely caused by incomplete mixing of liquid streams, resulting in a sample which contained more cesium than the bulk average.

Fission product concentrations in liquid contained within the drywell sump and the main containment vessel sump for Run A-12 are displayed in Figure 26. The rapid increase in liquid concentration following the beginning of injection was as expected for sprays which are efficient in removing airborne materials. The cesium concentration in the drywell rose to a value higher than expected on the basis of washout models based on the assumption that the gas phase was well mixed.

FIGURE 24. Iodine Mass Accounted for in Spray Liquid in Containment Vessel for Run A-10

FIGURE 25. Cesium Mass in Spray Liquid in Containment Vessel for Run A-10

FIGURE 26. Fission Product Concentration in Sump Liquid in Run A-12

The initial (pre-release) iodine concentrations in the sumps were somewhat higher than was observed for Run A-10. This was due to injection of methyl iodide into the vessel about 24 hours prior to time zero. During this time period, hydrolysis of the methyl iodide caused inorganic iodide to appear in the vessel sumps.

During the recirculation spray period, the drywell sump drained into the main vessel sump, mixing the two pools. After 120 minutes, only the liquid from the main vessel sump was analyzed.

Concentrations of fission products in spray liquid in Run A-12 as determined from samples of drops captured by four funnels and by a thief sampler are displayed in Figure 27. The behavior is similar to that observed in Run A-10. During the iodine release period the drop concentration increases to a maximum, and falls rapidly after elemental iodine injection is terminated. This decrease in concentration is caused by a decrease in airborne concentration of elemental iodine.

For Run A-12, the methyl iodide was injected 19 hours prior to the beginning of sprays. This sequence permitted absorption by spray of methyl iodide alone to be measured by means of the thief sampler. After about 30 minutes after time zero, the sprays are observed to remove iodine at a rate equal to the rate for methyl iodide alone. The thief sample yields concentrations which are in good agreement with the concentrations measured by means of the funnel collectors. For methyl iodide absorption alone, calculations of absorption by the wetted film on either the thief collector or funnel collector indicate that an appreciable fraction of the measured activity in the liquid would be accounted for by absorption by the surface film. Hence for methyl iodide absorption by drops of sodium thiosulfate solution, the data obtained here should not be considered as definitive of drop absorption.

FIGURE 27. Fission Product Concentration in Drop Liquid in Run A-12

Concentrations of iodine and cesium in the wall film liquid in Run A-12 are shown in Figure 28. Operating problems prevented collection of samples early in the spray period.

The masses of iodine in the drywell sump and the main vessel sump solutions for Run A-12 are shown in Figure 29. Twenty minutes after time zero, the injected iodine is fully accounted for in the liquid sumps. The indicated iodine mass increases to a value slightly greater than the mass injected. This was caused by non-representative sampling of the drywell pool. Inadequate mixing in the drywell pool resulted from failure of a mixing pump. The most important information portrayed in Figure 29 is that the injected iodine is rapidly absorbed by the spray, which confirms the gas phase concentration data. A small fraction of the iodine remains unaccounted for, and is presumably adsorbed onto solid surfaces within the vessel.

The mass of cesium accounted for in the two sumps is shown as a function of time in Figure 30. Essentially all injected cesium is accounted for in the liquid within the first 20 minutes after release was begun. Inadequate stirring in the drywell sump (caused by mixing pump failure) led to withdrawal of samples which were more concentrated than the bulk of the liquid in this pool. The rapid appearance of fission products within the liquid phase confirms the observed rapid removal from the gas phase.

FIGURE 28. Fission Product Concentration in Wall Liquid in Run A-12

FIGURE 29. Iodine Mass Accounted for in Liquid Pools in Run A-12

FIGURE 30. Cesium Mass Accounted for in Liquid Pools in Run A-12

V. COMPARISON OF OBSERVED WASHOUT WITH THEORY

In this chapter washout of the fission products present as several physical and chemical forms will be compared with theory.

