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Removal of Sarin Aerosol and Vapor by Water Sprays

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Abstract

Falling water drops can collect particles and soluble or reactive vapor from the gas through which they fall. Rain is known to remove particles and vapors by the process of rainout. Water sprays can be used to remove radioactive aerosol from the atmosphere of a nuclear reactor containment building. There is a potential for water sprays to be used as a mitigation technique to remove chemical or biological agents from the air. This paper is a quick-look at water spray removal. It is not definitive but rather provides a reasonable basic model for particle and gas removal and presents an example calculation of sarin removal from a BART station. This work is a starting point and the results indicate that further modeling and exploration of additional mechanisms for particle and vapor removal may prove beneficial.

Introduction

Falling water drops can collect particles and soluble or reactive vapor from the gas through which they fall. Rain is known to remove particles and vapors by the process of rainout. Water sprays can be used to remove radioactive aerosol from the atmosphere of a nuclear reactor containment building. There is a potential for water sprays to be used as a mitigation technique to remove chemical or biological agents from the air. This paper is a quick-look at water spray removal. It is not definitive but rather provides a reasonable basic model for particle and gas removal and presents an example calculation of sarin removal from a BART station. This work is a starting point and the results indicate that further modeling and exploration of additional mechanisms for particle and vapor removal may prove beneficial.

Collection Mechanisms

Particles are collected by falling drops by a number of mechanisms including diffusion, interception, impaction, thermophoresis, diffusiophoresis, and electrostatics. Diffusion loss occurs when the Brownian diffusion of a particle or vapor molecule causes it to encounter the droplet surface. Interception occurs when a particle follows the gas streamlines around a falling droplet but the particle's physical size brings it into contact with the droplet surface where it is captured. Impaction occurs when the particle, because of its inertia, can not follow the gas flow streamlines around the falling droplet and impacts on the droplet surface. Thermophoresis occurs when a temperature gradient exists in the gas at the droplet surface; a particle will tend to move down a temperature gradient. Thermophoresis can enhance particle collection if the droplet is colder than the surrounding gas. Diffusiophoresis occurs when condensation or evaporation are occurring at the droplet surface; a particle will move in the direction of the vapor flux. Thermophoresis and diffusiophoresis can be counteracting forces; when a droplet is evaporating it cools and thermophoresis acts to move particles toward the surface but the vapor flux acts to move particles away. We will assume for the purposes of this scoping calculation that the droplets are not evaporating (the atmosphere is saturated) and that they are at the gas temperature. This is not unreasonable for a large amount of water being sprayed through a confined volume. Electrostatic effects result when particles, droplets, or both are charged. These effects are more difficult to evaluate and will be ignored for the purposed of this scoping work. Subsequent modeling work should address thermophoresis, diffusiophoresis, and electrostatic effects and evaluate to what extent conditions might be manipulated to take advantage of these effects.

In an isothermal, non-evaporating, non-condensing, electrically neutral situation, the collection mechanisms are impaction, interception, and diffusion. A single drop-

let collection efficiency, $\varepsilon(d_p, D)$, is defined for collection of particles of size d_p by droplets of size D. This collection efficiency is defined as the fraction of the volume of gas swept by the falling droplet that is depleted of particles. This collection efficiency is the combined result of all collection mechanisms. Each collection mechanism can then have a specific single droplet collection efficiency and the collection efficiencies for the various mechanisms can be combined in a number of ways. The simplest combination is to add the single droplet collection efficiencies for all the mechanisms.

$$\varepsilon_{total} = \sum_{all\ mechanisms} \varepsilon_{mechanisms}$$

Another method of combination is to assume that particles are removed by each mechanism sequentially so that the combined (or total) single droplet collection efficiency is 1 minus the product of 1 minus the collection efficiency for each mechanism.

$$\varepsilon_{total} = 1 - \prod_{all\ mechanisms} (1 - \varepsilon_{mechanisns})$$

A number of correlations for these mechanisms are reported by Rimberg and Peng (1977), Hidy (1984), and Seinfeld (1986). Powers and Burson (1993) have developed a simplified model for the removal of aerosols from reactor containments by water sprays. The correlations selected for use in these scoping calculations are certainly adequate for that purpose but further searching of the literature would be warranted for follow-on work.

For the range of collector droplet that can be reasonably generated with a nozzle the flow regimes around the droplet range from viscous (Droplet Reynolds Number < ~1) to potential (Droplet Reynolds Number > ~1000). An interpolation formula developed by Langmuir (1948) for particle collection by droplet impaction is also used to interpolate for the mechanisms of interception and diffusion.

Vapor is also removed by Brownian diffusion to the surface of the collecting droplet in the same way that small particles are removed by Brownian diffusion. For particles, it is assumed with good reason, that once a particle contacts the surface, it is collected and that the concentration of particles at the droplet surface is zero; the rate-determining step for particle removal by Brownian diffusion is the transport of particles to the surface. Vapor removal must also consider a finite vapor concentration at the collector surface, the rate at which the gas goes into solution, the internal concentration and mixing within the collecting droplet and any chemical reaction occurring within the droplet to neutralize the material. Any of these processes could be a rate-limiting step.

Parameters

The parameters of interest in modeling the collection of particles and vapor by falling droplets are defined below.

The Stokes Number is based on the collector droplet radius and the relative velocity between the falling droplet and particle.

$$Stk = \frac{\tau \cdot V_{rel}}{D_{de}/2}$$

where

τ is the particle relaxation time defined as

$$\tau = \frac{\rho_p \cdot d_p^{\,2} \cdot C(d_p)}{18 \cdot \mu_{air}}$$

d_p is the particle equivalent spherical diameter

ρ_p is the particle material density

$C(d_p)$ is the Cunningham Slip Correction factor defined as

$$C(d_p) = 1 + \frac{2\lambda}{d_p} \cdot \left\{ 1.257 + 0.4 \cdot \exp\left(-0.55 \cdot \frac{d_p}{\lambda} \right) \right\}$$

