# ExxonMobil

# Use of Water to Mitigate a Bromine Loss of Containment Event

Soheil Hussain & Scott Clark

Academic Mentor: Dr. William Clark & Dr. Ray Mentzer

Industry Mentor: Silvio Esterellas

Purdue University Department of Chemical Engineering
Professional Master's Program
August 1, 2022

**Table of Contents**

**Abstract**

Water mitigation is an important safety precaution used for toxic chemicals such as hydrofluoric acid (HF). Though bromine ($Br_2$) is a toxic chemical with industrial uses, no data is available for water mitigation of $Br_2$ releases. This report aims to assess the feasibility of such a system, building off previous results for HF releases. Here two mathematical models are presented. The first is to determine the rainout of $Br_2$ upon release, which is the amount that drops out in the liquid phase. The second determines the efficiency of $Br_2$ absorption by water, which is the percent of post-rainout $Br_2$ absorbed. Several potential laboratory experiments are also suggested to further evaluate the model. Using the model to evaluate these experiments, initial results show that mitigation efficiencies above 90% can be achieved under the right conditions. These largely depend on the water:$Br_2$ ratio (volume of water contacting $Br_2$:volume of $Br_2$ after rainout); it is noteworthy that 3-4 times the amount of water is required to achieve 90% efficiency for $Br_2$ compared to HF. Larger water flow rates, lower $Br_2$ flow rates, smaller droplet sizes, and larger distances from the release point to the water curtain all increase the ratio and thus all increase efficiency. Overall, the results suggest water mitigation of bromine is a potentially useful strategy, and warrants further investigation.

## Introduction

Water mitigation is a common process used in emergency situations involving the loss of containment of a toxic chemical such as hydrofluoric acid (HF). ExxonMobil (EM) utilizes HF in their alkylation units, and employs water spray curtains and nozzles around HF storage tanks as a precaution. The main purpose of this project is to consider the application of water mitigation strategies to another toxic chemical, Bromine ($Br_2$), which is used by EM for manufacturing rubber. $Br_2$ is stored in tanks and delivered to the plant via a small pipeline, and water curtains and sprays could potentially be useful to absorb it in the event of a loss of containment. This project aims to model such a situation to gain a better understanding of its effectiveness.

In order to tackle this project, two different models were developed that are tailored to $Br_2$, since it has different properties to HF. The first model calculates rainout, the phenomena where a portion of the liquid release remains liquid and drops to the ground, and the second models the absorption of $Br_2$ by water. The rainout model takes into account many different variables, such as $Br_2$'s physical, chemical and thermodynamic properties, as well as interactions with air, to calculate the amount of $Br_2$ that remains in the liquid phase after release. The second model utilizes a set of equations in order to calculate the efficiency of $Br_2$ absorption into a water droplet. The equations follow a liquid drop model, which accounts for the absorption of $Br_2$ into discrete droplets rather than a jet spray. Due to the lack of data on $Br_2$, data from previous experiments using HF were utilized in order to validate the developed efficiency model.

The main results to consider from this project are the efficiency at which $Br_2$ is absorbed as well as the ratio of amount of water used to the amount of $Br_2$ released. Several experiments have also been designed for EM to potentially carry out on a lab scale in order to validate and further refine the model. These experiments will involve changing the release flow rate, distance from the orifice, water flow rate and droplet size.

**Literature Review**

One key parameter to consider for chemical releases before modeling water absorption is the rainout, the amount of the chemical that is released in liquid form and does not become airborne, since only the airborne part of the release requires mitigation. A model for predicting rainout for HF releases was developed by Muralidhar in 1995 [1] that uses mass, energy, and momentum differential equations to determine the effects of factors such as droplet size, amount of additive, temperature, and wind speed on rainout. This model was used by EM to create an Excel spreadsheet capable of predicting rainout under a variety of input parameters [2]. To determine rainout for $Br_2$ releases, this spreadsheet was used as a base, with relevant parameters to be discussed below changed from an HF/water/additive system to a release of pure $Br_2$.

To develop a model to calculate the absorption efficiency of $Br_2$ by water after rainout, several papers were referenced prior to building the set of equations. The first paper, written by Fthenakis, discusses the initial model developed in the 1990's for the experiments conducted in order to calculate HF absorption efficiencies. The second paper that was referenced was a memorandum from Krambeck, which outlined a set of equations that allowed for an improved water mitigation method.

In 1993, Fthenakis presented a model named HGSPRAY, which accounts for the physical and chemical phenomena that takes places when a heavy gas interacts with air and water sprays. [3] This model simulates mass, momentum, and energy interactions between water sprays and the heavy gas in air, where it predicts the flow fields of velocity, temperature, concentration of heavy gas and water vapor in two dimensional geometries. [3] HGSPRAY is split up into two sets of equations, the first being the gas phase, and the second the drop phase. The gas phase utilizes differential equations of mass, momentum, species and energy, where they are all solved iteratively to obtain a solution. The drop phase utilizes momentum, energy and mass transfer equations to solve for the heavy gas concentration, droplet trajectories and velocities. [3] Although these set of equations have been validated against various experiments and field tests, new and improved models have been developed since which are simpler and provide better results when looking at the absorption of a heavy gas by water sprays.

In 2000, a memorandum from Krambeck discussed an improved and simplified model that could be used to calculate the efficiency of water at mitigating HF loss of containment events. The equations that are used in this model are outlined in the model section of this report further down.

The paper starts off by calculating mass transfer coefficients. Two different equations with two different assumptions are used. The first equation, using the well-mixed assumption, assumes the air is stationary and the liquid drops are well-mixed, and uses the Schmidt number and the Reynolds number to calculate the mass transfer coefficient. The remaining constants and numbers are derived from Davies 1972, p321. [4] The second equation, using the slowly circulating drops assumption, assumes the drops are not well mixed, and that the diffusion time of the gas is significant compared to the contact time. It also accounts for the decay of the initial turbulence within the drops. [1]

Calculating the effect of wind used the approximation that the total density is equal to the air density, which allowed for a set of complicated equations to be derived. These equations can be approximated with a far simpler equation, which is outlined further down in the report. [3]

The memo then outlines the equation for efficiency of gas absorption by water, which takes all the different variables and physical properties and combines them into one given constant C. Another variable, k, which is the jet entrainment constant, is obtained via Ricou and Spalding, 1961 [5].

