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RATE PROCESSES FOR IODINE REMOVAL AND HYPOIODOUS ACID FORMATION IN THE PRESENCE OF CHEMICALLY REACTIVE CONTAINMENT SPRAYS*

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MASTER

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Abstract

The chemistry of the hydrolysis of iodine was reviewed based on available literature. Hypoiodous acid is formed during hydrolysis but the question of its volatility and methods of gas phase measurement have not been resolved. Based on a calculated Henry's Law constant and the kinetics of the reduction of iodine hydrolysis products with hydrazine, rates of mass transfer to liquid spray drops were calculated for several spray conditions at the peak LOCA temperature. The concentration of HOI relative to the total dissolved iodine at the interface decreases with decreasing pH and increasing iodide concentration. A detailed review of the kinetics of iodine hydrolysis indicates that the negative ion specie, I_2OH^-, may be the active substance in solution.

1. Introduction

The loss of coolant accident (LOCA) in a pressurized water reactor (PWR) would result in a rapid increase in temperature and pressure (because of the rapid production of steam from residual coolant) within the reactor containment vessel. Accompanying this would be the release of a major portion of the fuel element fission products as airborne gases, vapors, aerosols, and particulates of which the most important component from the standpoint of downwind dose is iodine.

Water spray systems within the containment, initially present to minimize the pressure rise during a LOCA, would only remove the airborne iodine at a modest rate because of the limited solubility. Most presently operating power reactors are equipped to handle a boric acid spray solution which serves as a soluble neutron poison for reactor shim control; it has been proposed that the same solution, but with certain reducing additives incorporated, be used to remove airborne iodine from the containment in the event of a LOCA. Spray solutions that have been experimentally investigated include boric acid-sodium hydroxide solutions with and without sodium thiosulfate(1-6) and boric acid with added hydrazine.(7,8)

To fully evaluate the effectiveness of chemically reactive sprays, the chemistry of the hydrolysis of iodine as well as its rate of reaction with added reducing agents plus the mechanism for mass transfer from the gas phase to the liquid droplet phase must be elucidated; the engineering and the chemistry are strongly interdependent as will be subsequently shown. This paper describes the chemistry involved, with special attention to the formation of hypoiodus acid, as well as methods for determining the rates of mass transfer to droplets containing chemically reactive additives.

2. The Chemistry of Iodine Hydrolysis

The predominant specie of iodine present in the steam-air environment of the containment following a LOCA would be elemental iodine vapor with minor amounts of both iodine adsorbed on particulates and organic iodides (mainly methyl iodide).

The equilibria involved in the hydrolysis of iodine were reviewed by Eggleton$^{(9)}$ for the reactions of importance at the pH of reactive sprays (pH of 5 to 9). These reactions include

$$I_{2(G)} \overset{K_1}{\rightleftharpoons} I_2 \qquad K_1 = \frac{[I_2]}{[I_2]_G} \qquad (1)$$

$$I_2 + I^- \overset{K_2}{\rightleftharpoons} I_3^- \qquad K_2 = \frac{[I_3^-]}{[I_2][I^-]} \qquad (2)$$

$$I_2 + H_2O \overset{K_3}{\rightleftharpoons} H^+ + I^- + HOI \qquad K_3 = \frac{[H^+][I^-][HOI]}{[I_2]} \qquad (3)$$

$$I_2 + H_2O \overset{K_4}{\rightleftharpoons} H_2OI^+ + I^- \qquad K_4 = \frac{[H_2OI^+][I^-]}{[I_2]} \qquad (4)$$

$$3I_2 + 3H_2O \overset{K_5}{\rightleftharpoons} 6H^+ + 5I^- + IO_3^- \qquad K_5 = \frac{[H^+]^6[I^-]^5[IO_3^-]}{[I_2]^3} \qquad (5)$$

where non-subscripted terms refer to the aqueous phase and concentrations are in moles/liter. Reaction 5 is very slow in acid media and slow enough even at a pH of 9 to be neglected.(9,10) Based on the data compiled, K_1 through K_4 can be represented as a function of temperature by

$$K = a\ e^{-\frac{b}{RT}} \qquad (6)$$

where R is the gas law constant (1.987 cal/mole °K), T is the temperature in degrees Kelvin, and a and b are given in Table 1.

Several experimenters have given evidence for the existence of a volatile inorganic iodine species which has been claimed to be HOI, hypoiodous acid. Keller(10,11) showed that on the basis of Eggleton's data HOI was the predominent specie in solution following iodine hydrolysis with the ratio of HOI to total dissolved iodine increasing with increasing pH and decreasing iodine concentration. Using a small glass vessel the existence of a volatile specie other than iodine was demonstrated by removing gas phase samples through a solid inorganic adsorbant claimed to preferentially adsorb HOI. Additionally, HOI was produced by a well-known reaction between iodine and mercuric oxide and an indirect chemical test based on the iodination of phenol(12) confirmed the volatility of the compound.

Russian investigators(13) reported an evaporation of hypoiodous acid which was most pronounced at higher pressure while Bachofner and Hesbol(14) noted a discrepancy between experimental and predicted results, indicative of hypoiodous acid evaporation, during the release of iodine from boiling water. Similar behavior was obtained by researchers at Oak Ridge(15) and the lack of material balance in the Battelle containment systems experiments(4,5) could be partly assumed to be due to HOI volatility.