λ is the molecular mean free path of the gas

μ_{air} is the air absolute viscosity

V_{rel} is the relative velocity between the droplet and the particle

D_{de} is the droplet equivalent spherical diameter

The Droplet Reynolds Number is defined as

$$Re = \frac{\rho_{air} \cdot U_T \cdot D_{de}}{\mu_{air}}$$

where

ρ_{air} is the density of the air

U_T is the terminal velocity of the droplet

The particle diffusivity is defined as

$$Df_p = k \cdot T \cdot \frac{C(d_p)}{3 \cdot \pi \cdot \mu_{air} \cdot d_p}$$

where

k   is Boltzmann's constant

T is temperature

The Schmidt Number is defined as

$$Sc = \frac{\mu_{air}}{\rho_{air} \cdot Df_p}$$

The Peclet Number is defined as

$$Pe = Re \cdot Sc = \frac{U_T \cdot D_{de}}{Df_p}$$

The Sherwood number is a dimensionless mass transfer coefficient and is defined as

$$Sh = \frac{k_m \cdot D_{de}}{Df_{gas\ phase}}$$

k_m is the mass transfer coefficient of the material (particles or vapor)depositing to the droplet

$Df_{gas\ phase}$ is the diffusion coefficient of the material (particles or vapor) in the gas phase

The particle terminal velocity is defined as

$$V_T = \tau \cdot g$$

where

g is the gravitational acceleration

Spray Droplet Terminal Velocity

Droplet terminal velocity is determined from a correlation for water droplets falling in air at ambient temperature and pressure cited in Clift, Grace, and Weber (1978) page 170. The terminal velocity is given as

$$U_T = \frac{\mu_{air}}{\rho_{air} \cdot D_{de}} \cdot \exp\{-3.16 + 1.01 \cdot \ln(N_D) - 0.019212 \cdot \ln(N_D)^2\}$$

where

D_{de} is the droplet equivalent spherical diameter

μ_{air} is the air absolute viscosity

ρ_{air} is the air density

N_D is the Best number defined as

$$N_D = C_D \cdot Re_T^2 = \frac{4 \cdot \rho_{air} \cdot (\rho_w - \rho_{air}) \cdot g \cdot D_{de}^3}{3 \cdot \mu_{air}}$$

C_D is the droplet drag coefficient

Re_T is the droplet Reynolds number at the terminal velocity defined as

$$Re_T = \frac{\rho_{air} \cdot U_T \cdot D_{de}}{\mu_{air}}$$

and is applicable over the range of $2.4 < N_D < 10^7$ and $0.1 < Re_T < 3550$.

This translates to a droplet size range from about 40 μm to 6 mm as seen in Figure 1. The droplet sizes from a spray nozzle should be within this range.

Spray Droplet Size Distributions

The calculations presented here will assume that the size distribution of the flux of spray droplets can be accurately described by a log-normal distribution function. The normalized distribution function is given as

$$m(D_{de}) = \frac{dM}{dD_{de}} \cdot \frac{1}{M_{total}} \cdot \frac{1}{\sqrt{2\pi} \cdot \ln(\sigma_g)} \cdot \exp\left\{ -\frac{\ln(DGM/D_{de})^2}{2 \cdot \ln(\sigma_g)^2} \right\}$$

where

     $m(D_{de})$ is the fraction droplet mass flux dM/M_{total} within the size range of D_{de} to $D_{de}+dD_{de}$