A. ABSORPTION OF IODINE BY FALLING DROPS

Spray drops were collected in four funnels located 8 ft and 23 ft below the nozzle header. Liquid collected was continuously withdrawn from the funnels and delivered to a sampling station outside the vessel. Also, "thief" samples were taken by inserting an open cup into the vessel through a May-pack sampling port. Several factors operate to make these samples less than ideal. One important factor is absorption at the surface of the collectors. This tends to enrich the liquid compared to the incident drops. A second factor is holdup of liquid in the delivery tubing. This holdup introduces uncertainty in assigning a collection time to liquid withdrawn. A third factor is mixing of liquid within the delivery tube. Although these factors are not negligible, liquid concentration data obtained are of benefit in interpreting the observed washout.

The ratios of iodine concentrations in collected drops to gas phase concentration are shown in Figures 31 and 32 as a function of spray time. Also shown is the theoretical value for elemental iodine and methyl iodide. The theory value for elemental iodine was based on a model which neglected back-pressure at the drop surface. For methyl iodide, a stagnant drop model was used. Drop diameter was taken as 1000 microns, and fall height was taken as 23 ft. An initial drop velocity of 1890 cm/sec was taken into account. The observed C_l/C_g ratios rise to values appreciably greater than predicted for elemental iodine during the injection period. After 20 minutes of spraying, C_l/C_g falls to a constant value, intermediate

FIGURE 31. Comparison of Measured Drop Absorption with Theory for Fresh Spray, Run A-10

FIGURE 32. Comparison of Measured Drop Absorption with Theory for Fresh Spray, Run A-12

between the theory values for elemental iodine and methyl iodide. The higher-than-theory values observed during injection are attributed primarily to absorption at the wetted surface of the collector.

The spray liquid concentration qualitatively follows the pattern expected, which confirms the other measurements of washout. For example, for Run A-12, initially the drop liquid concentration is low because airborne iodine is present as methyl iodide. Following initiation of injection of elemental iodine, the liquid enrichment increases sharply and remains high throughout the injection period. After elemental iodine injection was terminated, it rapidly disappeared from the gas phase, leaving behind methyl iodide. The drop concentration enrichment (C_ℓ/C_g) decreased rapidly to the value observed prior to injection of elemental iodine, at which time methyl iodide was the dominant species. As noted, the drop sampling techniques were too crude to give definitive data on drop absorption, and a more detailed analysis of these measurements is not warranted.

B. COMPARISON OF TOTAL IODINE WASHOUT WITH THEORETICAL PREDICTIONS

The gas phase concentration of total iodine was predicted from simple models, using as a basis the mass of iodine injected into the containment vessel as elemental iodine, and as methyl iodide. The run was divided into three time periods, each of which required a distinct theoretical model.

The first time period was the release period in which fission products were released into an atmosphere scrubbed by fresh spray. For this time period the gas phase concentration of elemental iodine was computed from

$$C_g = \frac{G}{(k_g A)_{\text{drop}} + (k_g A)_{\text{wall}}} \left\{ 1 - \exp - [(k_g A)_{\text{drop}} + (k_g A)_{\text{wall}}] t \right\}. \quad (57)$$

The generation rate, G , was obtained from the measured mass released from the generating equipment and the time interval of the release. Radiation level measurements made during the release period verified that the release was approximately linear over most of the release period. Hence G was taken as constant for the release period.

The product of the mass transfer coefficient and interfacial area for falling drops, $(k_g A)$ drops, was evaluated from the Frössling equation [Equation (13)] allowing for a decreasing drop velocity over the fall height [Equation (15)]. The mean drop size was the "effective size" defined by Equation (17). Based on the nozzle manufacturer's drop size distribution data, the effective mean size was calculated to be 980 microns. For simplicity, a drop size of 1000 microns was used in making absorption calculations.

The wall surface transfer coefficient was estimated from Equation (10), for the Grashov number evaluated using the temperature difference which exists under isothermal pre-spray conditions. This estimate of wall surface deposition is not rigorous because thermally and mechanically induced motion in the gas phase as a result of spray operation would play a role. Fortunately, the gas phase transfer coefficient to wall surfaces is not highly dependent on the temperature difference for the magnitudes of temperature differences of interest here. Also, the overall contribution of wall absorption during spray is relatively small. The relatively minor influence of the wall is predicted from theory and is borne out by measurements of fission product concentration in the wall liquid.