More recently, however, Schmitt(16) at ORNL concluded that a highly reactive iodine species in solution iodinated trace organic impurities in the sparging air stream and that it was the probable alkyl iodides formed which constituted the volatile iodine compounds noted in his work and others. The formation of iodoform (CHI_3) was confirmed by visible -UV spectrophotometry. Further, Davis, Jr., and Kibbey(17) measured the spectrum of $HgO-I_2$ filtered solutions and compared it with that from HgI_2 filtrates; the similarity was quite evident indicating that HgI_2 may also produce HOI or that the only product of HgO plus I_2 is HgI_2. The latter conclusion was substantiated by polarographic analyses showing the presence of IO_3^- but the absence of I^- and IO^-.

The techniques used to collect samples of airborne iodine and iodine compounds have consisted of coated substrates(18), maypacks(5) and modified versions of maypacks(11), and composite diffusion tube.(19,20) Until such time as when more sophisticated instrumental techniques become available for the direct determination of airborne iodine species, it appears unlikely that the question of the volatility of HOI will be resolved.

Further discussions relative to hypoiodous acid are contained in the section on mass transfer calculations and in the addendum where rates of hydrolysis of iodine are discussed.

3. Determination of Henry's Law Constant

The rate of mass transfer of iodine from the gas phase to the liquid spray droplet is controlled by the resistance in a gas film surrounding the drop as well as the resistance to diffusion within the drop. Usually one resistance is greater than the other such that the latter can be neglected; but a means of comparing the two values is dependent on Henry's Law which relates the gas phase and liquid phase iodine concentration.

Because of hydrolysis, the total dissolved quantity of iodine is given by

$$[I_2]_T = [I_2] + [HOI] + [I_3^-] + [H_2OI^+] \qquad (7)$$

The concentration of H_2OI^+ can be shown to be negligible under all circumstances and for pure water at neutral pH, I_3^- is also very small. Since there is no added I^-, reaction 3 states that $[H^+]$ equals $[I^-]$ equals $[HOI]$ and equation 3 can be solved for $[HOI]$:

$$[HOI] = (K_3[I_2])^{1/3} \qquad (8)$$

Henry's Law states that the concentration of iodine in solution is related to the partial pressure in the gas phase by

$$[I_2] = \frac{p_e}{H} \qquad (9)$$

where H is the Henry Law constant in atm liter/mole and p_e is the equilibrium partial pressure of iodine in atm. Combining equations 8 and 9 in 7 gives

$$[I_2]_T = \frac{p_e}{H} + (K_3\frac{p_e}{H})^{1/3} \qquad (10)$$

H can be determined at various temperatures from equation 10 using the solubility data of Seidell(21) and the equation for the vapor pressure of iodine

$$\log p = 7.2105 - \frac{3147.52}{T} \qquad (11)$$

where p is in atm and T is in degrees Kelvin (valid for temperatures between 20° and 135°C). Values for H are given in Table 2 including an extrapolated value of 4.5 atm liter/mole at 135°C (275°F), the maximum temperature of a postulated LOCA. Taylor(22) determined an experimental value of 0.206 at 20°C in relatively good agreement with that shown in Table 2.

4. Reaction between Iodine and Hydrazine

As indicated earlier, a number of chemically reactive sprays are proposed for use during a LOCA; the reducing agent incorporated in the spray would convert the dissolved iodine species to non-volatile iodide. For the purposes of developing and evaluating a mathematical model for the rate of removal of airborne iodine, the boric acid spray containing 50 ppm of hydrazine(7,8) was chosen as the modeling system because it appears to be the least corrosive of the reactive sprays and because it could be readily incorporated into existing plants and the present design plant. Of course, the calculation techniques developed here could be used to evaluate any reactive spray.

The kinetics of the reaction between hydrazine and iodine was determined by SenGupta and SenGupta(23); they found both an effect of pH and an effect of iodide concentration at the conditions of their experiments (pH from about 1 to 1.3, $[I^-]$ from

0 to 0.05 moles/liter, and temperatures from 25° to 45°C). The reaction was found to be first order with respect to the iodine concentration since the hydrazine was in excess by a factor of 5 of the stoichiometric amount as indicated by the overall equation

$$\tfrac{1}{2}N_2H_4 + I_2 \rightarrow \tfrac{1}{2}N_2 + 2H^+ + 2I^- \qquad (12)$$

For lack of other information, the rate of the reaction will be assumed to be proportional to the square root of the hydrazine concentration. Certainly the reaction cannot be zero order in hydrazine and if it were first order, it is unlikely the data of SenGupta and SenGupta would have conformed to first order in iodine up to the high extents of conversion they achieved. The square root dependency on hydrazine concentration was found for the reaction with oxygen(24) and is also suggested by the stoichiometry of equation 12. Further detailed information, however, should be obtained for this reaction.

Assuming that, during the reaction between the hydrazine and the iodine solution, the reactions given by equations 2, 3 and 4 were at equilibrium, it is possible to show that the rate was precisely proportional to the ratio of the concentration of HOI to H_2OI^+ which is inversely proportional to $[H^+]$. By emperical means the effect of iodide concentration was approximated; including the determinations made at several temperatures, the overall rate of reaction, in moles/liter min, is given by

$$-\frac{d[N_2H_4]}{dt} = \frac{2.35\text{x}10^5}{[H^+]e^{\frac{10000}{RT}}}\sqrt{[I_2]([I_2]+10\sqrt{K_2[I_2]}[I^-])[N_2H_4]} \qquad (13)$$

For zero concentration of iodide, it can be seen that the rate is proportional to the iodine concentration and the square root of the hydrazine concentration and inversely proportional to the concentration of H^+.