     M_{total} is the total droplet mass flux

     DGM is the geometric mass median droplet diameter

     σ_g is the geometric standard deviation

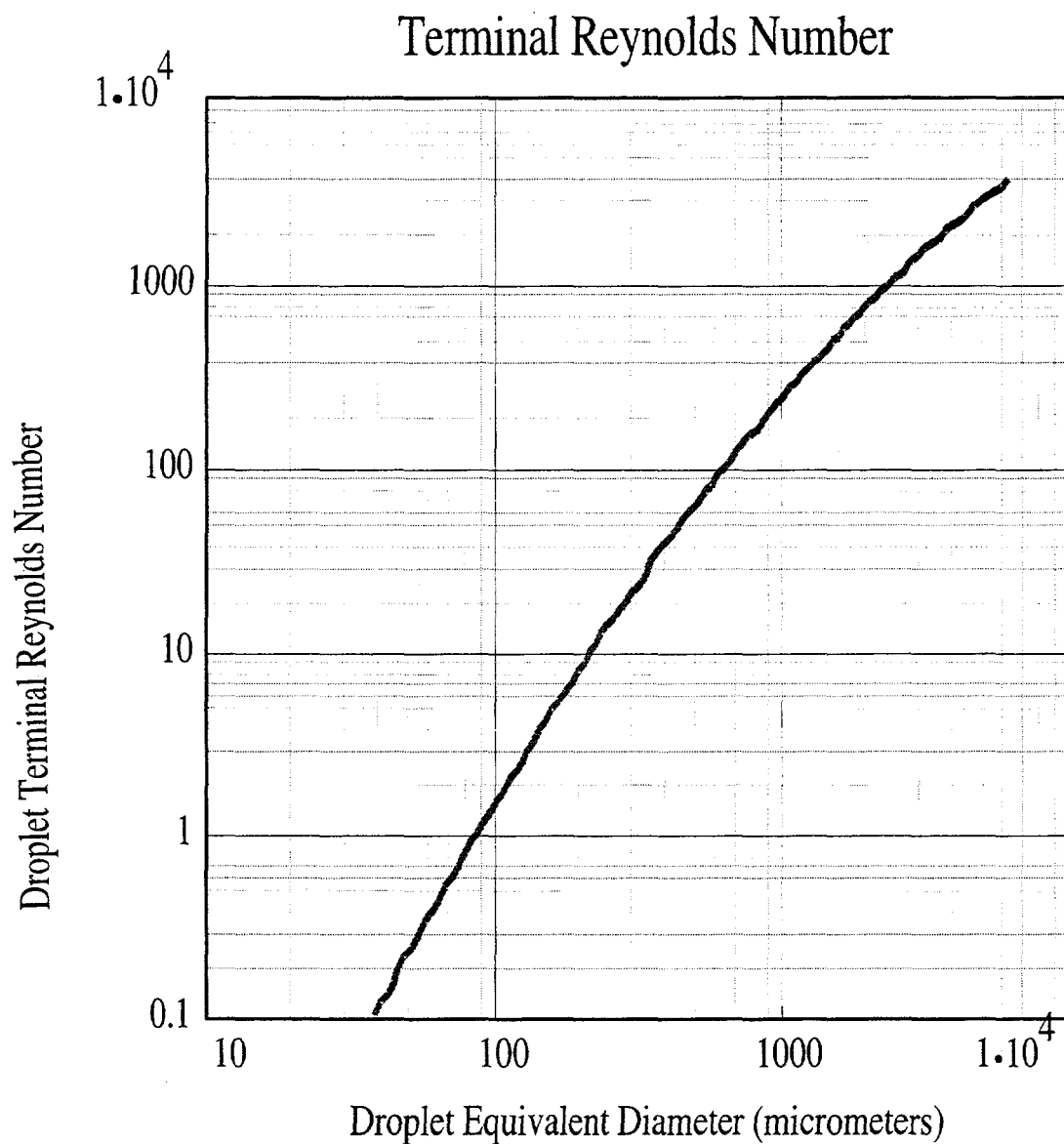Figure 1. The Reynolds number of a falling water droplet at the terminal velocity as a function of droplet equivalent spherical diameter based on the correlation from Clift, Grace, and Weber (1978).
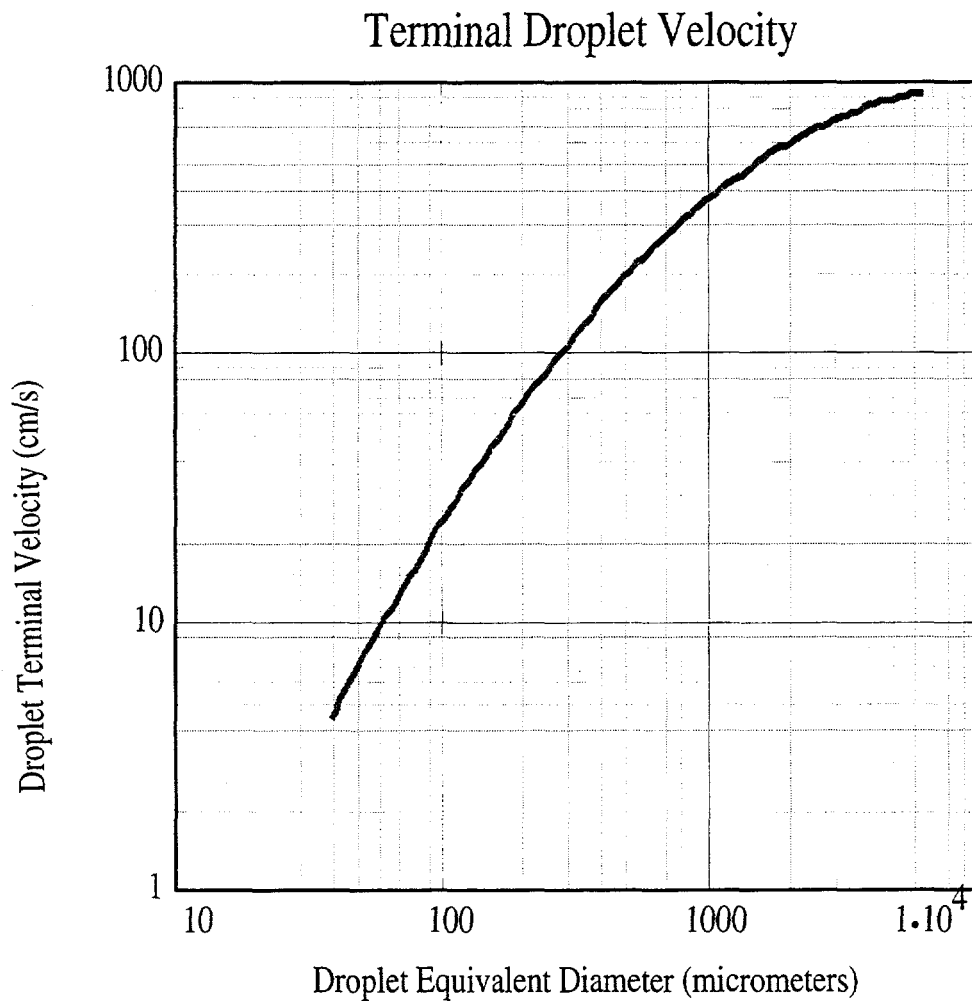
Terminal Droplet Velocity

Figure 2. The terminal velocity of a falling water droplet as a function of droplet equivalent spherical diameter based on the correlation from Clift, Grace, and Weber (1978).

The droplet number flux is then defined as

$$J(D_{de}) = \frac{M_{total} \cdot m(D_{de})}{\rho_D \cdot \frac{\pi}{6} \cdot D_{de}^3}$$

where

ρ_D is the density of the droplet material

The spread in droplet size will cause the droplets to coalesce as a result of different settling velocities. This will cause the droplet size distribution to shift to larger sizes as they fall. This effect is not included in the scoping calculation. Sprays usually do not have full coverage until some distance from the nozzle. The unsprayed volume will mix with the sprayed volume over time, but the effect of incomplete coverage will reduce the removal efficiency. The scoping calculation assumes complete coverage.

Particle Collection By a Falling Droplet

As a droplet falls, the gas flows around the droplet. Large particles in the path of the falling droplet are, because of their inertia, unable to follow the gas stream lines and will be impacted by the droplet. The correlation for impaction of particles on a falling sphere in the viscous flow regime is (Langmuir, 1948)

$$\varepsilon_{impaction\ visc} = \begin{cases} 0 & Stk \leq 1.214 \\ \left(1 + \dfrac{0.75 + \ln(2Stk)}{Stk - 1.214}\right)^{-2} & Stk > 1.214 \end{cases}$$

and in the potential flow regime is (Langmuir and Blodgett, 1946)

$$\varepsilon_{impaction\ pot} = \begin{cases} 0 & Stk \leq \dfrac{1}{12} \\ \dfrac{60}{7} \cdot \left(\dfrac{Stk}{Stk + 0.5}\right)^2 \cdot \left(Stk - \dfrac{1}{12}\right) & \dfrac{1}{12} < Stk \leq \dfrac{1}{5} \\ \left(\dfrac{Stk}{Stk + 0.5}\right)^2 & \dfrac{1}{5} < Stk \end{cases}$$

