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GAS ABSORPTION THEORY APPLIED
TO CONTAINMENT SPRAYS

L. F. Parsly, Jr.

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ABSTRACT

This report presents a brief review of the pertinent literature. We show how equilibrium and mass-transfer rate equations may be used to predict spray performance for removal of fission product compounds from building atmospheres. A simplified procedure for calculating the effect of condensation on the spray performance is presented; this gives an overly conservative answer.

INTRODUCTION

Sprays are being proposed for cooling many power reactor containment buildings, and it is desired to make use of these sprays to clean up airborne fission products as well. In order to do this, it is proposed that chemical additives be introduced to react with the fission products. The spray solution will be cooled and recycled through the containment building.

In view of the interest of the atomic power industry in taking advantage of sprays for containment cleanup, the U.S. Atomic Energy Commission has initiated a major research and development effort on the application of spray technology for this purpose. The program goal is to develop information to substantiate the possibility of using containment sprays for fission product cleanup as well as for containment building cooling by July 1968.

Gas absorption is one of the unit operations of chemical engineering and has been studied extensively over a period of more than 40 years.^{1,2,3} As a result, a considerable body of applicable knowledge exists. In addition, solvent extraction and heat transfer are closely related unit operations and technology developed for these is often applicable to absorption. By making an effort to apply this existing technology to the problem, we can find out what information we need and don't have and, therefore, what new data should be taken.

In this report, we have tried to pull together the theory which is important for the containment spray problem and to examine its implications. These lead to certain conclusions about the required R & D.

It is important to recognize that there are differences as well as similarities between industrial absorbers and containment building cleanup. In a normal industrial absorber the gas and liquid are in countercurrent flow and each makes one pass through the absorber. In the containment building case, the same body of air remains in the building for the entire time. In the industrial absorber, the contact time for gas is normally in the range of 0.5 to 5 minutes. For the containment building case, the contact time for the gas is very long. In the containment building, also, the liquid is recycled continuously, the mass of material to be absorbed is relatively small, and we can easily afford to use overwhelming excesses of chemical reagents to assure complete absorption. On the other hand, in the containment building case there are some problems unique to highly radioactive systems, such as radiolysis of the solution. An additional difference is that while most industrial absorbers are operated near ambient temperature, the containment sprays will normally run at elevated temperature (up to 140°C).

It is necessary to examine the behavior of a proposed absorption system from two viewpoints — that of equilibrium and that of rates. Of these, equilibrium is the more fundamental. Unless a favorable equilibrium exists it is pointless to be concerned about rates.

SUMMARY AND CONCLUSIONS

A containment building and the spray liquid used to cool it and remove fission products from its atmosphere form a system analogous to an equilibrium still. That is, there is a fixed inventory of non-condensable gases (unless it leaks, which we don't want), and a fixed inventory of spray liquid. At least we believe that both chemical shim requirements and the need for keeping in bounds the volume of contaminated liquid which ultimately will have to be disposed of will force everyone to use a limited amount of solution and to cool and recycle it. As a consequence, we expect the system ultimately to come to equilibrium.

The equilibrium equations are those given below: Since the atmosphere is fixed and the solution is recycled continuously, the solution and the building atmosphere will eventually come to equilibrium. In the body of the report, we have derived equations for the ultimate decontamination factor. These are:

For physical absorption only

$$DF = 1 + \frac{Q_L}{Q_G} H . \quad (1)^*$$

For the reversible chemical reaction in the liquid

*Definitions of the symbols used in the equations are found in the table of Nomenclature.

$$DF = 1 + \frac{Q_L}{Q_G} H \left[\frac{K_C Q_L C_B}{Q_G C_{Gi}} \right] . \quad (3)$$

For a more general chemical reaction:

$$DF = 1 + \frac{Q_L}{Q_G} \left[\frac{K_C^{1/a} C_B^{b/a}}{\frac{\ell}{a} \left(\frac{m}{a} \right)^{m/a} \left(\frac{Q_G}{Q_L} C_{Gi} \right)^{\frac{\ell+m}{a} - 1}} \right] . \quad (5)$$

The equations indicate several factors may be important. The ratio of gas to liquid volume (Q_L/Q_G) is one. This appears to be of the order of 10^{-2} for conventional dry containment and of unity for pressure suppression containment. A second is the distribution coefficient for physical absorption (H). Equation (1) shows that for the dry containment case, if we want a minimum DF of about 10^2 , we need an H of approximately 10^4 , while for pressure suppression containment, we need an H of about 10^2 .

Equations (3) and (5) show that a favorable equilibrium constant or an excess of solution reagent can significantly increase the equilibrium decontamination factor. Thus, by using an excess of a reagent with a favorable equilibrium constant, one can override an unfavorable distribution ratio and obtain an acceptable DF even for a relatively insoluble substance.