The equations were then used to compare different sets of data. A series of 3D model runs at set conditions were simulated and the results were compared to the model derived. Most of the data points seemed to almost exactly match the 3D model, a promising result.[1]

This paper was selected as a foundation to build on when developing a model to calculate the efficiency of $Br_2$ absorption by water sprays due to its simple approach as well as its good match of pre-existing data. The model section further down in the report goes into greater detail about the equations used as well as the values of several different constants and variables.

In late 1987 an industry program known as Industry Cooperative HF Mitigation/Assessment Program (commonly referred to as ICHMAP) took place in order to study and test techniques for mitigating accidental HF releases. [6] This program was sponsored and funded by 20 different companies from the chemical and petroleum industries which include BP, Dow, Exxon, and Mobil, to name a few. [6] The report constitutes several different studies which compromise a vapor barrier component, an ambient assessment component, and a water spray component.

The vapor barrier component involved literature review as well as simulations in a wind tunnel and computer simulations. Some of the conclusions drawn from this program include the fact that three dimensional vapor barriers reduce near and far-field concentrations of the released gas, as well as the fact that plant obstacles (such as pipes, towers, etc.) reduce near field concentrations by factors ranging from 3 to 25. [6]

The ambient assessment component developed and validated several computer models for accidental HF releases. These models could predict rates of release, jet flow and air entrainment from pressurized releases, while taking into account thermodynamic effects of HF/H2O/air mixtures and meteorological conditions. [6]

The water spray component was conducted on a larger scale with field equipment. 87 experiments were conducted, where 20 different variables were changed. [6] The results were then plotted on a graph, where the absorption efficiency was compared to water to HF ratios. Some of the factors that increased efficiency included smaller water droplets, upflow, a spray nozzle spacing of 2 to 3 ft, and a decreased spray distance of 16 ft from the release point, compared to 32 ft. It was also determined that additives to the spray water, air velocity, humidity and higher acid pressure had little or inconclusive effect on efficiency of absorption. [6] Various different plots were generated for the different parameters, and they compared to the base case results that are depicted in figure 1 below.

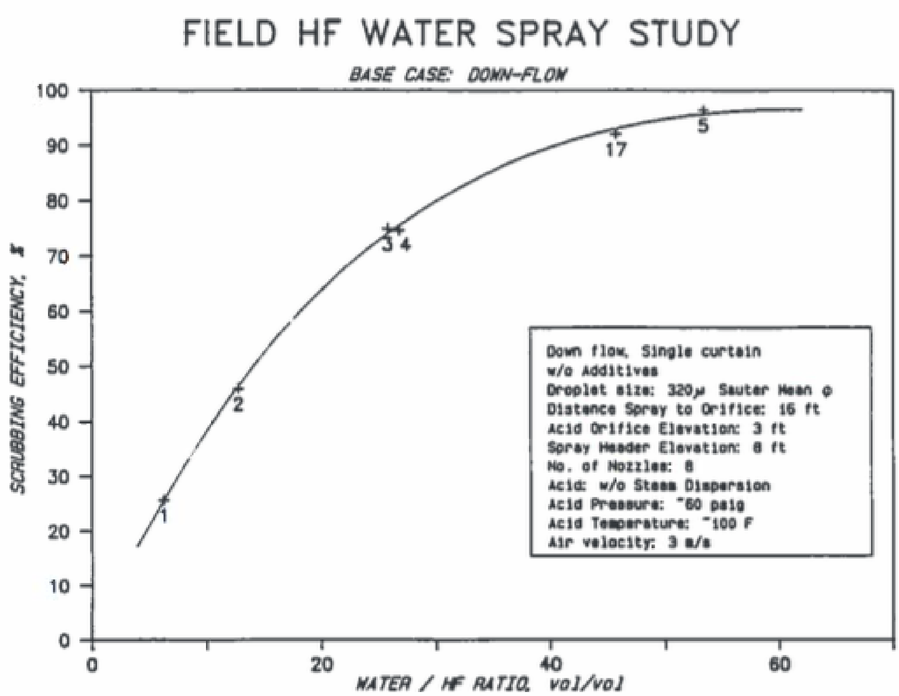


*Figure 1: Base case for water spray study with conditions outlined in the box above.[6]*

As seen in the figure above, water/HF ratios ranged between 6 and 60, and absorption efficiencies ranged between 15 and 95%. This data was very helpful when trying to validate the absorption efficiency model that is outlined further down in this report, and when determining which parameters could be changed experimentally to obtain useful information.

Another Mobil report outlining HF release tests was used to design the equipment and experimental conditions to test $Br_2$ absorption by water sprays, as it did the same for HF. The equipment used in the Mobil report involved a flow chamber, 41” long, 6” internal width, and 11.5” internal breadth. [7] A catch pan was attached to collect rainout, and a scrubber constructed of PVC was attached to the flow chamber to catch any material exiting the chamber. [7] The scrubber fan allowed for a supply of air into the chamber and generated wind speeds of

0.6 - 0.9 m/s. [7] The orifice holder used a ¼" Swagelok fitting, and Lexan was used for the side and roof of the enclosure. [7]

The experiments involved releasing an acid and additive mixture through the orifice at a rate of 6-8 g/sec, where it formed a jet. [7] Once the run was completed, the material in the catch pan was weighed to determine rainout, and the final water volume was measured in the scrubber to determine airborne HF reduction, which is a function of HF capture as well as the dilution of the amount of HF that is released by the additive. The amount of HF in both places was analyzed through an auto-titrator. [7]

Some of the parameters that were varied in the experiments include weight % of HF, additive, and water, temperature of release (90-115 F), and pressure of release. This paper was a great foundation for the experimental setup and testing procedure that will be used for $Br_2$. This is outlined later on in this report.