Combining these expressions in the interpolation formula of (Langmuir, 1948) gives the single droplet collection efficiency for particles by impaction over the range of

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flow regimes.

$$\varepsilon_{impaction} = \frac{\varepsilon_{impaction\ visc} + \varepsilon_{impaction\ pot} \cdot \dfrac{Re_T}{60}}{1 + \dfrac{Re_T}{60}}$$

Particles that follow the streamlines around a falling droplet can be collected by interception. This occurs when the physical size of a particle causes it to intercept the surface of the falling droplet and be collected. The correlation for interception of particles by falling spheres in the viscous flow regime is (Lee and Gieseke, 1980)

$$\varepsilon_{interception\ visc} = \frac{3}{2} \cdot \left(\frac{d_p}{D_{de}}\right)^2 \cdot \left(1 + \frac{d_p}{D_{de}}\right)^{-\frac{1}{3}}$$

and in the potential flow regime is (Ranz and Wong, 1952)

$$\varepsilon_{interception\ pot} = 3 \cdot \left(\frac{d_p}{D_{de}}\right)$$

Combining these expressions in the interpolation formula gives the single droplet collection efficiency for particles by interception over the range of flow regimes.

$$\varepsilon_{interception} = \frac{\varepsilon_{interception\ visc} + \varepsilon_{interceptiontion\ pot} \cdot \dfrac{Re_T}{60}}{1 + \dfrac{Re_T}{60}}$$

As a droplet falls, the Brownian motion of small particles will cause them to collide with the droplet and be collected. Expressions for the single droplet collection efficiency of particles by diffusion are in the viscous flow regime (Johnston and Robert, 1948),

$$\varepsilon_{diffusion\ visc} = \frac{4}{Pe} \cdot (2 + Re_T^{1/2} \cdot Sc^{3/8})$$

and in the potential flow regime (Ranz and Wong, 1952)

$$\varepsilon_{diffusion\ pot} = \frac{2.18}{\sqrt{Pe}}$$

Combining these expressions in the interpolation formula gives the single droplet collection efficiency for particles by diffusion over the range of flow regimes.

$$\varepsilon_{diffusion} = \frac{\varepsilon_{diffusion\ visc} + \varepsilon_{diffusion\ pot} \cdot \dfrac{Re_T}{60}}{1 + \dfrac{Re_T}{60}}$$

Two methods of combining the collection mechanisms are discussed above. The method chosen is

$$\varepsilon_{total} = 1 - (1 - \varepsilon_{impaction}) \cdot (1 - \varepsilon_{interception}) \cdot (1 - \varepsilon_{diffusion})$$

Particle Removal Efficiency

The time rate of change in particle concentration in an aerosol is related to the flux of droplets passing through the aerosol. For a given particle size, d_p, and a given droplet diameter, D_{de}, we can write

$$\frac{d}{dt} n_p(d_p) = -n_p(d_p) \cdot \varepsilon_{total}(d_p, D_{de}) \cdot J(D_{de}) \cdot \frac{\pi}{4} \cdot D_{de}^2$$

where

t is time

$n_p(d_p)$ is the particle number distribution dN/dd_p (#/volume/length).

$\varepsilon_{total}(d_p, D_{de})$ is the single particle collection efficiency for particle of size d_p by droplet of size D_{de}.

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$J(D_{de})$ is the droplet number flux of size D_{de} droplets through the aerosol (#/time/area/log interval)

For the time rate of change of the concentration of a particle of size d_p removed by the total flux of droplets we can write

$$\frac{d}{dt}n_p(d_p) = -n_p(d_p) \cdot \int_{D_{de}} \varepsilon_{total}(d_p, D_{de}) \cdot J(D_{de}) \cdot \frac{\pi}{4} \cdot D_{de}^{2} dD_{de}$$

Which when integrated with respect to time gives

$$\eta(d_p) = \exp\left\{-\left(\int_{D_{de}} \varepsilon_{total}(d_p, D_{de}) \cdot J(D_{de}) \cdot \frac{\pi}{4} \cdot D_{de}^{2} dD_{de}\right) \cdot t\right\}$$

where

$\eta_p(d_p)$ is the fraction of particles of size d_p remaining in the aerosol after time t

Recall that the number flux $J(D_{de})$ can be expressed in terms of the mass flux of the droplets and the normalized mass distribution of the droplets as

$$J(D_{de}) = \frac{M_{total} \cdot m(D_{de})}{\rho_D \cdot \frac{\pi}{6} \cdot D_{de}^{3}}$$

The total mass flux of droplets is defined as

$$M_{total} = \frac{\rho_D \cdot Q_D}{A_{floor}}$$

where

Q_D is the liquid volumetric flow rate

A_{floor} is the area through which the droplets flow, assumed to be equal to the floor area.

The above analysis assumes a steady-state liquid flux with steady-state aerosol re-

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moval.

With substitution we can express the fraction of particles of size d_p removed at the end of time t as

$$\eta_{removed}(d_p) = 1 - \exp\left\{-\frac{3}{2} \cdot \frac{Q_D}{A_{floor}} \cdot \lambda(d_p) \cdot t\right\}$$

where

$$\lambda(d_p) = \int_{D_{de}} \varepsilon_{total}(d_p, D_{de}) \cdot m(D_{de}) \cdot \frac{1}{D_{de}} dD_{de}$$

For the case in which air containing the particles is flowing down a tunnel in which the droplets are being sprayed, we can employ the following relationships.

$$t = \frac{L_{tunnel}}{U}$$

$$U = \frac{Q_{air}}{A_{tunnel}}$$

$$A_{floor} = L_{tunnel} \cdot W_{tunnel}$$

$$\frac{Q_D}{A_{floor}} \cdot t = \frac{Q_D}{Q_{air}} \cdot \frac{A_{tunnel}}{W_{tunnel}}$$

where

U is the average gas velocity down the tunnel

L_{tunnel} is the length of the tunnel

Q_{air} is the volumetric flow of gas through the tunnel

A_{tunnel} is the cross-sectional area of the tunnel

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A_{floor} is the area of the floor of the tunnel

W_{tunnel} is the width of the tunnel

This yields this relationship for aerosol removal from gas flow through a spray tunnel.

$$\eta_{removed}(d_p) = 1 - \exp\left\{-\frac{3}{2} \cdot \frac{Q_D}{Q_{air}} \cdot \frac{A_{tunnel}}{W_{tunnel}} \cdot \lambda(d_p)\right\}$$

It is worth noting that for a fixed amount of water delivery, removal depends on the flow rate of water and the flow rate of air; the tunnel length is not a parameter.