The above equations indicate a need to measure the distribution coefficient for all important fission product compounds over the range of temperatures from ambient up to the maximum expected in a containment building. In addition, they show that we need to know the equilibrium constant for any reversible reaction proposed for enhancing the removal of a fission product. If the reaction is irreversible, obviously the ultimate decontamination factor is infinite if an excess of reagent is present.

An example of the type of results we can get from equilibrium alone is the following with respect to iodine compounds:

Three important volatile iodine compounds likely to be present in containment buildings are elemental iodine (I_2), hydrogen iodide (HI), and methyl iodide (CH_3I). The distribution coefficient for I_2 at 25° is given as 80 by Griffiths⁹ at 10^{-1} g/l, increasing markedly as the concentration decreases. For HI, from vapor pressure data given in the Chemical Engineer's Handbook¹⁶ ($p = 6.4 \times 10^{-4}$ mm for a 4% solution at 25°) $H = 9.2 \times 10^6$. For CH_3I , we find¹⁷ that a saturated solution at 30° contains 1.4 g/100 g and that the vapor pressure is represented by

$$\log p = 7.56 - 1475/T.$$

From the above we calculate

$$H = 3.9 \quad .$$

Since $Q_L/Q_G \cong 10^{-2}$, equation (1) predicts decontamination factors of 2, 9×10^4 , and 1.04 for I_2 , HI, and CH_3I , respectively, by physical absorption, in PWR plants being designed today. Clearly, we need chemical absorption for removal of I_2 and CH_3I .

We present a review of equations for calculating transfer rates to the drop surface, inside the drop by diffusion, and inside the drop when chemical reaction is significant. In the latter, we show how the important case of instantaneous reaction with a large excess of reagent reduces to the gas film controlled case.

Also we present brief discussions of the effect of condensation on the performance of a spray and of the effect of drop size distribution. We show that experimental data

indicate that condensation promotes rather than hinders absorption. Our study of the effect of drop size distribution shows that the uniformity of the drops is of great importance in determining spray performance.

PREDICTION OF DECONTAMINATION FACTOR

Since the spray solution is recycled to the containment building, the solution and the building atmosphere will ultimately come to equilibrium.

If we define

$$HC_G = C_A \quad (6)$$

(and it should be noted that H is not necessarily a constant) we can write an overall material balance for the absorption process.

$$Q_G (C_{Gi} - C_{Gf}) = Q_L C_A \quad (7)$$

Then if we define a decontamination factor

$$DF = C_{Gi}/C_{Gf} \quad , \quad (8)$$

and do some simple algebra, we obtain

$$DF = 1 + \frac{Q_L}{Q_G} H \quad (1)$$

Since Q_L/Q_G is of the order of 10^{-2} for large PWR's currently under design, H needs to be at least 10^4 if the decontamination factor obtained by physical absorption is to be large enough to be of interest.

DECONTAMINATION FACTOR FOR EQUILIBRIUM CHEMICAL ABSORPTION

Assume that we use a spray containing an additive which reacts reversibly in the liquid phase with the constituent being removed, then part of the quantity which dissolves will react (call this fraction f_r), and part will remain in solution but not react (call this fraction f_p); and the total amount which enters the liquid phase is given by:

$$\frac{Q_L C_A}{f_p}, \quad (9)$$

and we can repeat the derivation of equation (1) to obtain

$$DF = 1 + \frac{Q_L}{Q_G} \frac{H}{f_p}. \quad (10)$$

Assume a relatively simple reaction:

The equilibrium constant will be:

$$K_c = \frac{C_L}{C_A} \frac{C_M}{C_B}. \quad (11)$$

Since we are not interested unless a high decontamination factor is achieved, it is not a bad approximation to assume that all of the constituent being cleaned up, $Q_G C_{Gi}$, is absorbed and removed by reaction.

$$\text{Thus: } C_L \cong \frac{Q_G C_{Gi}}{Q_L} \quad (12)$$

$$C_M \cong \frac{Q_G C_{Gi}}{Q_L} \quad (13)$$

Also we expect to provide a large excess of reagent B and can assume that C_B is a constant.

Using the above approximations:

$$K_c = \frac{\left(\frac{Q_G}{Q_L} C_{Gi}\right)^2}{C_A C_B} \quad (14)$$

$$C_A = \frac{\left(\frac{Q_G}{Q_L} C_{Gi}\right)^2}{K_c C_B} \quad (15)$$

$$f_p = \frac{C_A}{\left(\frac{Q_G}{Q_L} C_{Gi}\right)} \quad (16)$$

$$f_p = \frac{\frac{Q_G}{Q_L} C_{Gi}}{K_c C_B} \quad (17)$$

$$DF = 1 + \left(\frac{Q_L}{Q_G} H\right) \left(\frac{K_c Q_L C_B}{Q_G C_{Gi}}\right) \quad (3)$$

The term in the second parentheses is the product of the equilibrium constant times the ratio of total mols of reagent available to total mols of reactant to be removed.