For methyl iodide, washout during the generation time of about 3 minutes was predicted to be entirely negligible, hence the methyl iodide concentration was computed from

$$C_g = \frac{Gt}{V} \quad (58)$$

where

- t = time from beginning of methyl iodide generation,
 G = generation rate, equal to total release divided by
 3 minute release duration,
 V = total gas volume of CSE vessel.

The numerical values of parameters used in predictions for the release time period are summarized in Table X.

TABLE X. Values of Parameters Used in Theoretical Predictions for Fission Product Injection Period

	<u>Run A-10</u>	<u>Run A-12</u>
Time Period of Release for I_2 , min	8.7	9.1
Time Period of Release for CH_3I , min	3	(pre-spray release)
Mass of I_2 Released, grams	99	100
Mass of CH_3I Released, grams	1.2	0
Mass of CH_3I Airborne at Beginning of Release Period	0	1.65
Volume of Gas Space Assumed for I_2 , ft^3	21,048	21,048
Volume of Gas Space Assumed for CH_3I , ft^3	26,522	26,522
$(k_g^A)_{drop}$ for I_2 , min^{-1}	0.46	0.46
$(k_g^A)_{wall}$ for I_2 , min^{-1}	0.05	0.05
Washout Rate for CH_3I	0	0
Drop Flow Rate, gpm	46.7	47.7
Wall Film Flow Rate, gpm	2.3	2.3

The second time period for the continuous spray runs was from the end of the generation period to the end of the fresh spray period. During this time period, airborne fission products were scrubbed with fresh solution, with zero generation. For the fresh spray period, the elemental iodine concentration was calculated from

$$C_g = C_{gm} e^{-(k_g A/V)(t - t_R)} \quad (59)$$

where

C_{gm} = maximum I_2 concentration, predicted from
Equation (57) with $t = t_R$,
 t_R = time of release period for elemental iodine.

In this model, back pressure at the surface of the drop is ignored. Experimental measurements in previous CSE runs have shown that partition coefficients for elemental iodine are greater than 3×10^3 , and increase with time as a result of chemical reaction. The fractional saturation was judged to have a negligible influence on the total amount of iodine absorbed by a falling drop.

Perhaps the most serious limitation on the model is the neglect of desorption of dissolved iodine from liquid collected in the pool at the bottom of the main room. Desorption would occur if the concentration of liquid in the pool were higher than that of liquid in equilibrium with the gas phase. This release is of negligible importance in systems which contain appreciable quantities (>1%) of difficult-to-remove forms. This is so because the total concentration of iodine is little influenced by the presence of a slight desorption of elemental iodine from pools. The order of magnitude of the influence of desorption from the pool was investigated using a model in which it was assumed that the pool concentration remained at the theoretical maximum for the initial falling drops, and that the transfer coefficient was equal to that for a vertical wall surface. The equilibrium airborne iodine concentration was predicted to be approximately 0.1% of the release concentration of iodine. Although this concentration level is of little importance in determining the total iodine concentration including methyl iodide, pool desorption limits the

maximum decontamination factor for elemental iodine by fresh sprays. Allowance for pool desorption was not made in the calculations presented here.

Methyl iodide washout during the second calculational period was predicted from a model which accounted for wall film absorption, paint adsorption, and drop absorption. The wall film calculation was made assuming that the film was stagnant. For a stagnant wall film the removal half-time is

$$\frac{0.693}{t_{1/2}/\text{wall}} = \frac{A_W H \sqrt{kD}}{V} \tanh \left(\sqrt{\frac{k}{D}} \delta \right) \quad (60)$$

where

A_W = surface area of liquid film,

k = first order reaction rate constant of CH_3I in liquid film,

D = diffusivity of CH_3I in liquid film,

δ = thickness of liquid film.