5. Relationship between Gas and Liquid Mass Transfer Resistance

Based on the principle of steady-state transfer from the gas to the liquid

$$N_{I_2} = k_G(p-p_i) = k_L([I_2]_{Ti} - [I_2]_T) \qquad (14)$$

where N is the mass transfer in moles/min cm^2, k_G and k_L are the individual mass transfer coefficients, p and p_i are the partial pressures in the bulk gas and the gas-liquid interface, and $[I_2]_{Ti}$ and $[I_2]_T$ are the total iodine concentrations at the interface and in the main liquid in units of moles/liter. The rate of mass transfer is also defined in terms of the overall mass transfer coefficients by

$$N_{I_2} = K_G(p-p_e) = K_L([I_2]_{Te} - [I_2]_T) \qquad (15)$$

where p_e is the equilibrium partial pressure of iodine over a solution of concentration $[I_2]_T$, and $[I_2]_{Te}$ is the concentration of a solution in equilibrium with the gas phase partial pressure p. In practice, since interface concentrations and partial pressures are seldom known, it is important to be able to calculate the overall mass transfer coefficient from the individual film resistances (the resistance is the reciprocal of the mass transfer coefficient).

From equation 14 and 15

$$K_G(p-p_e) = k_G(p-p_i) \tag{16}$$

or

$$\frac{1}{K_G} = \frac{p-p_e}{k_G(p-p_i)} \tag{17}$$

By definition above

$$p-p_e = (p-p_i) + (p_i-p_e) \tag{18}$$

Substituting equations 18 and 14 in 17 gives

$$\frac{1}{K_G} = \frac{1}{k_G} + \frac{p_i-p_e}{k_G(p-p_i)} = \frac{1}{k_G} + \frac{p_i-p_e}{k_L([I_2]_{Ti}-[I_2]_T)} \tag{19}$$

By solving equations 2 and 3 for $[I_3^-]$ and [HOI], respectively, and combining with equations 7 and 9 (neglecting the concentration of H_2OI^+), the total iodine concentration in solution is

$$[I_2]_T = \frac{p_e}{H}\left(1 + \frac{K_3}{[H^+][I^-]} + K_2[I^-]\right) \tag{20}$$

Substituting equation 20, for p_e and p_i, in equation 19 gives

$$\frac{1}{K_G} = \frac{1}{k_G} + \frac{H}{k_L\left(1+\frac{K_3}{[H^+][I^-]} + K_2[I^-]\right)} \tag{21}$$

Similarly it can be shown that

$$\frac{1}{K_L} = \frac{1}{k_L} + \frac{\left(1 + \frac{K_3}{[H^+][I^-]} + K_2[I^-]\right)}{Hk_G} \tag{22}$$

In the absence of initial iodide in the spray, the total dissolved iodine can be calculated from

$$[I_2]_T = \frac{P_e}{H} + \sqrt{\frac{K_3 P_e}{[H^+]\ H}} \tag{23}$$

since the iodide and hypoiodous acid concentration would be equal.

Examination of equations 21 and 22 shows that they conform to the usual expressions relating k_G and k_L with K_G and K_L when the sum of terms in parenthesis is unity. For very soluble gases, H is small and the second term on the right in equation 21 becomes negligible; thus the overall gas phase mass transfer coefficient, K_G, is equal to the individual gas phase value, k_G, and the rate of mass transfer is said to be gas phase controlled.

For iodine, H is moderately large, and as the pH is lowered, $[H^+]$ increases; thus, the second term can be significant.

6. The Individual Gas Phase Coefficient, k_G

Extensive data on the rate of adsorption and desorption of very soluble gases (such that the resistance to mass transfer in the liquid could be neglected) from spheres and small drops has been correlated to the Froessling(25) semitheoretical equation

$$\frac{k_c D}{D_v} = 2.0 \left[1 + 0.276 \left(\frac{DV\rho}{\mu}\right)^{\frac{1}{2}} \left(\frac{\mu}{\rho D_v}\right)^{1/3}\right] \qquad (24)$$

where D is the spray drop diameter, D_v is the molecular diffusivity of the iodine vapor in the stream-air atmosphere, V is the velocity of the falling drop, and ρ and μ are the density and viscosity of the liquid in the drop. The units are chosen such that the terms in parentheses are dimentionless.

The diffusivity can be calculated from the semi-empirical equation(26)

$$D_v = 0.0069 \frac{T^{3/2}}{P(V_A^{1/3} + V_B^{1/3})^2} \sqrt{\frac{1}{M_A} + \frac{1}{M_B}} \qquad (25)$$

where T is the temperature(^oR), P is the total pressure (atm), V_A and V_B are the molecular volumes (cm^3/gmole), and M_A and M_B are the molecular weights. The other variables in equations 24 and 25 can be found in engineering tables. The molecular volume of iodine is given by Griffiths(27) as 71.5 cm^3/mole.