It is also of interest to note that although we derived the equation for a reversible reaction, if we allow K_c to become infinite we obtain the result for an irreversible reaction (DF becomes infinite).

We can do the same exercise for a more general reaction:

For this case, the equilibrium constant is given by

$$K_c = \frac{C_L^\ell C_M^m}{C_A^a C_B^b} \quad (18)$$

Assuming as above that the total mols of A reacted is approximately $Q_G C_{Go}$ and that C_B is approximately constant

$$C_L = \frac{\ell}{a} \frac{Q_G C_{Gi}}{Q_L} \quad (19)$$

$$C_M = \frac{m}{a} \frac{Q_G C_{Gi}}{Q_L} \quad (20)$$

Substituting into Eq. (21) and solving for C_A :

$$C_A = \frac{\left(\frac{\ell}{a}\right)^{\frac{\ell}{a}} \left(\frac{m}{a}\right)^{\frac{m}{a}} \left(\frac{Q_G}{Q_L} C_{Gi}\right)^{\frac{\ell+m}{a}}}{K_c C_B^{b/a}} \quad (21)$$

The overall material balance is given by:

$$Q_G (C_{Gi} - C_{Gf}) = Q_L \frac{C_A}{f_p} \quad (22)$$

For the case of nearly complete removal of A, this is approximately

$$Q_G C_{Gi} = Q_L \frac{C_A}{f_p} \quad (23)$$

or

$$\frac{1}{f_p} = \frac{Q_G C_{Gi}}{Q_L C_A} \quad (24)$$

Substituting for C_A from (24)

$$\frac{1}{f_p} = \frac{K_c^{1/a} C_B^{b/a}}{\left(\frac{\ell}{a}\right)^{\ell/a} \left(\frac{m}{a}\right)^{m/a} \left(\frac{Q_G C_{Gi}}{Q_L}\right)^{\frac{\ell+m}{a}} - 1} \quad (25)$$

Substituting (28) into (12)

$$DF = 1 + \frac{Q_L}{Q_G} H \left[\frac{K_c^{1/a} C_B^{b/a}}{\left(\frac{\ell}{a}\right)^{\ell/a} \left(\frac{m}{a}\right)^{m/a} \left(\frac{Q_G C_{Gi}}{Q_L}\right)^{\frac{\ell+m}{a}} - 1} \right] \quad (5)$$

What these equations show is that we can predict the decontamination factor provided we know the distribution coefficient for physical absorption, the chemical reaction involved, and the equilibrium constant for the chemical reaction.

Looking in particular at equation (3), since for PWR's presently under design Q_L/Q_G is of the order of 10^{-2} and if we assume $Q_L C_B/Q_G C_{Go}$ is made at least of the order of 10 (by design), we would need to have HK_c equal about 100 to get a DF of 10 and about 1000 to get a DF of 100. These seem to be reasonably attainable goals.

ABSORPTION THEORY

The absorption process involves transport in the continuous phase (containment building atmosphere) by diffusion or convection

to the drop surface, equilibrium between the two phases at the surface and transfer by diffusion or convection into the discontinuous phase (drop). The processes involved may be described either by differential equations or by the use of transfer coefficients. Transfer coefficients can be defined as follows:

$$k_c = \frac{N_A}{C_G - C_{Go}} \quad (26)$$

$$k_L = \frac{N_A}{C_{Ao} - C_A} \quad (27)$$

$$V_G = \frac{N_A}{C_G - C_A/H} \quad (28)$$

From the above equations and the definition of H , it is a matter of simple algebraic manipulation to show that:

$$\frac{1}{V_G} = \frac{1}{k_c} + \frac{1}{Hk_L} \quad (29)$$

In effect, the above equation states that the overall resistance is the sum of individual resistances.

In the discussion which follows, we shall discuss gas- and liquid-phase resistances for physical absorption, considering the drop as a rigid body. Then we will discuss the effect of internal circulation in the drops. Finally, we will discuss how chemical reaction in the liquid phase affects the rates.