For the case in which air containing the particles is contained within a volume in which the droplets are being sprayed, we can define a removal fraction as

$$\eta_{removed}(d_p) = 1 - \exp\left\{-\frac{3}{2} \cdot \frac{Q_D}{A_{floor}} \cdot \lambda(d_p) \cdot t\right\}$$

For the spray in a fixed volume, the removal is a function of the water flux and time.

Vapor Collection By a Falling Droplet

Just as small particles are removed by Brownian diffusion to the surface of the collecting droplet, vapor is also removed by Brownian diffusion to the surface. Modeling of vapor removal must consider a finite vapor concentration at the collector surface, the rate at which the gas goes into solution, the internal concentration and mixing within the collecting droplet, and any chemical reaction occurring within the droplet to neutralize the material. Any of these processes could be a rate limiting step.

Gas phase transport of diffusing material to the surface of a falling droplet is expressed below. The effect of a non-zero surface partial pressure is included. The rate

at which molecules of material are added to the droplet can be expressed as

$$\frac{dn}{dt} = \frac{(P - P_{surface})}{k \cdot T} \cdot k_m \cdot \pi \cdot D_{de}^{2}$$

where

n is the number of molecules added to the droplet

t is time

P is the partial pressure of material far from the droplet

$P_{surface}$ is the vapor pressure of the material at the surface

k is Boltzmann's constant

T is temperature

k_m is the mass transfer coefficient to the droplet surface

D_{de} is the droplet equivalent spherical diameter

Implicit in the partial pressure at the surface of the droplet is the effect of the rate of dissolution, neutralization, and internal transport by convective or diffusive mixing. If the rate of dissolution is low, this will be reflected in a higher surface partial pressure of the material. If the rate of mixing is low and internal mixing is the rate-limiting step, then the surface concentration is higher than the internal concentration and the surface partial pressure will be higher than that for a mixed droplet. It will be assumed that the rate at which the material goes into solution is fast compared to gas phase transport. It is also assumed that the vapor pressure at the surface can be determined from Raoult's Law.

$$P_{surface} = \chi_{surface} \cdot P_{sat}$$

where

$\chi_{surface}$ is the mole fraction of material at the surface

P_{sat} is the saturation vapor pressure of the material

The Kelvin effect is negligible for droplets greater than a few tens of micrometers and is not included.

The uncertainty is then the mole fraction of material at the surface. The internal transport of the material from the droplet surface to the interior and subsequent mixing is important. If the droplet contains a constituent that chemically neutralizes the collected material, then the internal transport of both the constituent and the collected material's is important. Transport and mixing are accomplished by diffusion and by internal circulation of the liquid in the droplet. If internal mixing is fast compared to the gas-phase transport, then the average mole fraction can be used to calculate transport; if not, then the rate-limiting step must be identified and used for the transport calculation.

The relative importance of gas-phase to condensed-phase transport can be expressed in the dimensionless ratio

$$\frac{k_m \cdot D_{de}}{Df_{condensed-phase}} \cdot \frac{P_{sat}}{R \cdot T} \cdot \frac{MW_{condensed-phase}}{\rho_{condensed-phase}}$$

which equals

$$Sh \cdot \frac{Df_{gas-phase}}{Df_{condensed-phase}} \cdot \frac{P_{sat}}{R \cdot T} \cdot \frac{MW_{condensed-phase}}{\rho_{condensed-phase}}$$

where

P_{sat}	is the saturation vapor pressure of the gas phase material
R	is the universal gas constant
T	is the temperature
$MW_{condensed-phase}$	is the mole weight of the droplet material
$\rho_{condensed-phase}$	is the material density of the droplet material
Sh	is the Sherwood number defined as

$$Sh = \frac{k_m \cdot D_{de}}{Df_{gas-phase}}$$

$Df_{condensed-phase}$ is the diffusion coefficient of the material in the condensed-phase of the droplet

$Df_{gas-phase}$ is the diffusion coefficient of the material in the gas-phase

If this ratio is less than about 1, then internal diffusion is faster than transport to the surface. If it is greater than 1, then internal diffusion is slower than gas-phase transport to the surface and internal diffusion is not sufficient to mix the material in the droplet. Typically, for small drops on the order of hundreds of micrometers falling through air, the Sherwood number is on the order of 2 to 10. The liquid-phase

diffusion coefficient is typically three or four orders of magnitude smaller than the gas-phase diffusion coefficient. Based on the method given in Reid, Prausnitz and Sherwood (1977) on page 568, the diffusion coefficient of sarin in water at 295 K is estimated at 7.5×10^{-6} cm^2/sec (about 4 orders of magnitude smaller than the diffusion coefficient in air of 6×10^{-2} cm^2/sec). The other terms are the ratio of gas-phase mole concentration to condensed-phase mole concentration, which is on the order of 10^{-6} for the materials considered here. The ratio is then on the order of 0.04 to 0.7 for the conditions and materials considered here, indicating that internal condensed phase diffusion is sufficient to mix the material within the droplet. The gas-phase transport to the droplet is the rate-limiting step, especially for smaller droplets, so that droplet scavenging of vapor can be modeled from the gas phase transport side.

Hydrodynamic mixing within a falling liquid droplet can be established by the friction of the gas flowing around the droplet at the outer edges promoting a toroidal circulation. Clift, Grace, and Weber (1978) pages 189-190, state that for Reynolds numbers greater than about 200, internal circulation in falling droplets can effectively mix the liquid. High surface active impurities in the droplet can impede internal circulation, and internal circulation occurs at lower Reynolds numbers in pure systems. Under typical ambient conditions, a 900 micrometer diameter droplet has a Reynolds number of 200.