**The Model**

Rainout Model:

Before determining the efficiency of water at mitigating airborne $Br_2$ from a release, the amount of rainout from the release must be determined since this value will determine how much airborne $Br_2$ there is. To this effect, a model for predicting rainout based on various parameters has been largely developed, with a few caveats that will need to be addressed at a later date. This model consists of an Excel spreadsheet, adapted from a spreadsheet used by EM to predict rainout for an HF/water/additive system [2]. The user inputs various parameters that may affect rainout, including orifice size, release height, temperature, and wind speed; a screenshot of this input window is included in the appendix. These values are then used as input for running scripts that will determine rainout. Many of these scripts calculate physical properties for a release; such scripts have been updated to reflect a release of a $Br_2$ system rather than an HF system. Variable names that included 'HF' were left as-is to avoid unnecessary confusion of the code, though all such variables now refer to bromine. Scripts that did not use or calculate values specific to HF were left unchanged to preserve the accuracy of the rainout calculations; as a result releases containing water and additive can still be examined. However, water and additive are not expected to be components of a $Br_2$ release; it is recommended to set their weight percentages as low as possible for the best rainout estimate. Though the constraints of the current project did not allow for an overhaul of the spreadsheet to remove these components and simplify the calculations, doing so would ultimately provide the best estimate for rainout in a bromine release.

Changes made from the original HF rainout spreadsheet model include molecular weight updates from HF's value of 20.01 g/mol to $Br_2$'s value of 159.81 g/mol [8] in the scripts CONASS, FLOW, HPFLSH, LIQPHY, MARS, RAINOUT, SCHOTTE, TPFLS2, TPHASE, and TPINIT. Other values changed were diffusivity in air, changed to 0.00001064 m^2/s for $Br_2$ in DROPINIT and SPHASE [9], and heat of vaporization, changed to 7420 cal/mol for $Br_2$ in HLIQ, HTOTIN, and HTOTT [9].

Calculations of physical properties of the release were conducted in the scripts CPHFLIQ, HFVOL, SIGHF, VISHF, and VPHF using proprietary equations provided by EM. These equations and/or their coefficients were used to replace the equations and coefficients for HF property calculations.

In CPHFLIQ, liquid heat capacity was calculated using the equation:

$$Y = A + BT + CT^2 + DT^3 + ET^4 \qquad \text{Equation 1}$$

where the coefficients were (in kcal/kmol*K) A = 42.8776, B = -0.15944, C = 0.00025576, and D = E = 0 and T was temperature in Kelvin.

In HFVOL, molar volume was calculated as 1/liquid density, with the equation below:

$$Y = A/(B^{1+(1-T/C)^D}) \qquad \text{Equation 2}$$

where the coefficients were (in kmol/m^3) A = 2.1872, B = 0.29527, C = 584.15, and D = 0.3295 and T was temperature in Kelvin.

In SIGHF, surface tension was calculated using the equation:

$$Y = A(1 - T_r)^{B+CT_r+D(T_r)^2+E(T_r)^3} \qquad \text{Equation 3}$$

where the coefficients were (in N/m) A = 0.09832, B = 1.2259, and C=D=E=0 and $T_r$ was the ratio of temperature in Kelvin to temperature in Celsius.

In VISHF, liquid viscosity was calculated using the equation:

$$Y = exp(A + B/T + Cln(T) + DT^E) \qquad \text{Equation 4}$$

where the coefficients were (in Pa*s) A = 16.775, B = -314, C = -3.9763, and D=E=0, and T was temperature in Kelvin.

In VPHF, vapor pressure was calculated using the equation:

$$Y = exp(A + B/T + Cln(T) + DT^E) \qquad \text{Equation 5}$$

where the coefficients were (in Pa) A = 108.26, B = -6592, C = -14.16, D = 0.016043, and E = 1 and T was temperature in Kelvin.

Thermal conductivity, required for the script SPHASE, was calculated using the equation

$$Y = A + BT + CT^2 + DT^3 + ET^4 \qquad \text{Equation 6}$$

where the coefficients were (in W/(m*K) A = -0.2185, B = 0.0042143, C = -0.000017753, D = 0.000000031041, and E = -0.000000000020108, and T was set to 298 K to obtain a single value as in the original spreadsheet. After unit conversion, this value was set to 0.00006688 Kcal/(m*sec*K).

Finally, the scripts HTOTIN, HTOTT, HVAP, SPHASE, TPHASE, and TPINIT all used the mean specific heat of air, nitrogen, and ideal gaseous HF (6.96 kcal/kmol*K) originally [7]. This value was recalculated for air, nitrogen, and bromine using an even weighting and values of 6.992, 6.965, and 9.549 kcal/kmol*K, respectively [10], to obtain a specific heat of 7.835 kcal/kmol*K for use in the listed scripts.

The final difference in properties for HF and $Br_2$ was in VLE data and NRTL parameters. The scripts RNRTLP and RNRTLH use the NRTL liquid activity coefficient model described in Murhalidar Appendix A [11] to calculate vapor pressure and molar excess enthalpy, respectively, for an HF/water/additive solution. In the new model, the NRTL coefficients (labeled a, b, and alpha) were changed to reflect the bromine system, to b = 1756.70 for $Br_2$/Water and b = -1972.37 for Water/$Br_2$ as well as alpha = 0.0509 for $Br_2$/Water and alpha = 0 for Water/$Br_2$ (values provided by EM). The other coefficients do not change between the systems. However, it is worth noting that this system is overly complicated since a bromine release would not contain any additive or water. The VLE calculations performed in these scripts as well as SCHOTTE will need to be simplified for the best estimate of $Br_2$ rainout. Though the constraints of the current project did not allow for this, the model presented here can still be used to get a general feel for probable rainout amounts during a loss of containment event.

<u>Absorption Efficiency model:</u>

Efficiency was defined as the percent of airborne $Br_2$ (after rainout) absorbed by water. In order to estimate the efficiency for $Br_2$ mitigation, a model was developed based on Krambeck, 2000 [1]. This model was validated against ICHMAP HF data, and it fits the results fairly well.