Gas Film

For forced convection in the gas film, equations can be derived^{1,2,3} showing that:

$$N_{Sh} = \phi(N_{Re}, N_{Sc}) \quad . \quad (30)$$

The following equation proposed by Ranz and Marshall⁴ appears to be a reasonably good representation of the data:

$$N_{Sh} = 2.0 + 0.6 N_{Re}^{1/2} N_{Sc}^{1/3} \quad (31)$$

This equation is semi-empirical, since it is shown by Ranz and Marshall⁴ and by others,^{1,2} that for the case of pure conduction or pure diffusion:

$$N_{Sh} = N_{Nu} = 2.0 \quad (32)$$

Liquid Phase Resistance - Rigid Drop Model

The process in the liquid phase, if this is considered as a rigid spherical drop, is unsteady-state diffusion. For the case of heat transfer, Jakob⁵ derives the equation:

$$\alpha \left(\frac{\partial^2 \Theta}{\partial r^2} + \frac{2}{r} \frac{\partial \Theta}{\partial r} \right) = \frac{\partial \Theta}{\partial t} \quad (33)$$

$$\Theta = T - T_e$$

with the boundary conditions

$$1. \quad \Theta = \Theta_i \quad \text{at } t = 0$$

$$2. \quad \frac{\partial \Theta}{\partial r} = -g\Theta \quad \text{at } r = a$$

$$g = h_g/k_{(liquid)} \quad .$$

For the mass-transfer case, it is convenient to define a new concentration variable analogous to Θ :

$$\gamma = HC_{Gi} - C_A \quad . \quad (34)$$

Now if one writes the equations for the flux in the gas- and liquid-phases at $r = a$:

$$N_A = - D_A \frac{\partial C_A}{\partial r} = k_c (C_{Gi} - C_{Go}) \quad , \quad (35)$$

From (34)

$$\frac{\partial \gamma}{\partial r} = - \frac{\partial C_A}{\partial r} \quad . \quad (36)$$

Also

$$C_{Gi} = \left[\frac{\gamma + C_A}{H} \right]_{r=a} \quad (37)$$

$$C_{Go} = \left[\frac{C_A}{H} \right]_{r=a} \quad (38)$$

$$D_A \frac{\partial \gamma}{\partial r}_{r=a} = k_c \left[\frac{\gamma + C_A}{H} - \frac{C_A}{H} \right]_{r=a} \quad . \quad (39)$$

Therefore

$$\left(\frac{\partial \gamma}{\partial r} \right)_{r=a} = \left(\frac{k_c}{HD_A} \gamma \right)_{r=a} \quad . \quad (40)$$

Thus by analogy with the boundary conditions for equation (33) the parameter $g = k_c/HD_A$ for mass transfer.

The solution for equation (33) is given by Jakob⁵ as:

$$\frac{\theta}{\theta_i} = 2 \sum_{n=1}^{\infty} \frac{\sin \psi_n - \psi_n \cos \psi_n}{\psi_n - \sin \psi_n \cos \psi_n} e^{-\psi_n^2 \frac{\alpha t}{r_o}} \frac{\sin \psi_n \frac{r}{r_o}}{\psi_n \frac{r}{r_o}} \quad (41)$$

The eigenvalues ψ_n are the solutions of the equation:

$$gr_o = 1 - nr_o \cos nr_o \quad (42)$$

The first four eigenvalues for values of gr_o ranging from 0 to ∞ are published by Jakob⁵ (page 279), based on the solutions of the equations by Groeber.⁶

If we let $\bar{\theta}$ designate a mean value of θ , we have

$$\bar{\theta} = \frac{\int_0^{r_o} 4 \pi r^2 \theta dr}{\frac{4}{3} \pi r_o^3} = \frac{3}{a^3} \int_0^{r_o} r^2 \theta dr \quad (43)$$

Substituting (41) into (43) and integrating, we obtain:

$$\frac{\bar{\theta}}{\theta_i} = \sum_{n=1}^{\infty} \frac{6}{\psi_n^3} \frac{(\sin \psi_n - \psi_n \cos \psi_n)^2}{\psi_n - \sin \psi_n \cos \psi_n} e^{-\frac{\psi_n^2 \alpha t}{r_o^2}} \quad (44)$$

By analogy for mass transfer:

$$\frac{\bar{\gamma}}{\gamma_i} = \sum_{n=1}^{\infty} \frac{6}{\psi_n^3} \frac{(\sin \psi_n - \psi_n \cos \psi_n)^2}{\psi_n - \sin \psi_n \cos \psi_n} e^{-\frac{\psi_n^2 D_A t}{r_o^2}} \quad (45)$$

If $C_{Ai} = 0$, from the definition of γ , we have:

$$\frac{\bar{\gamma}}{\gamma_i} = 1 - \frac{\bar{C}_A}{HC_{Gi}} \quad (46)$$

$\bar{C}_A/HC_{Gi}$ is the fractional saturation

$$\frac{\bar{C}_A}{HC_{Gi}} = 1 - \sum_{n=1}^{\infty} \frac{6}{\psi_n^3} \frac{(\sin \psi_n - \psi_n \cos \psi_n)^2}{\psi_n - \sin \psi_n \cos \psi_n} e^{-\psi_n^2 \frac{D_A t}{r_o^2}} \quad (47)$$

A number of writers⁷ indicate that equations 41, 44, 45 and 47 may be truncated to the first term of the infinite series without too great an error. For instance, Vermeulen⁸ suggests:

$$E_m = \left[1 - \exp \left(- \frac{\pi^2 \alpha t}{r_o^2} \right) \right]^{1/2} \quad (48)$$

and comparisons are given in the literature indicating that this is not a bad approximation.