The mass transfer coefficient can then be calculated from

$$k_G = k_c/RT \tag{26}$$

7. The Individual Liquid Phase Coefficient, k_L

With chemically reactive sprays, the liquid phase coefficient must be determined on the basis of simultaneous diffusion and reaction. Since, for a reactive liquid drop, there is no accumulation of iodine or its hydrolysis products in the bulk of the drop, the rate of diffusion into the drop must equal the rate of reaction. By substituting the definition of k_L in equation 14

$$k_L = \frac{D_L}{z} \tag{27}$$

where D_L is the liquid diffusivity (liter/cm min) across a thin film of thickness, z (cm), at the surface of the drop and multiplying by the surface area of the drop, A_D, the rate of diffusion in moles/min is obtained.

The rate of disappearance of hydrazine occurs at half the rate of diffusion of the iodine as indicated by the stoichiometry of equation 12. The former can be calculated from equation 13, as moles per minute, by multiplying the volume of the thin film given as

$$\frac{zA_D}{1000} = \text{volume, liters} \tag{28}$$

where A_D is the surface area of the drop in cm^2 (πD^2).

Equating the rate of diffusion of $[I_2]_T$ with twice the rate of reaction of hydrazine, z can be calculated from

$$z = \left(\frac{500\ D_L [I_2]_{Ti}\ [H^+]}{k\sqrt{[\overline{I_2}]([\overline{I_2}]+10\sqrt{K_2[\overline{I_2}][\overline{I^-}]})[\overline{N_2H_4}]}} \right)^{\frac{1}{2}} \qquad (29)$$

where the line over the concentration terms indicates that average concentrations in the film are used and k is the reaction rate velocity constant

$$k = 2.35\text{x}10^5\ e^{-\frac{10000}{RT}} \qquad (30)$$

Equation 29 is valid for z/D of less than 0.05. Because the rate of diffusion of iodine into the drop must be balanced by a stoichiometric rate of diffusion out from the center of the drop into the reaction zone, the average hydrazine concentration can be calculated from

$$[\overline{N_2H_4}] = [N_2H_4] - \frac{D_{I_2}[I_2]_{Ti}}{4\ D_{N_2H_4}} \qquad (31)$$

Solution of equation 29 is by a trial-and-error procedure. First, from an assumed partial pressure (p_i) of iodine at the interface determined by

$$p > p_i > 0 \qquad (32)$$

where p is the iodine partial pressure in the main gas phase, $[I_2]_{Ti}$ can be calculated from equation 20 or 23, $[I_2]_i$ from equation 9, $[HOI]_i$ from the second term of equation 20 or 23, and $[I_3^-]_i$ from the third term of equation 20 or from equation 2. The iodide concentration is either equal to that of the HOI or the amount initially present. The average hydrazine concentration in the thin film is calculated by equation 31 and the average concentrations of I_2, I_3^-, and total dissolved iodine are half the interface concentrations since chemical reaction within the bulk of the drop prevents any accumulation. Since iodide is a product of the reaction, only at time zero is the average concentration half the interface value or equal to the initial concentration if present originally.

The thickness of the mass transfer and reaction zone film can then be calculated from equation 29 and k_L from equation 27. Having calculated k_G from equations 24 and 26, equation 14 can be evaluated to determine if the equality based on the assumed value of p_i is satisfied; if not a new value of p_i must be assumed and the process repeated.

8. Initial Rate of Iodine Removal at Peak LOCA Conditions

Based on an averaging of several PWR's, design criteria for evaluation of spray performance have been tabulated.(7)

Pertinent information necessary to perform the calculations presented in the previous section are given in Table 3 for the peak LOCA conditions. For a chemically reactive spray assumed to contain 50 ppm (1.562×10^{-3} moles/liter) N_2H_4, the initial rates of iodine removal at the point where the spray drops first enter the containment were evaluated at a pH of 7 and 5 both with and without an initial iodide concentration of 508 ppm (0.004 moles/liter); the results of the iterative calculations are shown in Table 4.

The fraction of dissolved iodine which is present as hypoiodous acid, $[HOI]_i/[I_2]_{Ti}$, is seen to be nearly unity at a pH of 7 and slightly less at pH5. But with the addition of a small amount of iodide to the spray solution (0.004 moles/liter), the fraction of HOI present at the drop surface was further suppressed, especially at pH5. This, of course, would substantially reduce any possibility of HOI evaporation. It should be noted that even in the absence of initial iodide, at any time greater than zero the iodide concentration at the surface of the drop will be 0.00625 moles/liter as a result of complete conversion of the available N_2H_4 at the surface. Thus, the extent of HOI volatility, even if it has a low, partition coefficient, should be insignificant with 50 ppm hydrazine sprays at a pH of about 6 or less.

The overall coefficients, K_G and K_L, were calculated from equations 21 and 22 and the fractional contribution of k_G. For neutral pH(=7) in the presence of 0.004 moles/liter of iodide, the calculated value of this fraction is 0.890 (cf. Table 4) which compares very well with the measured value of 0.88 obtained from short exposure time experiments$^{(7)}$ using a midget impinger cascade.

Based on the total volume of the drop, the rate of disappearance of hydrazine can be calculated by

$$-\frac{d[N_2H_4]}{dt} = \frac{K_G A_D p}{2V_D} \qquad (33)$$

where A_D and V_D represent the surface area and total volume of the drop, respectively. For the range of variables investigated in Table 4, the maximum rate occurs at a pH of 7 - 0.01268 moles/liter min - and the minimum at pH 5 - 0.00210 moles/liter min - both in the absence of initial iodide. For a drop fall time of seconds the initial hydrazine concentration in the spray, assuming gas phase control, should be 0.0021 moles/liter or 68 ppm N_2H_4 for an initial containment gas phase iodine concentration of 10 ppm.