As a droplet falls through and collects a vapor, the dissolved vapor concentration builds up in the droplet, increasing the vapor pressure at the surface of the droplet and reducing the removal efficiency of the droplet. For this reason, removal of vapor from a gas is treated differently from removal of diffusing particles from the gas. If the surface partial pressure of the material is always negligible compared to the material's partial pressure in the gas and the build-up within the droplet is low, then removal of particles with the same diffusion coefficient as the vapor material is a reasonable estimate of vapor removal. These assumptions should not be made without justification. In this case, for droplets larger than about 200 micrometers, this is a good assumption; the mole fraction of sarin in the droplet after a fall of 18 feet will not exceed 0.1 and sarin build-up in the droplet does not greatly affect scavenging. For a 100 micrometer droplet at these conditions, the sarin mole fraction may be as high as 0.4 and solubility limits must be considered.

Spray Removal of Particulate and Gaseous Material for BART

Station Conditions

Station Volume = 2,400,000 ft^3

Tunnel Cross Section, A_{tunnel}, = 200 ft^2

Tunnel Height, H_{tunnel}, = 17 to 19 ft (average 18 ft)

Tunnel Width, W_{tunnel}, = $\frac{4}{\pi} \cdot \frac{A_{tunnel}}{H_{tunnel}}$ = 14 ft

     (assumes an elliptical cross section)

Air Flow, Q_{air}, = 100,000 ft^3/min (cfm)

Average Air Velocity Through Tunnel, U, = 500 ft/min

Water Volumetric Flow Rate Through Sprays, Q_D, 795 gallon/min (gpm)

    At these conditions this is comparable to 1.22 gpm/m^2

Temperature, T, = 295 K (71 F)

Pressure, P, = 1 atm

Gas and Water Properties

Air Viscosity, μ_{air}, = 1.82×10^{-4} poise

Air Density, ρ_{air}, = 1.196×10^{-3} gm/cm^3

Water Viscosity, μ_{water}, = 1.0×10^{-2} poise

Water Density, ρ_{water}, = 1.0 gm/cm^3

Water Surface Tension, σ_{water}, = 69 dyne/cm

Sarin Properties (from *Alternative Technologies* and *Army Field Manual FM 8-9*)

Molecular Weight of Sarin = 140.1 gm/mole

Liquid Density @ 293K, ρ_{sarin} = 1.0887 gm/cm^3

Molecular Volume @ 293 K, vm_{sarin} = 2.137×10^{-22} cm^3

Kinematic Viscosity @ 298 K, ν_{sarin} = 0.0128 cm^2/s

Absolute Viscosity @ 298 K, μ_{sarin} = 0.0139 poise

Surface Tension @ 293K, σ_{sarin} = 26.5 dynes/cm

Diffusion Coefficient (vapor in air) @ 293K, Df_{sarin} = 0.061 cm^2/s

Assume a T^2/P dependence for diffusion coefficient

$$Df_{sarin} = 0.72 \cdot \frac{T^2}{P} \cdot \frac{dyne}{K^2 \cdot s}$$

Vapor Pressure @ 273.15 K, P_{sarin} = 0.498 torr

Vapor Pressure @ 298.15 K, P_{sarin} = 2.92 torr

Vapor Pressure @ 431.15 K, P_{sarin} = 760 torr

Sarin equilibrium vapor pressure fit

$$P_{sarin} = \exp\left(22.47 - \frac{7007K}{T + 29.3K}\right) \cdot torr$$

Spray Drop Distributions for Particulate Removal

Case 1: DGM = 900 μm σ_g = 2.2

Case 2: DGM = 400 μm σ_g = 1.6

Case 3: DGM = 200 μm σ_g = 1.6

Case 4: DGM = 100 μm σ_g = 1.6

The droplet distribution for Case 1 is typical for a spray nozzle operating at a supply pressure of about 30 psig. To get smaller droplets, higher line pressures are required. The same nozzle would require about 100 psig to produce the droplet sizes in Case 2. Other nozzle designs can produce smaller droplets at lower line pressures and nozzle performance can be addressed in follow-on work.

Particle removal in the tunnel at a gas flow of 100,000 cfm and a water flow of 795 gpm is calculated with the basic model for the four spray droplet distributions. These results are presented in Figure 3. Removal of sarin particles 10 micrometers and larger in diameter is very efficient. Vapor scavenging by the smaller droplets in

the distribution may be very effective. A 10 micrometer sarin particle will evaporate in a few seconds, so that removal of dispersed sarin will be by efficient collection of larger particles and by removal of the vapor. Particle sizes that are not efficiently removed by the spray will not be present for more than a few seconds. This situation makes the removal of sarin vapor an important issue.

Particle removal in the station is calculated for a water flux of 1 gpm/m^2. The removal efficiencies at the end of 1 minute are presented in Figure 4 for the four spray droplet size distributions used in the tunnel calculation. The results are almost the same because, the tunnel has an effective water flux of 1.2 gpm/m^2 for an exposure time of 1 minute. A spray duration of longer than 1 minute would increase the removal; for example, cumulative removal of 50% after 1 minute would increase to 75% after 2 minutes, 94% after 4 minutes, 99.6% after 8 minutes, etc.

It is not immediately clear that sarin vapor will be removed with the same efficiency as particles having the same diffusion coefficient. Figure 5 shows the calculations for sarin vapor removal by a 1 gpm/m^2 flux of single sized droplets of 200, 400, and 900 micrometers in diameter. Complete mixing is assumed. In these cases, the mole fraction of sarin in the droplets was small compared to the ambient concentration. If complete mixing within the droplet can be justified, as in these cases, sarin vapor can be efficiently removed.

The results in Figure 5 assume that the reductions in concentration of airborne sarin result from continuous flow of clean water in to the sarin containing atmosphere and ignores the droplets once they hit the floor. In actuality, the finite vapor pressure of sarin collected in the droplets will introduce a level of vapor concentration which translates into a lower limit of removal effectiveness. The water can be treated with agents that will neutralize the sarin and remove this limitation.