It is possible to show that under special conditions there is a very simple relationship between the diffusivity and the liquid film coefficient. It is necessary to accept approximation of the infinite series by one term. Then, as shown in the Appendix, one can derive:

$$\frac{k_L r_o}{D_A} = \frac{\psi_1 \cos \psi_1 - \sin \psi_1}{\sin \psi_1 - \frac{3}{\psi_1^2} (\sin \psi_1 - \psi_1 \cos \psi_1)} \quad (49)$$

For the special case of $gr_o = \infty$ (no gas-film resistance), $\psi_1 = \pi$ and the equation reduces to

$$\frac{k_L r_o}{D_A} = \frac{\pi^2}{3} \quad (50)$$

This is the equation derived by Griffiths.⁹

Effect of Circulation within the Drops

It is a well-known fact that a drop moving in a viscous fluid will tend to circulate internally due to the shear stress applied at its interface by the ambient fluid. Sideman⁷ presents a well-documented discussion of this effect. This shows that heat and mass transfer are augmented both in the continuous and discontinuous phases.

In the continuous phase, circulation inside the drop apparently reduces the boundary layer thickness. The correlations presented by Sideman⁷ indicate that the transfer coefficients are higher than for rigid drops by factors ranging up to 4; 2 appears to be a reasonable average.

Sideman⁷ also reports a number of solutions for transfer inside the drops. These include solutions for internal flow models. The simplest approach appears to be to use an effective diffusivity in the rigid drop equations. Appropriate multipliers for the diffusivity are recommended by several writers.^{10,11,12}

It is clear from reviewing the work on drop circulation that if we neglect it we will underestimate the transfer coefficients. Since errors introduced by doing so will always be on the conservative side, we can afford to use the simpler rigid drop model.

Simultaneous Absorption and Chemical Reaction

Probably the best available discussions of the problem of absorption with chemical reaction are those of Astarita.^{13,14} He states that for the case where the reaction rate R depends essentially only on the concentration of the transferring reactant, the differential equation for diffusion and reaction takes the form:

$$D_A \left(\frac{\partial^2 C_A}{\partial r^2} + \frac{2}{r} \frac{\partial C_A}{\partial r} \right) = \chi(r) \frac{\partial C}{\partial t} + R(C_A) \quad (51)$$

The function $\chi(r)$ depends on the shape of the velocity distribution within the liquid phase. It is of the order of unity. The function $R(C)$ is the function of concentration describing the reaction rate. General solutions to this equation are not available.

Defining:

$$k_L = \sqrt{D_L/t_D} \quad (52)$$

$$t_R = \frac{C_{Ao} - C_A}{R(C_{Ao})} \quad (53)$$

$$\tau = t/t_D \quad (54)$$

$$\beta = \frac{C_A - \bar{C}_A}{C_{Ao} - \bar{C}_A} \quad (55)$$

Equation (51) can be transformed to

$$D_A \left(\frac{\partial^2 \beta}{\partial r^2} + \frac{2}{r} \frac{\partial \beta}{\partial r} \right) = \frac{1}{t_D} \left[\chi(r) \frac{\partial \beta}{\partial \tau} \right] + \frac{1}{t_R} \left[\frac{R(C_A)}{R(C_{Ao})} \right] \quad (56)$$

Astarita¹³ points out that the terms in brackets are both of the order of unity. Therefore, if the reaction time is much greater than the diffusion time we can drop the second term and if the diffusion time is much greater than the reaction time, we can drop the first.

Depending on the relative reaction and diffusion rates, Astarita defines five possible regimes.

1. Kinetic: Reaction rate is so slow that the drops become saturated with component A. This applies if

$$t_R \gg \frac{V}{Sk_L} \quad (57)$$

For spherical drops $V/S = d/6$, and k_L can be approximated by: $\frac{D_A}{d} \cdot \frac{2}{3} \pi^2$, so that the criterion becomes:

$$t_R \gg \frac{d^2}{4\pi^2 D_A} \quad (58)$$

Using $d = 0.1$ cm and $D_A = 10^{-5}$ cm²/sec

$t_R \gg 25$ sec is required for this regime to apply in the case of containment sprays.

2. Diffusional regime: The reaction rate is low enough not to interfere with diffusion but fast enough to consume all of the transferring component in the bulk of the drop. Astarita gives:

$$t_D \gg t_R \gg \frac{V}{Sk_L} \quad (59)$$

as the criterion for this case.