Calculations and results similar to those shown in Table 4 should be performed over the total drop fall time at perhaps 1 second intervals as well as at other initial iodine containment concentrations and containment temperatures. Similar calculations would show the effect of the termination of fresh spray and the commencement of recirculated spray.

For the conditions assumed in these example calculations and the degraded operation numbers given in Table 3, an estimate of the iodine half-life in the containment atmosphere can be made. The rate of conversion of iodine to iodide is twice the rate of reaction of the hydrazine with an average value during the half-life time of 0.015 moles/liter min. Therefore the amount of iodine removed is

$$\frac{(0.015)(10)(6.579\mathrm{x}10^{-7})}{60} = 1.645\mathrm{x}10^{-9} \text{ moles/drop}$$

The total number of drops in the containment is

$$\frac{1500}{(7.42)(2.323\mathrm{x}10^{-8})} = 8.702\mathrm{x}10^{9} \text{ drops/min}$$

and the total amount of iodine in the containment is

$$\frac{(1\mathrm{x}10^{-5})(453.6)(4)(273.16)(1\mathrm{x}10^{6})}{(359)(408.16)} = 33.8 \text{ moles}$$

The time to remove half is

$$\frac{16.9}{(1.645\mathrm{x}10^{-9})(8.702\mathrm{x}10^{9})} = 1.18 \text{ min}$$

which is in good agreement with experimental values of from 0.4 to 5 minutes.

9. Reaction Between Oxygen and Hydrazine

Because there is a significant amount of oxygen in the containment the rate of oxidation of the hydrazine by oxygen must be compared to that with the iodine. Additionally, atmospheric oxidation during storage and refueling operations may also be significant.

Studies on the auto-oxidation of hydrazine were performed by Gilbert(24) and the use of N_2H_4 as an oxygen scavenger was evaluated by Stones.(28) From the meager amount of kinetic data the rate equation was determined to be

$$-\frac{d[N_2H_4]}{dt} = k[O_2]\sqrt{[N_2H_4]} \qquad (34)$$

where the concentrations are in moles/liter and k is

$$k = 1.8\text{x}10^9 e^{-\frac{13000}{RT}} \qquad (35)$$

for a pH of 7. Both investigators found the rate to be pH-dependent, increasing by an order-of-magnitude on raising the pH from 7 to between 9 and 10. The rate decreased more slowly upon lowering the pH. The reaction rate has been shown to increase markedly in the presence of catalyzing agents such as small amounts of particulates and dissolved metals such as iron and copper;(28) the rate constant given in equation 35 is that in the absence of such catalysts and for a pH of 7.

10. Air Oxidation of Hydrazine at Peak LOCA Conditions

The gas phase coefficient, k_G, as determined by equations 24 and 26 is 0.01723 moles/min cm^2 atm at the peak LOCA conditions (275°F).

Experimental results with wetted-wall columns(26) has shown that the absorption of oxygen is liquid-film controlled. On this basis, the oxygen partial pressure at the interface is the same as that in the containment atmosphere, namely, 0.203 atm and the oxygen concentration in the liquid at the interface is

$$|O_2|_i = \frac{p}{\Pi} = \frac{0.203}{1361} = 1.492\text{x}10^{-4} \text{ moles/liter}$$

The rate of diffusion into a liquid film of thickness z surrounding the drop equals the rate of oxidation of hydrazine assuming no accumulation of oxygen within the mass of the drop until the hydrazine has been depleted. Thus,

$$\bar{A}_f N_{O_2} = V_f R \tag{36}$$

where $\bar{A}_f$ is the log mean average area for mass transport within the film (cm^2), N_{O_2} is the rate of oxygen mass transfer (moles/cm^2 min), V_f is the volume of the film (liter), and R is the rate of hydrazine oxidation (moles/liter min).

The log mean average area is

$$A_f = \pi \left(\frac{2z}{\ln \frac{D}{D-2z}} \right)^2 \tag{37}$$

and the volume is

$$V_f = \frac{\pi}{6000} \left[D^3 - (D-2z)^3 \right] = \frac{2z\pi}{6000} (3D^2 - 6Dz + 4z^2) \tag{38}$$

where D is the drop diameter (cm). The oxygen mass transfer rate is

$$N_{O_2} = \frac{D_{O_2}}{z} [O_2]_i \tag{39}$$

Substituting equations 34, 37, 38, and 39 in 36 and rearranging gives

$$z^2 = \left(\frac{2z}{\ln \frac{D}{D-2z}} \right)^2 \frac{3000 \, D_{O_2} [O_2]_i}{(3D^2 - 6Dz + 4z^2) k [\overline{O_2}] \, [\overline{N_2H_4}]} \tag{40}$$

where the oxygen and hydrazine concentrations in the denominator represent average film concentrations approximated by

$$[\overline{O_2}] = \frac{[O_2]_i}{3} \tag{41}$$

and

$$[\overline{N_2H_4}] = [N_2H_4] - \frac{D_{O_2} [O_2]_i}{3 D_{N_2H_4}} \tag{42}$$

and k is given by equation 35.