Sarin is neutralized in water by hydrolysis. The -OH hydroxyl ion breaks down sarin. The half-life in water is about 200 to 300 hours but if the pH is above 10, the half-life drops to minutes. Other non-toxic, non-corrosive formulations that Sandia National Laboratories are developing will neutralize not only sarin but other nerve agents as well in a matter of minutes.
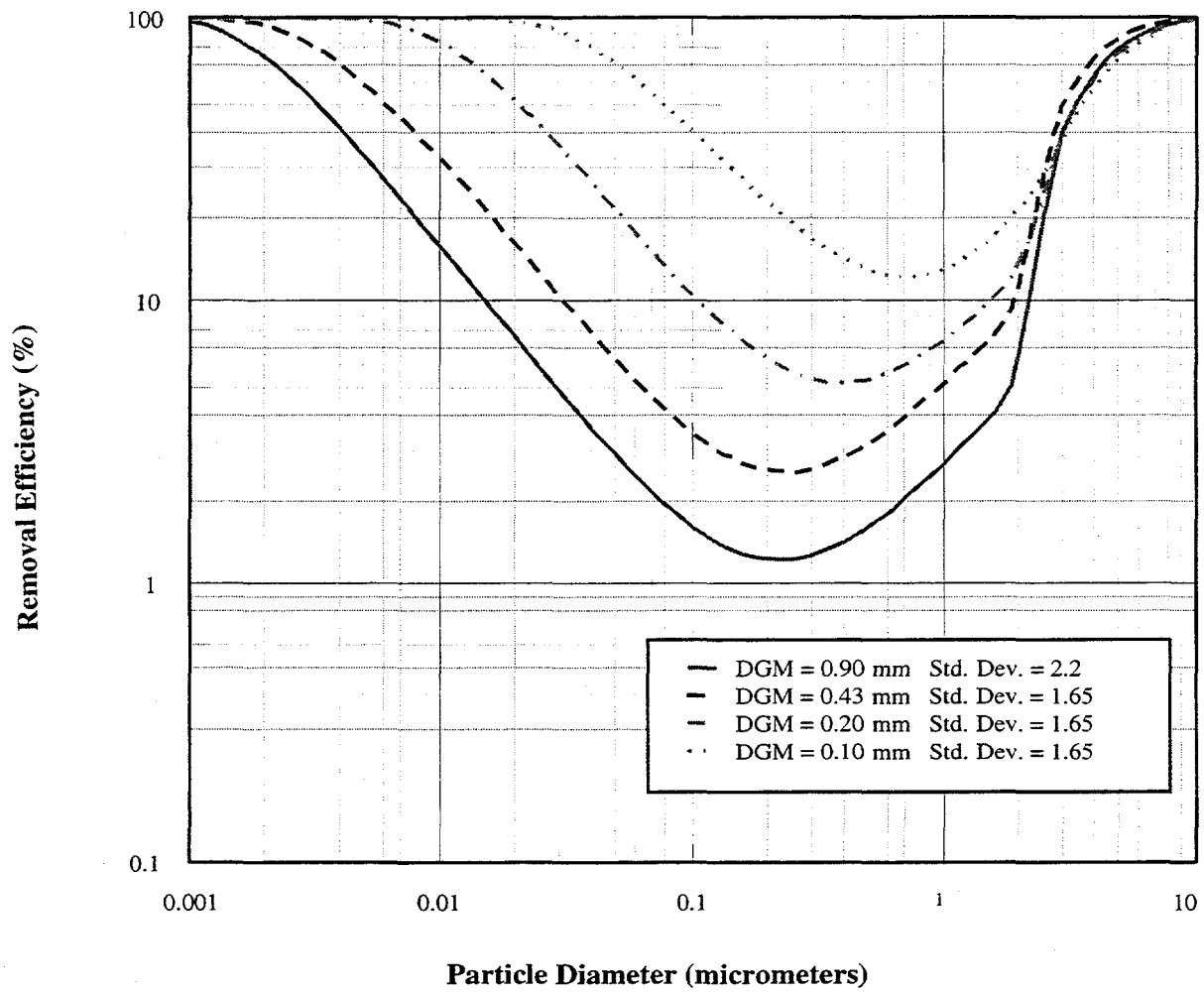
Removal Efficiency by Spray in Tunnel

Figure 3. Spray removal in the tunnel.

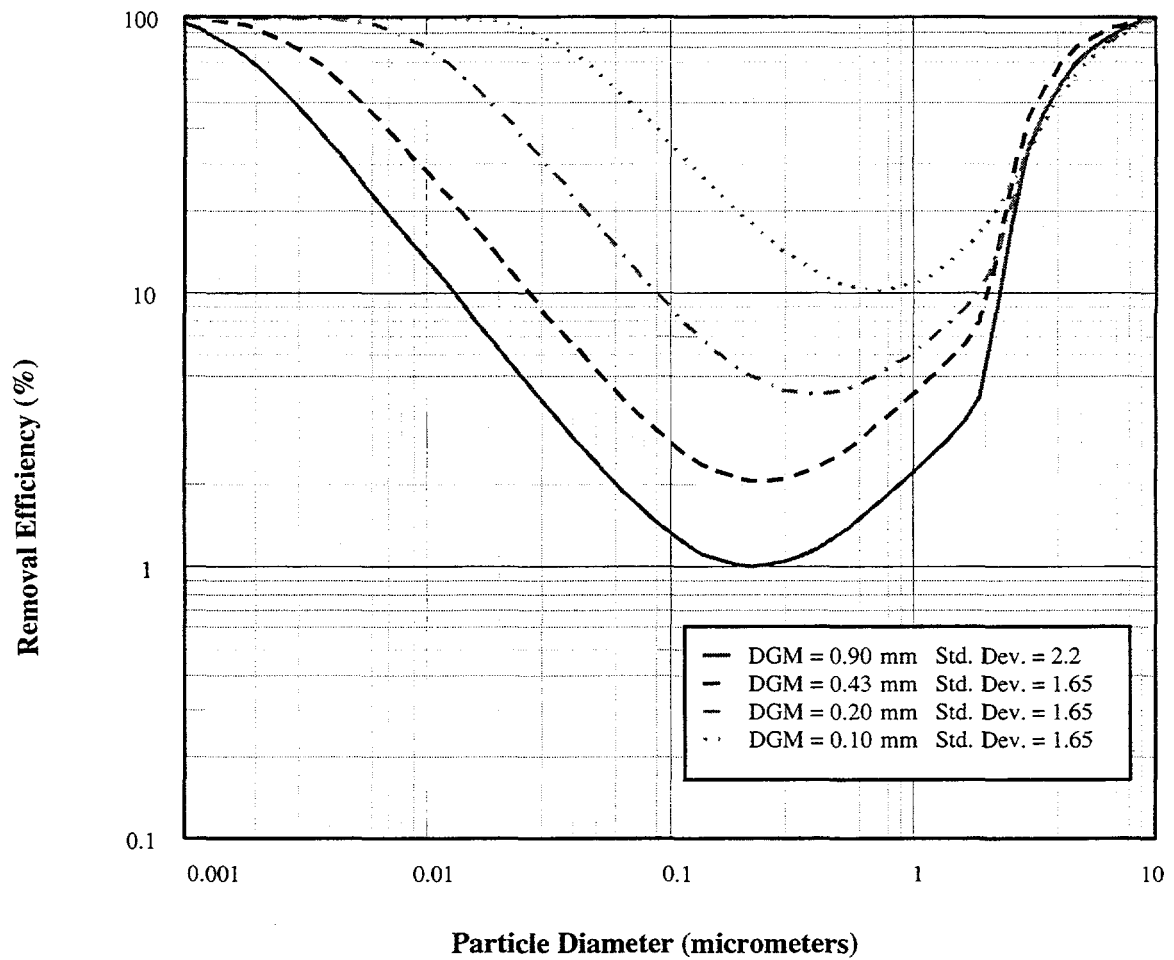**Removal Efficiency by Spray in Station**