Given that t_D is of the order of 10^{-1} sec $V/S = d/6$ and k_L is of the order of 10^{-2} , this criterion cannot be satisfied for drops of the order of 10^{-1} cm diameter.

3. Fast reaction regime: The bulk of the drop is at its equilibrium value. For this case, Astarita indicates that an equation of the form

$$N = \sqrt{\frac{D}{t_R}} (C_{Ao} - \bar{C}_A) \quad (60)$$

should be applicable. Intermediate cases between diffusional and fast reaction can be handled by equations of the form:

$$\frac{k'_L}{k_L} = \sqrt{\frac{t_D + t_R}{t_R}} \quad (61)$$

4. Instantaneous reaction: Up to this point, we have been discussing kinetics based on the assumption that the reaction rate depended only on the concentration of the reacting component, C_A . Although a good many problems can be handled on this assumption, it is not generally true and the concentration distribution of the transferring component (A) and the reaction rate may depend in a complicated way on the diffusion of the liquid phase reactant and the reaction products. One extreme case is found when the reaction between A and the solution reagent (B) is instantaneous. Then at no point in the liquid can A and B exist at non-negligible

concentration levels. If we assume that the diffusivities of A and B are equal, then the mass flux is given by

$$N = k_L \left[C_{Ao} + \frac{a C_B}{b} \right] . \quad (62)$$

Astarita indicates a criterion for equation (62) to be valid is:

$$t_R \gg t_D \left(\frac{b C_{Ao}}{a C_B} \right) . \quad (63)$$

Intermediate cases between fast reaction and instantaneous reaction have been studied. The problem is very complex and it is difficult to choose from among the models proposed.

5. Surface reaction: If it turns out that

$$N_A^* = k_L \frac{a C_B}{b} > k_C C_G \quad (64)$$

which is the limit of equation (62) as C_{Ao} tends to 0, the reaction in the liquid phase will take place at the drop surface and the rate will be governed by the gas-phase transfer rate.

$$N_A = k_C C_G . \quad (65)$$

The criterion for (65) to hold is

$$C_B > \left(\frac{b k_C}{a k_L} \right) C_G . \quad (66)$$

For the case of clean-up of iodine by 1% sodium thiosulfate solution, equation (66) is satisfied whenever C_G is less than 8×10^{-8} g mols/cm³ or 2×10^4 mg/m³ (in other words, all the time).

Therefore it appears that for elemental iodine absorption by reactive sprays using a large excess of the solution reagent, the surface reaction model is applicable, so that it can be treated as a pure gas-film-controlled process. For HI, the same should be true, particularly if the solution is basic.

In the case of methyl iodide, the experimental results obtained to date in the ORNL wind-tunnel tests¹⁵ indicate that the gas-film is not controlling. The results are substantially higher than would be predicted for the liquid-film coefficient according to a rigid-drop model, even in the case of pure water. The latter fact suggests that internal circulation exists in the drops, and observation of the drops in the tunnel confirms this. The dependence of the rate coefficient on concentration indicates a significant effect of the reaction in improving the mass-transfer rate; however, none of the models listed above account for the maximum in the mass transfer rate which has been reported.

EFFECT OF CONDENSATION ON THE SPRAY DROPS

A question which has been raised several times is:
"How does condensation on the drops affect their performance

for iodine removal?" One can obtain a very pessimistic answer to this by assuming that a layer of condensate forms on the outside of the drops and in effect forms a diffusion barrier for the dissolving iodine. However, we have experimental evidence¹⁸ which indicates that condensation enhances rather than inhibits iodine absorption by sprays. We carried out an experiment in which we scrubbed elemental iodine from a steam-air atmosphere (130°C, 45 psig) using borated alkaline sodium thiosulfate solution at room temperature and then repeated the experiment with the same solution preheated to 120°C. We found a half-life for I₂ removal of 31 sec with cold solution and of 48 sec with hot solution. The explanation is that iodine is transported by convection as well as by diffusion.¹⁹ When condensation is eliminated by using hot spray, we also eliminate convection and have only diffusion.

EFFECT OF DROP SIZE DISTRIBUTION ON SPRAY PERFORMANCE

We encountered a significant discrepancy between the removal half-life observed in some of our early experiments¹⁸ and that predicted by theory.²⁰ Of the assumptions made in our theoretical model, the most likely source of the difficulty appeared to be the assumption that all drops were the same size. In order to get at this, we extended our model to investigate the performance of sprays which have a log-normal size distribution. This distribution is characterized

by a mean diameter and by a geometric standard deviation (σ_G).