The film thickness, z, is computed from equation 40 by trial-and-error and for peak conditions of the LOCA, z is found to be 0.04192 cm from which k_L is

$$k_L = \frac{D_{O_2}}{z} = \frac{7.05\times10^{-6}}{0.04192} = 0.000168 \text{ liter/cm}^2 \text{ min}$$

Substituting k_G and k_L in

$$\frac{1}{K_L} = \frac{1}{k_L} + \frac{1}{Hk_G} \tag{43}$$

gives a K_L of 1.67999×10^{-4} or $K_L/k_L = 0.99999$; thus the diffusion is liquid phase controlled.

The rate of removal of the hydrazine is

$$-\frac{d[N_2H_4]}{dt} = \frac{k_L[O_2]_i\bar{A}_f}{V_D} \tag{44}$$

where V_D is the total drop volume. Substituting the appropriate values into equation 44 gives a rate of hydrazine removal of 0.0003745 moles/liter min which, when compared to the rates shown in Table 4, amounts to about 3 to 18% of the rate of removal by iodine.

Based on these results it would appear that oxidation of hydrazine by the air in the containment could possibly amount to a significant fraction of that by iodine especially if the initial containment I_2 was 1 ppm by volume instead of the assumed 10 ppm or if the reaction rate between oxygen and hydrazine was higher because of catalytic effect by trace constituents.

A similar calculation of the rate of reaction of oxygen and hydrazine but at 250°F gave a rate of 0.000289 moles/liter min or 9.2 ppm/min which compares reasonably well with a value of 3.5 ppm/min obtained experimentally by Postma.(7) More detailed information of the effects of temperature, pH, and impurities on this reaction should be obtained.

11. Oxidation of Hydrazine during Storage and Refueling Operations

In order to determine the feasibility of using a boric acid spray containing 50 ppm of hydrazine, long term stability tests(7) were performed by determining the rate of hydrazine air oxidation in a stagnant, open 50 gallon drum. The experimenters suggested that the rate of reaction and not mass transfer was the controlling factor; however, experience of other investigators(26) has shown that the rate of oxygen mass transfer in the liquid should be the controlling factor, especially since the rate of chemical reaction with hydrazine is only moderate.

Assuming the storage experiment was performed at 25°C and that the gas film resistance is negligible, the concentration of oxygen at the surface of the liquid (at steady-state) is the equilibrium solubility, 2.562×10^{-4} moles/liter. Since the hydrazine concentration in the bulk liquid is 50 ppm (1.562×10^{-3} moles/liter) and that of the oxygen is zero because of chemical reaction, the average oxygen concentration in a thin film of thickness z at the surface of the liquid in the drum is one-half the surface concentration, i.e., 1.281×10^{-4} moles/liter and that for hydrazine is calculated from equation 42 giving $[\overline{N_2H_4}] = 1.486\times10^{-3}$ moles/liter.

For a drum of surface area, A_f, the volume of the film is $zA_f/1000$ (liters); equation 36 becomes

$$\frac{D_{O_2}}{z}\,[O_2]_i = \frac{z}{1000}\,k[O_2]\,[N_2H_4] \qquad (45)$$

and rearranging gives

$$z = \left(\frac{1000\,D_{O_2}\,[O_2]_i}{k[\bar{O}_2]\sqrt{[N_2H_4]}}\right)^{\frac{1}{2}} \qquad (46)$$

At 25°C, the diffusivity, D_{O_2}, is 1.02×10^{-6} liter/cm min and k, from equation 35, is 0.532 $(\text{liter/mole})^{\frac{1}{2}}$/min. Solving equation 46 gives a film thickness, z, of 0.316 cm and

$$k_2 = \frac{D_{O_2}}{z} = \frac{1.02\text{x}10^{-6}}{0.316} = 3.23\text{x}10^{-6} \text{ liter/cm}^2 \text{ min}$$

Assuming that the surface area of the 50 gallon (189.2 liters) drum is about 2375 cm^2, the rate of removal of hydrazine can be estimated from equation 44 as

$$-\frac{d[N_2H_4]}{dt} = \frac{(3.23\text{x}10^{-6})(2.562\text{x}10^{-4})(2375)}{189.2} = 1.04\text{x}10^{-8} \text{ moles/liter min}$$

which is equal to 0.48 ppm/day; the value obtained experimentally by Postma(7) was 1.2 ppm/day!

In a normal refueling operation using the refueling water with the hydrazine additive, it is anticipated that with the degree of turbulence and mixing occurring throughout the entire cycle, the solution would be nearly saturated with oxygen from the containment air; thus the solution reaction rate would play a controlling role. Based on the reaction rate given by equation 34, the half-life can be calculated from

$$t_{\frac{1}{2}} = \frac{0.586\sqrt{[N_2H_4]}}{k[O_2]} \qquad (47)$$

Using the rate constant and concentrations determined previously at 25°C, evaluation of equation 47 gives a half-life of 170 minutes or about 3 hours. More than half the hydrazine would be destroyed for a refueling cycle taking several hours.

12. Conclusions

The important points which have been covered in this report are summarized below with indications as to the direction future work should take where information is the most sparse or completely lacking.

1. Numerous investigators have attributed volatization of an iodine component as being related to the volatization of HOI but recent studies indicate that the loss occurs by formation of volatile alkyl iodides from organic contaminents in air. Instrumental methods including chromatographic and spectrophotometric techniques should be developed for identification of these species.

2. The reaction between hydrazine and hydrolyzed iodine has only been studied at temperatures near room temperature and then only in very low pH solutions. Because of the complexity and pH-dependence of the hydrolysis reactions, extrapolation of rate data over very large pH and temperature ranges is not desirable. Data on the rate of reduction of iodine with the desired reductant should be experimentally obtained.