To start off, a general equation from Krambeck, 2000 was selected in order to calculate efficiency [1]. This assumes that the partial pressure of $Br_2$ in water is negligible.

$$\eta = 1 - exp(\frac{-6k_m w' \rho_a A}{m \rho_w u_w d_w}) \qquad \text{Equation 7}$$

This equation will be rearranged after different variables have been calculated and plugged in.

In order to calculate many of the equations defined below, several different constants were needed. These were pulled from literature [1, 8, 9] as well as EM's database, and listed out in the table below.

*Table 1: Constants used in different equations in the model.*

| Variable | Definition | Value | Unit |
|---|---|---|---|
| $C_0$ | Orifice CD | 0.62 | - |
| $D_a$ | Diffusivity of $Br_2$ in air | $10.64*10^{-6}$ | $m^2/s$ |
| $D_w$ | Diffusivity of $Br_2$ in water | $1.3*10^{-9}$ | $m^2/s$ |
| H | Henry's Law constant for $Br_2$ in water | 133.749 | $(Pa*m^3)/mol$ |
| $v_a$ | Kinematic viscosity of air | $1.5*10^{-5}$ | $m^2/s$ |
| $v_w$ | Kinematic viscosity of water | $1.0038*10^{-6}$ | $m^2/s$ |
| $\rho_a$ | Density of air | 1.225 | $kg/m^3$ |
| $\rho_w$ | Density of water | 1000 | $kg/m^3$ |
| $\rho_0$ | Density of Br | 3102.3 | $kg/m^3$ |
| φ | Cloud spread angle | 100 | degrees |
| $g_c$ | Gravitational Constant | 1 | $(kg*m/s^2)/N$ |

Calculating release velocities and flow rates:

In order to calculate the velocity of the $Br_2$ release the following equation was used:

$$u_0 = C_o * \sqrt{\frac{2*g_c*P_0}{\rho 0}}$$ Equation 8

The $C_0$ value of 0.62 was selected as it was assumed that the fluid had a high Reynolds number and exited a sharp-edged orifice. This value was also used by EM's prior spreadsheets.

$$m_0 = \rho_0 * u_o * A$$ Equation 9

Equation 9 was then used to calculate the mass flow rate of the $Br_2$ out of the orifice, where A is the area of the orifice calculated using the equation below:

$$A = \frac{\pi}{4} * d_0^2$$ Equation 10

In order to determine the release cloud spread distance, equation 11 below was used:

$$\delta = x * 2 * tan(\frac{\varphi}{180} * \frac{\pi}{2})$$ Equation 11

The value obtained from equation 11 was then used to determine the amount of water that would be contacting the $Br_2$ cloud through equation 12:

$$w' = w * \delta$$ Equation 12

Equation 13 below then calculates the velocity of the water spray that is used to absorb the Br.

$$u_w = (\frac{2*P_w}{\rho_w})^{0.5}$$ Equation 13

The equation above uses the pressure of the water out of the nozzle, which can be as low as 50 psi, as well as the density of water in order to obtain the water velocity out of the nozzle.

Mass transfer coefficients:

There are two possible ways of calculating the mass transfer coefficient - the well-mixed drops assumption and the slowly circulating drops assumption. Both cases are explained below. Krambeck recommends the use of the slowly circulating drop assumption due to the well mixed assumption overestimating absorption efficiencies [1]. The model developed for $Br_2$ absorption efficiencies also uses the slowly circulating drop assumption; however, it was noted that in some scenarios the well mixed assumption can be used. This is discussed further down in this report in the validation section.

Well Mixed Drops:

The equation below assumes that all the mass transfer resistance is in the gas phase. It utilizes the Reynold's and Schmidt numbers to obtain the final value. The constants, 20, 0.37, and 0.5 in the equation are obtained from Davies, 1972 [4]. The equation also assumes that the air is stationary, which reduces the mass transfer coefficient by a certain factor, which in Krambeck, 2000 is taken account for when the data is fitted [1].

$$k_b = 20 * (\frac{v_w}{v_a})^{0.37} * (\frac{D_a}{v_w})^{0.5} * u_w \qquad \text{Equation 14}$$

Slowly circulating drops:

$$k_m = C_1 * H * (\frac{D_w u_w}{d_j})^{0.5} \qquad \text{Equation 15}$$

The equation above assumes that the drops are not well-mixed, and that the diffusion time is far greater than the contact time. [1] The constant $C_1$ was approximated by using known numbers from HF data and back-calculating in order to estimate a value. It was noticed that since the Henry's Law constant for $Br_2$ was roughly 10 times larger under the same conditions, the value of $C_1$ was made smaller by a factor of 10 and set to $C_1$=124030.7828. This is a rough estimate of what the value is, and further improvements to this constant should be made in the future in order to determine a more accurate value. $d_j$ is the jet diameter, and it is described by equation 19 below.

<u>Rainout:</u>

In order to calculate rainout, a value would need to be obtained from the rainout model described further up in this report. This value is labeled as the greek letter χ, and plugged into equation 16 to obtain the mass flow rate of $Br_2$ that remains as a mist in the air after the release.

$$m'_0 = m_0 * (1 - \chi) \qquad \text{Equation 16}$$

<u>Air entrainment by released jet:</u>

The following equations were obtained from Krambeck, 2000, and will then be used in the efficiency equations [1]. The two variables calculated look at air and $Br_2$ properties, as well as the orifice diameter.

$$q = \left(\frac{\rho_a}{\rho_0}\right)^{1/2} \frac{kx}{d_0} \qquad \text{Equation 17}$$

$$\beta = \frac{q}{1 - \frac{\rho_a}{\rho_0} + \left(\left(1 - \frac{\rho_a}{\rho_0}\right)^2 + 4q^2\right)^{1/2}} \qquad \text{Equation 18}$$

Equation 19 below depicts the method for calculating the jet diameter. The jet entrainment constant k is set to 0.32 [5]. Although this was the same value used for HF, it did not need to be changed since both $Br_2$ and HF are heavy gasses.