Methyl iodide absorption by falling drops was predicted from a stagnant drop model, allowing for a first order chemical reaction. The removal half-time for drop absorption is

$$\frac{0.693}{t_{1 \text{ drops}}} = \frac{F}{V} \left(\frac{C_\ell}{C_g} \right)^* \quad (61)$$

where

F = spray drop flow rate,

$$\left(\frac{C_\ell}{C_g} \right)^* = \frac{\text{concentration in drop at end of fall}}{\text{concentration in gas}}$$

$\left(\frac{C_\ell}{C_g} \right)^*$ was evaluated numerically using the stagnant drop model described by Equation (33).

Paint adsorption of methyl iodide was accounted for by use of a deposition velocity. The removal half-time for paint adsorption was calculated from

$$\frac{0.693}{t_{1/2 \text{ paint}}} = \frac{k'A}{V} \quad (62)$$

where

k' = deposition velocity of methyl iodide on Phenoline-302 paint,

A = total painted surface area exposed to gas.

The deposition velocity used was the initial deposition velocity reported by Rosenberg⁽³⁸⁾ for Phenoline-302 paint. Based on the reactive capacity of this paint⁽³⁸⁾ and the amount of methyl iodide used in CSE tests, only a few percent of the reactive sites were used to combine with methyl iodide. Hence use of an initial deposition velocity for the entire CSE spray tests appears reasonable.

The numerical values of the important parameters for this second calculational period are tabulated in Table XI.

TABLE XI. Values of Parameters Used in Theory Predictions for Washout by Fresh Spray Following the Termination of Fission Product Injection

Parameter	Numerical Value for Run A-10	Numerical Value for Run A-12
Time period for I_2 , min	$\left[(t_o + 8.7) \text{ to } (t_o + 40) \right]$	$\left[(t_o + 9.1) \text{ to } (t_o + 40) \right]$
Time period for CH_3I , min	$\left[(t_o + 3) \text{ to } (t_o + 40) \right]$	$\left[(t_o + 0) \text{ to } (t_o + 40) \right]$
Volume of gas space for I_2 , ft ³	26,522	26,522
Volume of gas space for CH_3I , ft ³	26,522	26,522

TABLE XI. (contd)

Parameter	Numerical Value for Run A-10	Numerical Value for Run A-12
$\frac{(k_g A)}{V}$ drops for I_2 , min^{-1}	0.46	0.46
$\frac{(k_g A)}{V}$ wall for I_2 , min^{-1}	0.05	0.05
Paint deposition rate constant for CH_3I ,* ft/min	2.2×10^{-3}	0
First order reaction velocity for CH_3I in wall film, sec^{-1}	3.3×10^{-3}	1.35
Drop flow rate, gpm	46.7	47.7
Wall film flow rate, gpm	2.3	2.3

* From **Reference 38**.

The third calculational period covered the time of spray recirculation. For this interval, elemental iodine absorption was calculated by assuming that the sump liquid was well mixed, and that the gas phase concentration was constant for a given drop. Wall film transfer was accounted for by assuming a well mixed liquid film. The buildup of elemental iodine is given by

$$C_g = C_{go} e^{-Eht/V} + \frac{C_{l1}}{H}(1 - e^{-Eht/V}) \quad (63)$$

where

$$\begin{aligned}
 E &= F(1 - A) + L_w(1 - B), \\
 F &= \text{drop flow rate}, \\
 A &= \exp - \left(\frac{6k_g t_e}{Hd} \right), \\
 L_w &= \text{wall flow rate}, \\
 B &= \exp - \left(\frac{k_w z_w}{\Gamma H} \right), \\
 k_w &= \text{gas phase mass transfer coefficient to wall},
 \end{aligned}$$

Γ = wall flow rate per unit width of perimeter,
 H = gas-liquid partition coefficient,
 t_e = drop fall time,
 z_w = length of wall film.

From a practical standpoint this treatment gives a near-instantaneous attainment of equilibrium between the gas volume and the spray liquid after recirculation has begun.

For methyl iodide, the washout was predicted from the same model used during the fresh spray period after injection had ceased. This is justified because the long holdup time of liquid in the sump (40 minutes) permits nearly complete reaction of dissolved methyl iodide, even for the base-borate solution used in Run A-10. The numerical values of parameters used in calculating absorption during the recirculating spray period are summarized in Table XII.