3. Calculations of chemical reaction and mass transfer rates should be performed under a variety of conditions of airborne iodine concentration, pH of spray, temperature in the

containment, drop fall time and drop size, and concentration of reductant and added iodide. These calculations would include a determination of the HOI concentration in the liquid film at the surface of the drop which would then permit an estimation of the extent of the HOI volatility problem.

4. The magnitude of the rate of oxidation of hydrazine by the oxygen in the containment is, under conditions of low iodine vapor concentration (1 ppm or less) and/or the presence of catalytic metallic ions, of the same order as the rate with iodine. The kinetics of the reaction of the reductant with the containment oxygen should be more precisely defined.

5. Kinetic data on the rate of hydrolysis of iodine (cf. Addendum) indicates the importance of the negative ion specie, I_2OH^-. Rate data on the hydrolysis reactions at temperatures higher than room temperature must be experimentally determined in order to fully understand the mechanisms of the reactions with reductants such as hydrazine.

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Table 1

Temperature Dependence for Hydrolysis Equilibrium Constants

$$K = a\,e^{-\frac{b}{RT}}$$

Equilibrium constant, K[1]	a	b
K_1	1.388×10^{-3}	-6516
K_2	7.76	-2722
K_3	0.976	16720
K_4	4.227×10^{-3}	3474

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[1] (cf. p. 2 of text)

Table 2

Calculated Henry's Law Constant for Iodine

$$[I_2]_T = \frac{p}{H} + \left(K_3 \frac{p}{H}\right)^{1/3}$$

Temperature, °C	Iodine solubility $[I_2]_T$, moles/liter	I_2 Vapor pressure p, atm	Henry's Law constant H, atm liter/mole
20	0.001124	0.000298	0.267
25	0.001324	0.000451	0.343
90	0.01241	0.03495	2.840
100	0.01753	0.0597	3.433
112.3	0.02837	0.111	3.942
135			4.50[1]

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[1] (extrapolated value)

Table 3

Parameters for Iodine Absorption by Spray Drops

Typical Reactor and Containment Description	
Type	PWR
Volume above Main Deck	10^6 ft^3
Drop fall distance	100 ft
Spray System Minimum Capacity	
Flow rate	1500 gpm
Duration of fresh spray	62 minutes
Mean drop diameter	0.108 cm
Drop surface area	0.0366 cm^2
Drop volume	6.596×10^{-7} liters
Hydrazine concentration	50 ppm
Peak LOCA Conditions	
Iodine partial pressure	4×10^{-5} atm (10 ppm)
Temperature	135°C (275°F)

Table 4

Results of Iterative Determination of Iodine Mass Transfer
Time zero[1] (min) at Peak LOCA Conditions
All Concentrations are in moles/liter

pH	7	5	7	5
$[I^-]_o$	0	0	0.004	0.004
pi, atm	2.41×10^{-6}	3.38×10^{-5}	4.38×10^{-6}	2.82×10^{-5}
$[I_2]_{Ti}$	7.68×10^{-5}	3.61×10^{-5}	4.48×10^{-6}	1.21×10^{-5}
$[I_2]_i$	5.33×10^{-7}	7.50×10^{-6}	9.73×10^{-7}	6.28×10^{-6}
$[I^-]_i$	7.61×10^{-5}	2.85×10^{-5}	0.004	0.004
$[HOI]_i$	7.61×10^{-5}	2.85×10^{-5}	2.64×10^{-6}	1.70×10^{-7}
$[I_3^-]_i$	9.05×10^{-9}	4.77×10^{-8}	8.68×10^{-7}	5.60×10^{-6}
$[N_2H_4]_i$	1.54×10^{-3}	1.55×10^{-3}	1.56×10^{-3}	1.56×10^{-3}
$[HOI]_i/[I_2]_{Ti}$	0.993	0.792	0.589	0.014
z, cm	6.00×10^{-4}	1.69×10^{-3}	3.69×10^{-3}	3.01×10^{-4}
k_G	0.01212	0.01212	0.01212	0.01212
k_L	0.00592	0.00209	0.09621	0.01181
K_G	0.01139	0.00189	0.01079	0.00356
K_L	0.00036	0.00177	0.01054	0.00834
$k_G(p-p_i)$	4.55×10^{-7}	7.55×10^{-8}	4.32×10^{-7}	1.42×10^{-7}
$k_L[I_2]_{Ti}$	4.55×10^{-7}	7.55×10^{-8}	4.32×10^{-7}	1.42×10^{-7}
K_G/k_G	0.940	0.156	0.890	0.294
$-d[N_2H_4]/dt$	0.01268	0.00210	0.01201	0.00396

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[1] (spray drop has just entered the containment atmosphere)

Table 5

Rate Constants for the Kinetics of Iodine Hydrylysis[1]

k_{10}	8.85×10^{-4} mole/liter sec
k_{01}	1.3×10^{11} liter/mole sec
k_{12}	≈ 0.1 sec^{-1}
k_{21}	$\approx 1.0 \times 10^{10}$ liter/mole sec
k_{13}	2.1 sec^{-1}
k_{31}	1.6×10^{10} liter/mole sec
k_{03}	$\approx 1.0 \times 10^{10}$ liter/mole sec
k_{30}	$\approx 6.0 \times 10^{5}$ sec^{-1}
k_{24}	$\approx 2.0 \times 10^{7}$ sec^{-1}
k_{42}	$\approx 5.0 \times 10^{9}$ liter/mole sec
k_{34}	$\approx 3.0 \times 10^{7}$ sec^{-1}
k_{43}	$\approx 6.0 \times 10^{9}$ liter/mole sec