$$d_j = kx \qquad \text{Equation 19}$$

Before obtaining the final efficiency equation, many of the variables can be collected and bunched up into a constant C. This was obtained by back-calculating from the efficiency equation in the Krambeck model for HF. The Krambeck report sets this value to 1.478; however, after many runs, it was determined to set this as a variable. This is due to the fact that this allows for a more accurate estimation of absorption efficiencies, especially when the mass transfer coefficient can vary by a large degree. The equation for C differs depending on the assumption. For the well-mixed assumption, $k_b$ is used and a square root is neglected:

$$C = \frac{3*\boldsymbol{\pi}*k_b*\rho_a*d_0*q*(u_0+(u_a*q))}{2*\rho_w*u_w*u_0*d_w*(\frac{x}{d_w})} \qquad \text{Equation 20}$$

For the slow circulating assumption, $k_m$ is used and a square root is included on the $(x/d_w)$ term:

$$C = \frac{3*\boldsymbol{\pi}*k_m*\rho_a*d_0*q*(u_0+(u_a*q))}{2*\rho_w*u_w*u_0*d_w*(\frac{x}{d_w})^{1/2}} \qquad \text{Equation 21}$$

<u>Efficiency Formula:</u>

After combining all the equations above and rearranging, the following two efficiency equations are obtained. The first one neglects a square root, and this is for when the well mixed drop assumption is used:

$$\eta = 1 - exp(- C\frac{w'd_o}{m_o}(\frac{x}{d_w}) \frac{\beta}{(1+q\frac{u_a}{u_o})}) \qquad \text{Equation 22}$$

The equation below accounts for the slow circulating drop assumption, and the only difference is that the $(x/d_w)$ term is to the power of a half.

$$\eta = 1 - exp(- C\frac{w'd_o}{m_o}(\frac{x}{d_w})^{1/2} \frac{\beta}{(1+q\frac{u_a}{u_o})}) \qquad \text{Equation 23}$$

<u>Water:Br Ratio:</u>

The ratio of total water coming into contact with the $Br_2$ cloud to total airborne $Br_2$ (after rainout) was calculated on a volumetric basis for comparison with efficiency.

$$\theta = \frac{w'\rho_o}{m'_o\rho_w} \qquad \text{Equation 24}$$

The volumetric basis is achieved by dividing the flow rate for each term by its density.

Validation:

The extensive data collected during the ICHMAP tests, and the understanding derived from them, make HF the best chemical candidate for validation of the current model. In order to do this, parameters corresponding to the baseline ICHMAP tests (Figure 1) [6] were entered into the new model (using HF's chemical properties as well). The amount of rainout was calculated by entering the relevant values to the original HF-based rainout spreadsheet. The Isolated Drop mode of release was used, with the following parameters:

- Release height 3 feet
- Release pressure 60 psig
- Release temperature 100 deg F
- Orifice diameter 0.00635 m (0.25 in)
- Distance from orifice 16 feet
- Ambient pressure 14.7 psia (1 atm)
- Ambient temperature 25 deg C
- Relative humidity 40%
- Wind speed 3 m/s
- Weight percentages 90 HF, 0.1 additive, 0.9 water, 5 ASO, 4 dissolved hydrocarbons

Under these conditions, rainout was calculated to be 1.5%.

After this, the new model was used to evaluate the effect of changing water:HF ratio on efficiency of mitigation, which was achieved by varying water mass flow rates. Parameters used were the same as for the above rainout calculation, along with the following constants [12, 13]:

- HF release density of 986.7 kg/m^3
- HF diffusivity in water 1.68*10^-9 m^2/s

- HF diffusivity in air 7.53*10^-5 m^2/s
- Henry's Law Constant for HF 10.538 (m^3*Pa)/mol
- Water droplet diameter 320 um

Air and water density, cloud spread angle, $g_c$ and $C_0$ were as in Table 1. $C_1$ was 1240307.828, a factor of 10 greater than for Br as explained earlier. Rainout was 1.5%, calculated as above. Water flow rate was varied to obtain efficiency results for several different water:HF ratios. The values used for Figure 2 were 1.8, 3.7, 7.5, 9, and 10 kg/(s*m).

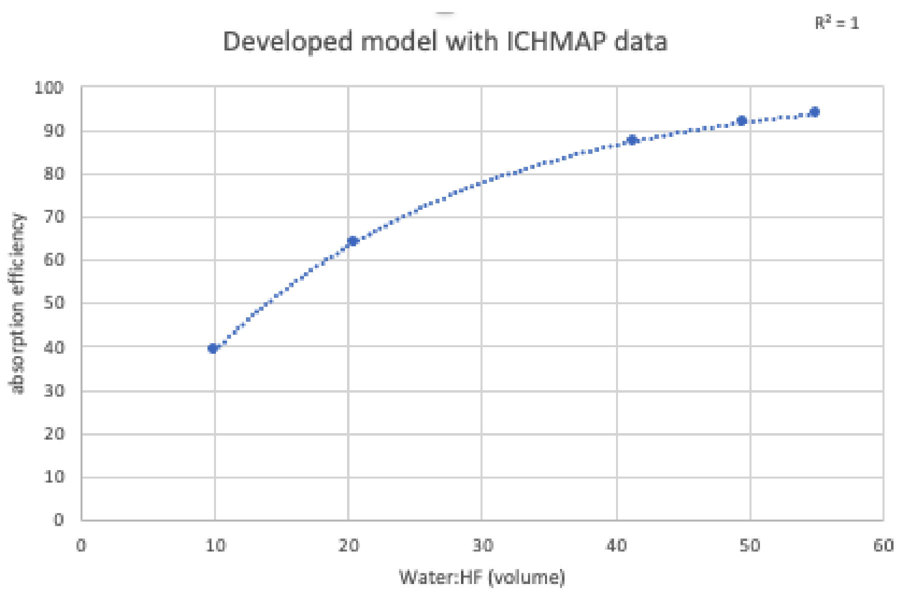


*Figure 2: Water:HF ratio vs absorption efficiency for validation of the new model*

It can be seen from comparison between Figure 1 and Figure 2 that the absorption efficiencies for given water:HF ratios are very similar, starting around 40% for a ratio of 10 and leveling off between 90 and 100% beginning around a ratio of 50. The close match between the graphs obtained via the model and the experimental data demonstrate the model's use as a predictive tool.