TABLE XII. Numerical Values of Parameters Used in Theory Predictions for Fission Product Absorption by Recirculating Spray

Parameter	Numerical Value for Run A-10	Numerical Value for Run A-12
Time period, min	$\left[\begin{matrix} (t_o + 50) \text{ to} \\ (t_o + 1140) \end{matrix} \right]$	$\left[\begin{matrix} (t_o + 50) \text{ to} \\ (t_o + 1310) \end{matrix} \right]$
Volume of gas space, ft ⁵	26,522	26,522
Volume of liquid (liters) at beginning of recirculation	9000	9200
Partition coefficient for I ₂	1×10^4	1×10^5
Paint deposition velocity for CH ₃ I, ft min ⁻¹	2.2×10^{-3}	0
First order reaction rate constant for CH ₃ I in wall film, sec ⁻¹	3.3×10^{-5}	4.5
Wall film flow rate, gpm	2.3	2.3
Drop flow rate, gpm	46.7	47.7

The theoretical predictions for total iodine are compared to measured concentrations in Figures 33 and 34. In the predictions, all iodine is assumed to be present as elemental iodine and methyl iodide.

The predicted iodine concentration increases to a value larger than measured, for both spray runs. Several factors may contribute to this discrepancy between theory and experiment. First, washout theory is based on the assumption that 100% of the injected iodine becomes airborne as either elemental iodine or methyl iodide. Condensation of water within the iodine delivery line, formation of large fog drops containing CsI, and imperfect mixing of iodine in the vessel during injection are factors which could cause the peak concentration to be lower than predicted. Isolation of the specific contribution of each of these factors is not possible.

After iodine injection, the predicted concentration rapidly falls to the value for methyl iodide. In Run A-10 the measured concentration did not decrease to the methyl iodide concentration as predicted. It appears that a third species containing iodine was either injected or formed in the containment vessel. Since this species was not observed in previous spray tests which used the same iodine generation method, it is concluded that the third species, possibly HOI, was formed in containment. In Run A-12, this species was not formed, or else reacted rapidly in solution with sodium thiosulfate.

During recirculation, the gas phase concentration of iodine decreased more rapidly in Run A-10 than predicted. Two factors may account for this. First, an appreciable fraction of the iodine was present as a third species which was removed faster than methyl iodide. Second, the partition coefficient for elemental iodine was taken as equal to 10^4 and invariant with time. In truth, the partition coefficient increased with time and attained a value greater than 10^4 . For the thiosulfate

FIGURE 33. Comparison of Measured Washout of Iodine with Theory for Run A-10

FIGURE 34. Comparison of Measured Washout of Iodine with Theory for Run A-12

run, A-12, the predicted behavior follows closely the measured concentration for about 600 minutes following termination of injection. At longer times the theory curve depends primarily on the partition coefficient for elemental iodine. Use of a partition coefficient greater than 10^5 would improve agreement between the theory and experiment.

The good agreement between theory and experiment for Run A-12 shows that the methyl iodide model works well for the thiosulfate spray. In Run A-10, the methyl iodide washout is influenced by both paint adsorption and reaction with water. The predicted and measured rates of methyl iodide removal both correspond to half-times of about 720 minutes for Run A-10.

C. COMPARISON OF CESIUM PARTICLE WASHOUT WITH THEORY

Cesium-containing particles were generated by heating cesium carbonate. The cesium aerosol was mixed with iodine vapor and passed through the uranium furnace so that chemical reactions could be expected between the iodine and the cesium. Injection of the cesium was accompanied by formation of a dense fog within the containment vessel. This was expected because cesium is soluble in water.

Aerosol samples were withdrawn from the vessel through a round-jet cascade impactor," and the stages analyzed to determine the mass distribution. Results of this sizing are shown in Figure 35 for Run A-10, and Figure 36 for Run A-12. All samples withdrawn at times less than 500 minutes indicate a mass median diameter of 0.3 to 0.5 microns. The samples withdrawn at long times indicate that the particles were too small to be sized by the impactor, the mass median diameter being less than 0.25 microns. As discussed earlier in this report, particle size measurements in saturated steam-air atmospheres are difficult to obtain in a fully satisfactory

* *Model CI-S-8, Scientific Advances Inc., Columbus, Ohio.*

FIGURE 35. Cascade Impactor Samples of Cesium Particles - CSE Run A-10

FIGURE 36. Cascade Impactor Samples of Cesium Particles - CSE Run A-12

manner. The cascade impactor is easy to use and analyze, but particle growth or evaporation may occur. For the low gas flow rates encountered, one would expect appreciable heat transfer during the sample withdrawal. Heat transfer, combined with expansion, would cause a decrease in relative humidity which would cause drop evaporation. The measured particle sized would be smaller than the size in containment.