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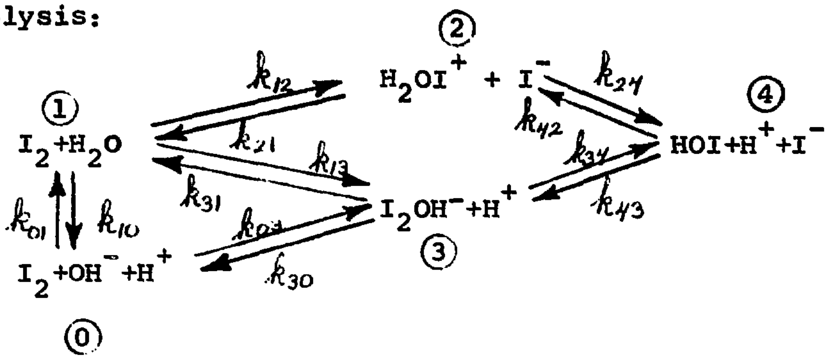
[1] (cf reference 29)

Addendum: The Kinetics of Iodine Hydrylysis

The very pertinent results of Eigen and Kustin(29) on the hydrolysis of iodine were uncovered after the evaluation of the kinetics and mass transfer calculations were made in this paper. On the basis of their thorough investigation it appears that the mechanism for the reduction of iodine by hydrazine can be more easily explained as involving the negative ion intermediate, I_2OH^-.

They considered the following overall mechanism for the hydrolysis:



Based on the work of Bell and Gelles(30), it was determined that the formation of HOI by the reaction path through H_2OI^+, ①→②→④, was not significant since the H_2OI^+ is present to too small an extent. Using the T- jump relaxation method to carry out experiments, the kinetic constants for each of the above important steps were carefully evaluated; the results are given in Table 5.

The equilibrium constant for the reaction between states ③ and ④ is

$$K_{34} = \frac{k_{34}}{k_{43}} = \frac{[HOI][I^-]}{[I_2OH^-]} = 0.005 \qquad (48)$$

For an iodide concentration of 0.005 moles/liter, which is about the expected level in the presence of 50 ppm N_2H_4, the equilibrium concentration of I_2OH^- is approximately equal to that of the HOI, thus this mechanism must be given consideration in the evaluation of the reduction of iodine and its hydrolysis products (It appears that Eggleton's evaluation(9) of his reaction 7 was incorrect; I_2OH^- should not have been eliminated from consideration.)

Using a steady-state approach for calculating the concentration of I_2OH^-, Eigen and Kustin obtained

$$[I_2OH^-] = \frac{(k_{03}[OH^-]+k_{13})[I_2]+k_{43}[HOI][I^-]}{k_{30}+k_{34}+k_{31}[H^+]} \qquad (49)$$

For the condition at which Sen Gupta and Sen Gupta(23) measured the rate of iodine reduction by hydrazine, pH of about 1 and an iodide concentration between 0 and 0.05 moles/liter, $k_{31}[H^+] >> k_{30}+k_{34}$ and $k_{13} >> k_{03}[OH^-]$. Equation 49 becomes

$$[I_2OH^-] = \frac{k_{13}[I_2]+k_{43}[HOI][I^-]}{k_{31}[H^+]} \qquad (50)$$

If I_2OH^- is the reacting specie in the reaction with hydrazine then equation 50 predicts that the rate would be inversely proportional to the hydrogen ion concentration; this has been shown to be the case for the results of Sen Gupta and Sen Gupta. Furthermore, at their experimental conditions it can be shown that $k_{13}[I_2] > k_{43}[HOI][I^-]$ and that $[I_2]$ decreases as $[I^-]$ increases because of reaction 2 which forms the triiodide; thus the effect of iodide concentration that was noted by the experimenters is qualitatively explained as a reduction in the concentration of I_2OH^- as the iodide concentration increases.

At the pH expected for sprays (pH from 5 to 7), $k_{34} >> k_{31}[H^+]$ and $k_{03}[OH^-] >> k_{13}$. Equation 49 becomes

$$[I_2OH^-] = \frac{k_{03}[OH^-][I_2] + k_{43}[HOI][I^-]}{k_{34}} \qquad (51)$$

Furthermore, the second term in the numerator is much larger than the first, so equation 51 reduces to that shown as equation 48. In this range of pH, the $[I_2OH^-]$ is not a function of the hydrogen ion concentration. Therefore, the rate equation 13 is not strictly correct in the light of this negative ion specie which has up to the present, not been considered.

Most importantly, if indeed I_2OH^- is a precursor to HOI and is the specie which reacts with hydrazine (and, incidentally, is probably the specie which iodinates phenols since for the conditions of Cofman's experiments(12) the I_2OH^- concentration was about 40 times that of the HOI), then a chemically reactive spray may remove the I_2OH^- before HOI can be formed. An investigation of the kinetics of these reactions in the presence of hydrazine or other reducing agents should be made before attempting to evaluate the volatility of HOI - especially since methods of measuring the vapor phase concentration of HOI have not been validated.