Though the Krambeck report recommends the use of the slowly circulating assumption ($k_m$ and the equations based on it), it was found that in this model both assumptions could be useful in different situations. In particular, the ratio of $k_b$:$k_m$ can indicate which assumption should be used. As long as the ratio is around 1, the assumption used does not make much of a difference to the final results, with a ratio of exactly 1 achieving exactly the same efficiency. In cases where the ratio was much less than 1 (<~0.5), the slowly circulating assumption resulted in a higher estimate of efficiency. The opposite was true when the ratio was much greater than 1 (>~0.5), with the well-mixed assumption resulting in the higher estimate. Since it is safer when designing systems such as this to underestimate the efficiency that will be achieved, it is recommended to evaluate this ratio before deciding which assumption will be used for a given set of release conditions. Note the only equations that change are for C and efficiency; both have the $x/d_w$ term raised to an additional 0.5 power in the slow circulating case but not well-mixed, and the C equation includes a $k_b$ or $k_m$ term. These are the only changes that need to be made to switch between assumptions.

Water solubility values and reactivity in water have the potential to make a difference to the mitigation efficiency. Bromine is capable of undergoing a reaction in water to form hydrobromic and hypobromous acid in the following disproportionation reaction:

$Br_2 + H_2O \rightarrow HBr + HOBr$

Bromine is soluble in 25 C water at 0.2141 mol/L, with the formation of 0.00115 mol/L of HOBr [8]. Since each chemical in the equation reacts at a 1:1 ratio, this means that 0.00115 mol of $Br_2$ reacts to form HOBr for every 0.2141 mol that dissolves. Ultimately this is a very small proportion of the total $Br_2$ (0.5%), which was deemed negligible for the purposes of this project.

**Experimental Design**

Although common practice is to run experiments and use the results to develop a model, due to the nature of this project, an initial model was developed which experiments can be based off. The experiments can then be used to further refine and improve the developed model in order to accurately predict the efficiency of water mitigation for a $Br_2$ loss of containment event. The following section outlines equipment design and several different experiments, as well as $Br_2$ safety for EM to use in the future.

In order to model small-scale experiments with the developed efficiency model, several small modifications had to be made. The equations used to calculate $Br_2$ release velocities and flow rates were removed, since this would be a controlled parameter and the flow rate would be set to a specified value in the experiments. The same is true for the water spray flow rates. All other equations and parameters described above were kept the same.

Equipment:

The basic equipment to be used for the set of experiments involving $Br_2$ widely resembles the Mobil report that discusses the small scale HF experiments. The $Br_2$ is released into a flow chamber 41" long, 6" in internal width, and 11.5" in internal breadth. [7] These dimensions are identical to the flow chamber used in the Mobil report, and this allows for the same parts to be used without the need to fabricate any new flow chambers. Catch pans are set underneath the flow chamber to collect the $Br_2$ rainout. A scrubber is attached to the end of the flow chamber, where the packing section is 5 ft long, and has a diameter of 1.5 ft. [7] These were the same dimensions used in the Mobil report; however, it is recommended that further investigations are conducted to ensure that the sizing and packing type of the scrubber is adequate for $Br_2$. A fan is also attached to the scrubber outlet to draw air into the flow chamber and simulate wind speed. The orifice used for the $Br_2$ release is a ¼" swagelok fitting, which allows for smaller flow rates of the release to be experimented with. Figure 3 below depicts a rough approximation of what the lab scale equipment looks like.