In this model, we also take into account the slowing down of the drops from the time they enter until they attain terminal velocity. We find that fine drops reach terminal velocity within a few cm of the nozzle, but very large drops do not attain terminal velocity in falling to the bottom of the model containment vessel of the Nuclear Safety Pilot Plant (about 5 M total weight). We plan to report details of our model in a separate report.

We don't have experimental data on size distribution for the spray nozzles used in our tests. Such data are not readily available from manufacturers, and we have not had a size-measuring capability.

We have made a sensitivity analysis of the influence of σ_G on half-life for iodine removal for drops of 100 μ mean diameter at 30°C and 700 μ mean diameter at 120°C (corresponding to experiments we have run. The results are given in Table 1.

The table shows that the half-life for I removal increases by a factor of the order of 6 as the geometric standard deviation increases from 1 (complete uniformity) to 2. Thus the uniformity as well as the size of drops needs to be considered in predicting spray performance.

Table 1. Effect of Geometric Standard Deviation
on Spray Performance

Number Mean Drop Dia, μ	Temperature $^{\circ}\text{C}$	σ_G	Half-Life for I_2 Removal, sec
100*	30	1.0	6.4
100	30	1.5	11.4
100	30	1.8	23.2
100	30	2.0	38.7
700**	120	1.0	32.3
700	120	1.2	36.8
700	120	1.4	49.9
700	120	1.6	74.1
700	120	1.8	115.2
700	120	2.0	181.7

*Total flow of 0.25 gpm through 12 nozzles.

**Total flow of 9.5 gpm through one nozzle.

EFFECT OF VARIABLE VELOCITY

As noted above, for the larger sizes of drops, the drops may not attain terminal velocity in the NSPP containment vessel. Therefore we must consider what effect the varying velocity may have on our data. According to equation (31)

$$\frac{k_c d}{D} = 2.0 + 0.6 N_{Re}^{1/2} N_{Sc}^{1/3} . \quad (31)$$

And for the case we are considering

$$0.6 N_{Re}^{1/2} N_{Sc}^{1/3} \gg 2 \quad (67)$$

and we may write:

$$k_c = C_1 v^{1/2} d^{-1/2} . \quad (68)$$

The contact area is given by

$$A = \frac{6L}{\rho_L v d} \quad (69)$$

$$\text{Hence } A = C_2 v^{-1} d^{-1} . \quad (70)$$

The removal time constant is

$$k_c A = C_3 v^{-1/2} d^{-3/2} . \quad (71)$$

This means that we should measure a smaller time constant or longer half-life in our experiments than would be valid if all of the fall were at terminal velocity. In other words, any errors introduced because the drops haven't slowed down to terminal velocity will lead to conservative results.

NOMENCLATURE

a	=	Number of mols of constituent A required in reaction.
a	=	Specific area of sprays, cm^{-1}
A	=	The constituent being absorbed.
b	=	Number of moles of constituent B required in reaction.
B	=	The reagent used in solution to react with A.
C_A	=	Concentration of A in the liquid, g mols cm^{-3} .
C_{Ao}	=	Concentration of A in the liquid at the drop surface g mols cm^{-3} .
$\overline{C_A}$	=	Average concentration of A in the liquid g mols cm^{-3} .
C_G	=	Concentration of A in the gas, g mols cm^{-3} .
C_{Gi}	=	Initial value of C_G .
C_{Go}	=	Value of C_G at surface of drop.
C_L	=	Concentration of L in liquid g mols cm^{-3} .
C_M	=	Concentration of M in liquid g mols cm^{-3} .
C_p	=	Specific heat, $\text{cal g}^{-1} \text{ deg C}^{-1}$.
d	=	Diameter, cm
D_A	=	Diffusivity of A in liquid, $\text{cm}^2 \text{ sec}^{-1}$.
D_G	=	Diffusivity of A in gas, $\text{cm}^2 \text{ sec}^{-1}$.
DF	=	Decontamination factor, dimensionless.
e	=	Base of natural logarithms.
f_p	=	Fraction of total A entering liquid phase which is not reacted.
f_R	=	Fraction of total A entering liquid phase which reacts.

g	=	Parameter defined by boundary conditions of equation (33).
h	=	Heat transfer coefficient, $\text{cal cm}^{-2} \text{sec}^{-1} \text{deg C}^{-1}$.
H	=	Distribution coefficient ($= C_A/C_G$).
k	=	Thermal conductivity, $\text{cal cm}^{-1} \text{sec}^{-1} \text{deg C}^{-1}$.
k_c	=	Mass transfer coefficient in gas based on concentration driving force, cm sec^{-1} .
K_c	=	Equilibrium constant, defined in equations (11) and (18).
k_L	=	Mass transfer coefficient in liquid cm sec^{-1} .
l	=	Number of mols of L produced by reaction.
L	=	A reaction product.
L_v	=	Latent heat of vaporization of water at T_b .
m	=	Number of mols of M produced by reaction
M	=	A reaction product.
n	=	1, 2, 3, ...
N_A	=	Mass flux of A, $\text{g mols cm}^{-2} \text{sec}^{-1}$.
Q_G	=	Total volume of gas in system, cm^3 .
Q_L	=	Total liquid in system, cm^3 .
r	=	Radius, cm.
r_o	=	Drop radius ($= d/z$).
R	=	Reaction function in equation (51).
t	=	Time, sec.
T	=	Temperature, deg. C.
T_b	=	Buildup temperature.
T_s	=	Spray temperature.
v	=	Velocity, cm sec^{-1} .