The cascade impactor data is the only size data available from the CSE spray tests, hence it was used in arriving at numbered values of the theoretically predicted concentration. A particle size of 0.4 micron was assumed to exist for all time periods of both Runs A-10 and A-12. During the injection period, cesium concentration was evaluated using Equation (57) with the transfer coefficient being evaluated from Equation (24), for a particle size of 0.4 micron. The release was assumed to be linear after the 10 minute release period. For the remainder of the fresh spray period, the washout coefficient was taken to be the same as during the injection period. For the recirculation period the washout was calculated allowing only for Brownian diffusion and interception. The numerical values of parameters used in the calculations are summarized in Table XIII.

TABLE XIII. Numerical Values of Parameters Used in Cesium Particle Washout Predictions

Parameter	Numerical Value for Run A-10	Numerical Value for Run A-12
Time internal of release period, min	0 to 10	0 to 10
Mass of Cs released, grams	7.1	4.7
Target efficiency due to diffusiophoresis	0.55×10^{-2}	0.55×10^{-2}
Target efficiency for Brownian diffusion	0.7×10^{-4}	0.7×10^{-4}
Target efficiency for interception	0.995×10^{-3}	0.995×10^{-3}
Drop diameter, microns	1210	1210
Particle diameter, microns	0.4	0.4

The measured cesium particle concentrations are compared with the predicted values in Figures 37 and 38. For both runs, the measured particle concentrations fall below the predicted values. The maximum airborne concentration attained in both cases is only about 10% of the maximum predicted on the basis of theory. Hence, it is obvious that more washout has occurred than expected on the basis of the theory used. This is likely due to two factors. First, it is likely that the cesium particles in the containment atmosphere are appreciably larger than indicated by the cascade impactor sample. The larger particles would be removed more rapidly due to inertial impaction. The observed curve would be explainable if the impaction efficiencies were initially about 0.05, which corresponds to a particle size of about 3.5 microns. A second factor is potential condensation of steam within the delivery line which would cause some deposition within this line. The latter effect is expected to be relatively small because only a small surface area of the delivery line is exposed to spray.

It should be noted that this faster-than-predicted removal is consistent with particle washout measurements in all prior CSE experiments.

FIGURE 37. Comparison of Cesium Washout with Predictions - CSE Run A-10

FIGURE 38. Comparison of Cesium Particle Washout with Predictions - CSE Run A-12

VI. ACKNOWLEDGMENTS

Safe and successful completion of the large scale experiments described required the devoted efforts of skilled craftsmen of many disciplines, laboratory and engineering technicians and professional engineers whose names do not appear. The cooperation and teamwork of these personnel is gratefully acknowledged. Special recognition is due our associates, R. K. Hilliard, J. D. McCormack and G. J. Rogers, for considerations given to the experimental planning, performance and reporting of these experiments; Dr. J. G. Knudsen, Oregon State University; Tom H. Row, Oak Ridge National Laboratory; and to our sponsor, the Research and Development Branch-Nuclear Safety, Reactor Development and Technology, U.S. Atomic Energy Commission.