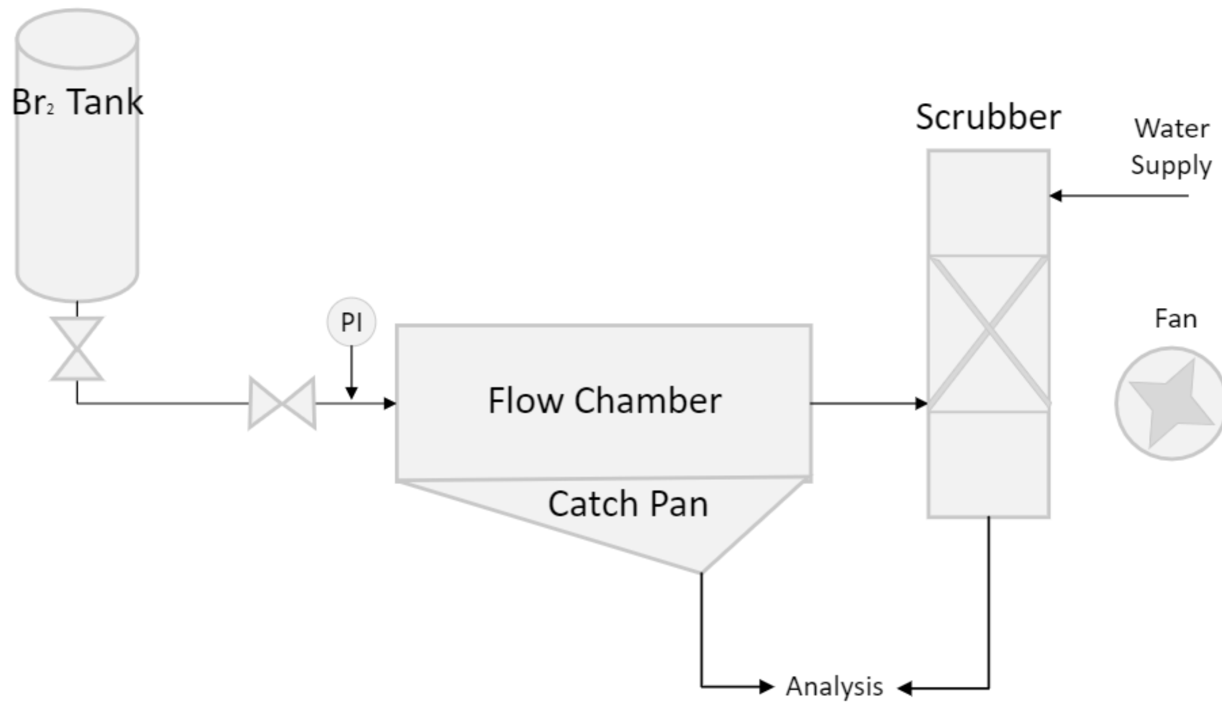


*Figure 3: A diagram of the lab scale equipment to be used.*

<u>Experimental procedure:</u>

Several experiments have been developed in order to test the efficiency (percent of airborne $Br_2$ absorbed by water). To start off, a brief description of a general experimental run is outlined. Firstly, pressurized $Br_2$ is allowed to flow from the cylinder through a series of lines into the flow chamber. The $Br_2$ is released at a controlled flow rate out of the orifice, which is the hole in a metal plate with the ¼" swagelok fitting. A jet of $Br_2$ is propelled through the flow chamber, and whatever rains out is collected in the catch pans, where it is then weighed. Any remaining aerosol droplets are drawn into the scrubber, where a set amount of water is sprayed out, and the $Br_2$ water mixture is collected in a pan below that. This sample is then sent to be analyzed for the amount of $Br_2$. Based on the collected values, the amount of rainout can be detected via the mass of $Br_2$ in the catch pans, and the amount of $Br_2$ absorbed can be calculated from the sample taken at the scrubber. The water for the scrubber is a fresh stream that will need to be supplied, and it is not planned to recycle the water and $Br_2$ mixture until it has been treated. One other factor that has not been taken into account is the time for which the experiments will run for. This is due to the fact that the dispersion time for $Br_2$ across the flow chamber into the scrubber is unknown. Once this is determined, a rough idea of how long the experiment should be run for will be known.

The experiments developed can be found in table 2 below, where the following parameters are changed and tested for:

- Amount of rainout
- Flow rate of the release
- Amount of water used in scrubber
- Distance from orifice
- Water droplet size

Each of the steps, as well as theoretical results based on the lab-scale efficiency model, are described in detail below.

*Table 2: list of experiments to test the effects of different parameters on absorption efficiency.*

| Experiment # | Variable | Values set to | $Br_2$ flow rate kg/s |
|---|---|---|---|
| 1,2,3,4,7 | Release flow rate | 0.02, 0.04, 0.06, 0.08, 0.1, 0.15, 0.2 kg/s | - |
| 8,9,10,11,12,13,14,15, 16,17,18,19,20,21,22 | Distance from orifice | 1, 0.75, 0.5 m | 0.02, 0.05, 0.08, 0.125, 0.2 |
| 23,24,25,26,27,28,29,30, 31,32,33,34,35,36,37 | Change in water flow rate | 0.03, 0.06, 0.09 kg/s | 0.02, 0.05, 0.08, 0.125, 0.2 |

| | | | |
|---|---|---|---|
| 38,39,40,41,42,43,44,45, 46,47,48,49,50,51,52 | Water droplet size | 280, 300, 320 microns | 0.02, 0.05, 0.08, 0.125, 0.2 |

<u>Rainout:</u>

In order to determine the amount of rainout, experiments can be run where $Br_2$ is released at various flow rates without considering the water absorption efficiency. The amount of $Br_2$ collected in the catch pans can be weighed, and the amount of rainout determined as the fraction of the weight in the catch can out of the total amount of $Br_2$ released. This will allow for a better understanding of how much $Br_2$ rains out at different release conditions.

<u>Flow rate of the release:</u>

In this set of experiments, the goal is to test the absorption efficiency while varying the release flow rate, and keeping the water flow rate in the scrubber constant to 1 gpm (0.06 kg/s). The flow rate of the $Br_2$ out of the orifice is set to 0.02, 0.04, 0.06, 0.08 0.1, 0.15, and 0.2 kg/s, where this value can be controlled via a flow meter. This was determined from Mobil's set of experiments, where a similar range of flow rates were used. [14] Experiments should be repeated and an average value taken. Figure 4 below represents a theoretical prediction of the absorption efficiency against the water:$Br_2$ ratio.

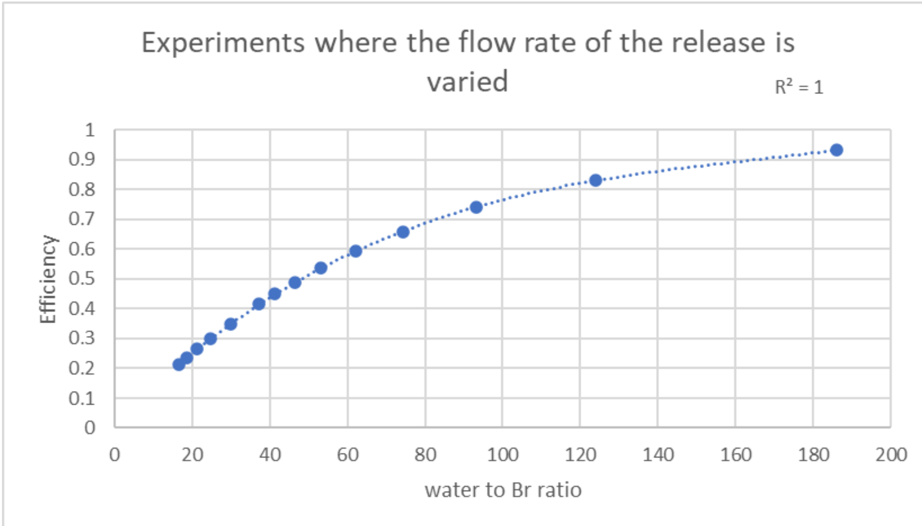


*Figure 4: Results of simulated experiments varying the release flow rate*

<u>Water mass flow rate:</u>

The next set of experiments looks at varying the water flow rate that is sprayed. Three different flow rates, 0.5, 1, and 1.5 gpm, are used, and absorption efficiencies are evaluated at the following $Br_2$ flow rates: 0.02, 0.05, 0.08, 0.125, 0.2 kg/s. Figure 5 below represents the best absorption efficiency that can potentially occur, when the water flow rate is set to 1.5 gpm. Figures A2 and A3 in the appendix show the results when 0.5 and 1 gpm of water is used.