Figure 4. Spray removal in the station after 1 minute.
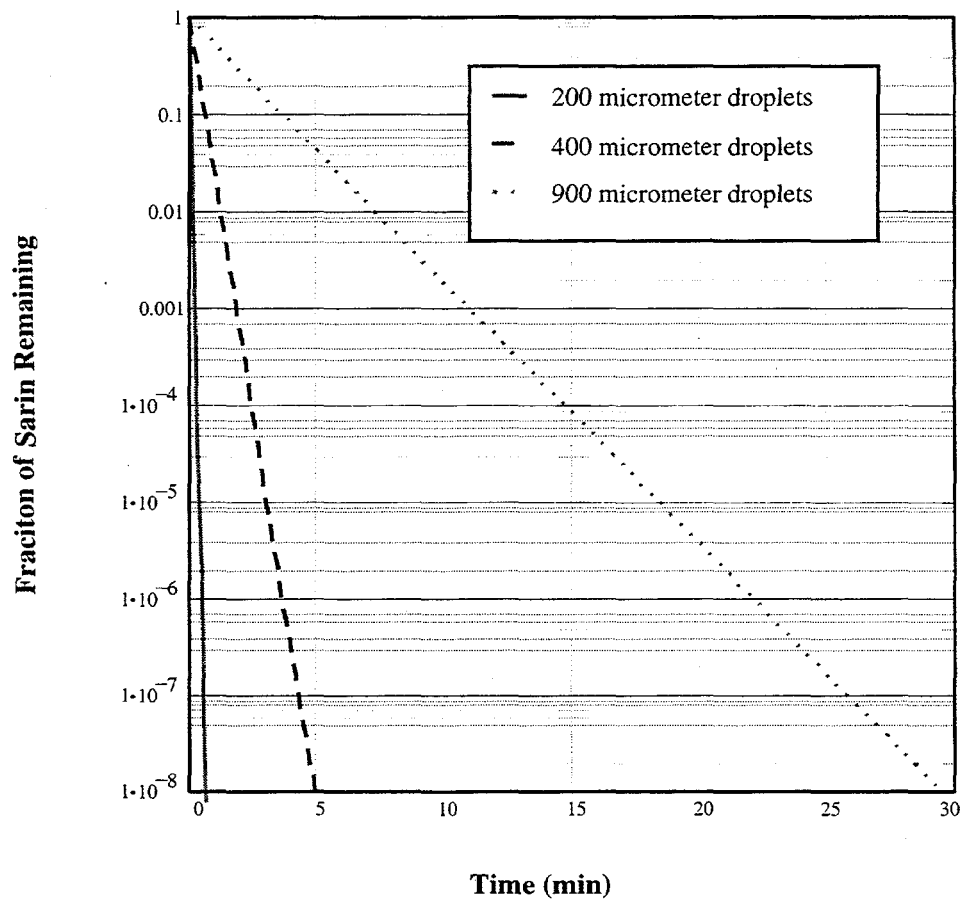
Sarin Removal by Water Droplets

Figure 5. Removal of sarin vapor by monodisperse droplet flux of 1 gpm/m^2 for three droplet sizes.

The above plot shows the decline in sarin concentration as a function of time for three water sprays composed of 200 µm, of 400 µm and of 900 µm droplets. The water flux is 1 gallon per minute per square meter over a fall height of 18 feet. The key assumptions made in these calculations are 1.) that the water in the droplet is mixed (either by internal convection or diffusion), i.e., that gas-phase transport of sarin vapor to the droplet surface is the rate limiting step, and 2.) that an effective neutralizing agent is used in the water so that the collected sarin is neutralized and the used water provides no source of sarin vapor. Based on the above discussion of vapor transport to droplets, this assumption is not unreasonable. The purpose of the example is to illustrate the potential removal capabilities of a water spray. Under these conditions, the mole fraction of sarin in the droplets was low so that build-up of sarin in the droplets had very little effect on the removal of the vapor. Smaller droplets may be more effective in removing sarin even though sarin concentration build-up in the droplet may retard collection. For a given water volume flux, there are more small droplets and even though sarin removal by individual droplets will be limited, the total removal will be increased over that of larger droplets. This is an area that should receive further investigation.

An initial concentration of 17,240 mg/m^3 corresponds to the sarin saturation vapor pressure at 295 K (71 degrees F). In this case the remaining fraction of $1x10^{-8}$ corresponds to $1.7x10^{-4}$ mg/m^3. A concentration of 10^{-4} mg/m^3 corresponds to the Permissible Hazard Level (PHL) for a worker's 8 hour exposure. The LCt_{50}, the concentration exposure time integral for sarin, that has a 50% lethality is 70 to 100 $mg\text{-}min/m^3$. Note that in this case, the 400 µm droplet flux would have reduced the sarin concentration to the PHL in about 5 minutes and the 200 µm would take about 1 minute.

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