VII. NOMENCLATUREA. SYMBOLS

- a = radius
 A = surface area
 A_F = floor area (horizontal projection)
 A_W = effective wall surface area
 B = particle mobility
 B_{12} = exchange coefficient for inter-room transport
 C_g = mass concentration in gas phase
 C_ℓ = mass concentration in liquid phase
 C_P = heat capacity
 d = drop diameter
 d_P = diameter of spherical particle
 d_1 = diameter of water molecule
 d_2 = diameter of air molecule
 D = drop diameter or diffusivity
 D_ℓ = liquid phase diffusivity
 D_P = diffusion coefficient for particle
 D_v = gas phase diffusivity
 E = total collection efficiency of drop
 E_{BD} = drop target efficiency for Brownian diffusion
 E_D = effective target efficiency for diffusiophoresis
 E_{INT} = drop target efficiency for interception
 F = volumetric generation rate of spray drops
 f = fraction of contained volume not washed by sprays

f_A = ratio of air volume in containment to volume at standard temperature and pressure

f_R = correction factor for rotameter reading

g = acceleration due to gravity

G = generation rate of FP (or simulant) mass

AG = free energy of nucleation

G_d = generation rate of drops of diameter d

Gr = Grashov number

h = fall height of drop

H_e = gas-liquid partition coefficient for a single species

H = gas-liquid partition coefficient, including fast chemical reactions

ΔH_C = latent heat of condensation (per mole)

k = first order reaction rate constant, or Boltzmann constant

k_C = natural convection mass transfer coefficient

k_g = gas phase mass transfer coefficient

k_g^* = mass transfer coefficient under high transfer rate

k_l = liquid phase mass transfer coefficient

k_s = mass transfer coefficient due to condensing steam

K_g = overall mass transfer coefficient

K_1, K_2 = equilibrium constants for chemical reactions

L = volume of liquid held in sump, or length of vertical surface

L_F = volumetric flow rate of liquid wall film

L_O = volume of liquid in containment initially

L_s = volume of fresh liquid sprayed
 m = mass of particle
 M = molecular weight
 M_d = airborne mass of drops of diameter d
 M_o = molecular weight of solute in a fog droplet
 n = number of molecules per unit volume of liquid
 n_s = mass flux of steam to wall
 N = mass transfer flux
 N_{Ao} = mass transfer flux of component A at interface
 N_{Bo} = mass transfer flux of component B at interface
 p_s = vapor pressure of water
 P = total pressure in vessel
 q = mass absorbed per unit area
 Q = generation rate of drops
 R = gas constant, or rotameter reading
 R^* = critical radius of nucleating particle
 R_d = removal rate of drops of diameter d from the gas phase
 Re = Reynolds number
 R_G = gas phase reaction rate
 R_o = initial radius of nucleating particle
 Sc = Schmidt number
 t = time
 t_e = exposure time of drops to atmosphere
 t_s = sample duration time
 $t_{1/2}$ = concentration half-life

- T = absolute temperature
 AT = temperature difference
 $u_{\max}$ = gas velocity at gas-liquid interface
 v_g = terminal settling velocity of drop or particle
 v_s = gas sample volume (containment conditions)
 v_t = terminal settling velocity of a particle
 v_w = wall deposition velocity for particle
 V = free gas volume in containment vessel
 V_D = diffusio-phoretic velocity at interface
 V_{go} = initial containment gas volume
 V_{WF} = volume of liquid held up on wall as film
 x = distance from surface of film
 y = distance measured along film
 z_w = length of wall film

B. GREEK SYMBOLS

- γ_1 = mole fraction of water vapor
 $\nabla\gamma_{1\infty}$ = gradient in water vapor mole fraction at drop surface
 γ_2 = mole fraction of air
 δ = film thickness
 θ = mass transfer parameter, enhancement factor due to high transfer rate
 λ_c = first order removal rate constant ~~or~~ latent heat of condensation
 λ_N = removal rate constant due to natural processes
 λ_s = removal rate constant due to spray drops
 ν = kinematic viscosity

ρ = density

a = interfacial free energy per unit area between liquid and vapor

a_{12} = slip factor

ϕ = mass transfer parameter, ratio of flux to transfer coefficient or wetting angle between gas and liquid

C. PRIMES

Refer to property of solution.

D. SUBSCRIPTS

a = average value

A,B = solute species

b = bulk phase

d = value for drops of diameter d

D = value for drops of diameter D

f = final value

g = gas phase

i = refers to i th subgroup; interface or species type

l = liquid phase

m = value for correct mean

o = initial condition

p = value for paint

t = terminal value

0 = value at zero time or interfacial position

2 = second chamber

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