- V_G = Overall mass transfer coefficient based on concentration.
 W = Mass of spray drop, g.
 α = Thermal diffusivity = $k/\rho c_p$.
 β = Concentration variable defined in equation (55).
 γ = Concentration variable defined in equation (34).
 δ = Boundary layer thickness, cm.
 Θ = Temperature variable defined in equation (33), $^{\circ}\text{C}$.
 μ = Viscosity $\text{g cm}^{-1} \text{ sec}^{-1}$.
 π = 3.14159 ...
 ρ = Density, g cm^{-3} .
 τ = Dimensionless time variable in equation (56).
 ψ_n = Nth eigenvalue for solution to the diffusion equation.
= Velocity function in equation (51).

Dimensionless Groups

- N_{Nu} = Nusselt number hd/k
 N_{Pr} = Prandtl number $C_p\mu/k$
 N_{Re} = Reynolds number $dv\rho/\mu$
 N_{Sc} = Schmidt number $\mu/\rho D$
 N_{Sh} = Sherwood number $k_c d/D_G$ or $k_L d/D_A$

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APPENDIX

Relation Between Differential Equation
Solutions and Film Coefficient

We can write the equations for mass flux at the drop surface in both transfer coefficient and differential form:

$$N_A = k_L (C_{Ao} - \bar{C}_A) = -D_L \frac{\partial \gamma}{\partial r} \bigg|_{r=r_o} \quad (A1)$$

From this we can derive from the definition of γ

$$N_A = k_L (\gamma_{Ao} - \bar{\gamma}_A) = D_L \frac{\partial \gamma}{\partial r} \bigg|_{r=r_o} \quad (A2)$$

If we assume that the infinite series can be approximated by their first terms, we can write:

$$\gamma = \gamma_i A_1 e^{B_1 t} \frac{\sin \psi_1 \frac{r}{a}}{\psi_1 \frac{r}{a}} \quad (A3)$$

$$\bar{\gamma} = \gamma_i \frac{3}{\psi_1^3} A_1 e^{B_1 t} (\sin \psi_1 - \psi_1 \cos \psi_1) \quad (A4)$$

Differentiating (A3) with respect to r

$$\frac{\partial \gamma}{\partial r} = \gamma_i A_1 e^{B_1 t} \left[\frac{1}{r} \cos \left(\frac{\psi_1 r}{a} \right) - \frac{\alpha}{\psi_1 r^2} \sin \left(\frac{\psi_1 r}{a} \right) \right] \quad (A5)$$

Evaluating (A5) at $r=a$

$$\begin{aligned} \frac{\partial \gamma}{\partial r} &= \gamma_i A_1 e^{B_1 t} \left[\frac{1}{a} \cos \psi_1 - \frac{1}{\psi_1 a} \sin \psi_1 \right] \\ &= \gamma_i A_1 e^{B_1 t} \left[\frac{1}{\psi_1 a} (\psi_1 \cos \psi_1 - \sin \psi_1) \right] \end{aligned} \quad (A6)$$

Appendix (continued)

Now substituting back into A2, noting that $\gamma_1 A_1 e^{B_1 t}$ conveniently cancels out:

$$\begin{aligned} k_L \left[\frac{\sin \psi_1}{\psi_1} - \frac{3}{\psi_1^3} (\sin \psi_1 - \psi_1 \cos \psi_1) \right] \\ = \frac{D_L}{\psi_1 a} (\psi_1 \cos \psi_1 - \sin \psi_1) \end{aligned}$$

$$\frac{k_L a}{D_L} = \frac{\psi_1 \cos \psi_1 - \sin \psi_1}{\sin \psi_1 - \frac{3}{\psi_1^2} (\sin \psi_1 - \psi_1 \cos \psi_1)} \quad (A7)$$

For the case where $ba = \infty$, $\psi_1 = \pi$ and equation A-7 reduces to:

$$\frac{k_L a}{D_L} = \frac{\pi^2}{3} \quad \text{or} \quad (A-8)$$

$$\frac{k_L d}{D_L} = \frac{2\pi^2}{3} \quad (A-9)$$

as derived by Griffiths.⁹

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