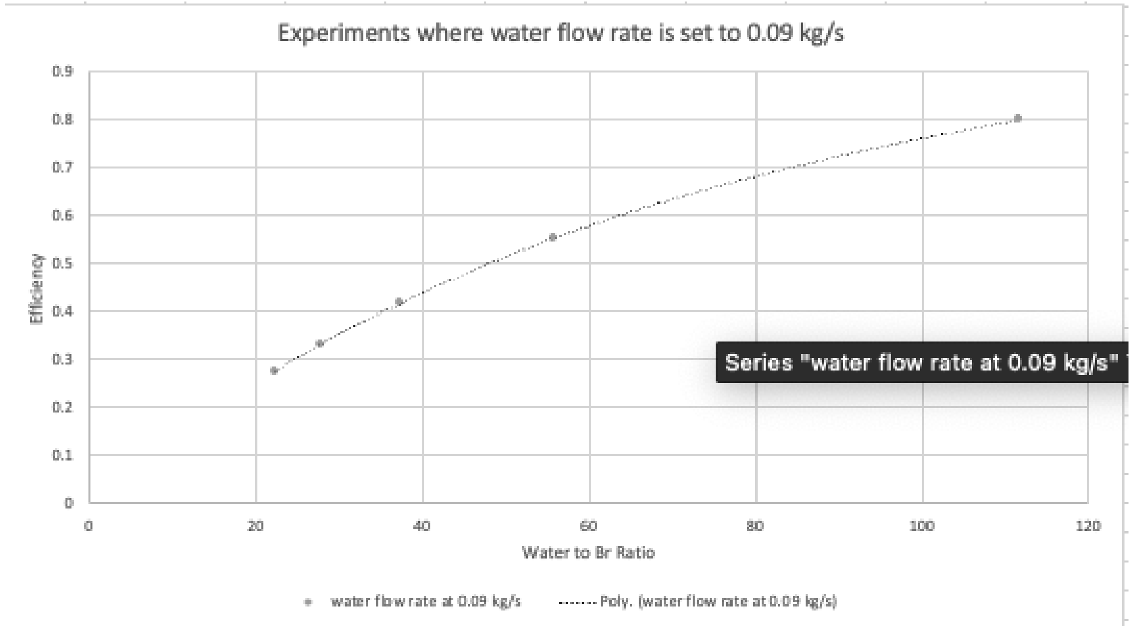


*Figure 5: Results of simulated experiments when 1.5 gpm (0.09 kg/s) of water is used.*

Distance from Orifice:

The following experiments look at the effect distance has on how efficiently $Br_2$ can be absorbed by water. The orifice will have to be moved in the flow chamber, and set to three distances from the scrubber: 1m, 0.75m, and 0.5m. Figure 6 below presents results based on the model, where as the distance increases, the absorption efficiency increases too. The amount of rainout based on distance would need to be tested experimentally, and this can be measured by weighing the amount of $Br_2$ in the catch can.

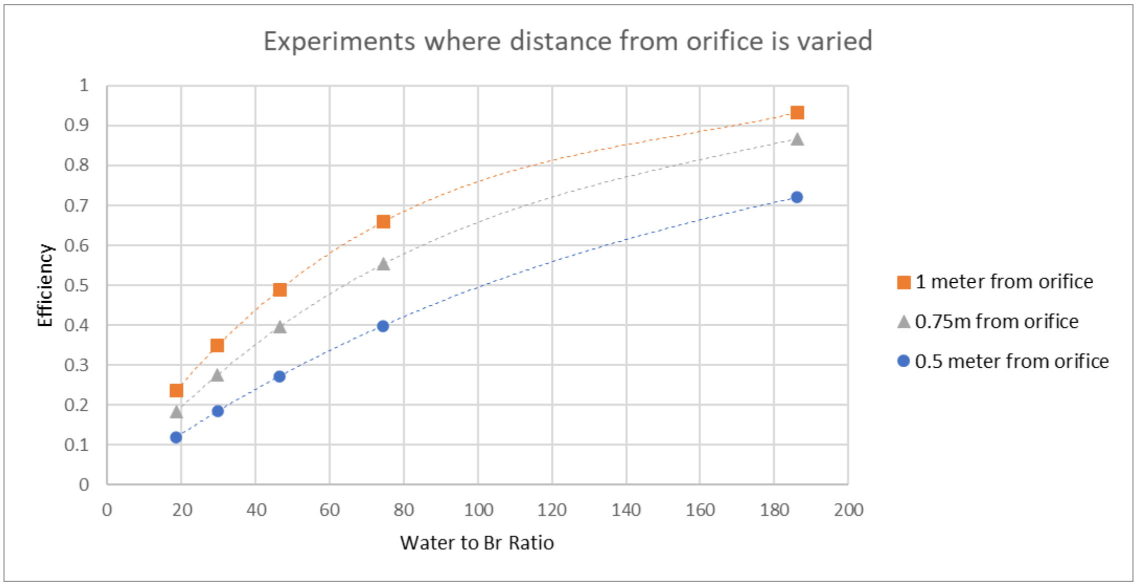


*Figure 6: Results of simulated experiments varying the scrubber (water curtain) distance from orifice*

<u>Water droplet size:</u>

The last set of experiments that have been developed is the change in water droplet size. This could require the change in the nozzle head in the scrubber. The three sizes looked at here are 280, 300, and 320 microns. Again, $Br_2$ flow rates of 0.02, 0.05, 0.08, 0.125, and 0.2 kg/s are used. Figure 7 below shows the model's results under these conditions, where the use of smaller droplet sizes resulted in better absorption efficiencies.

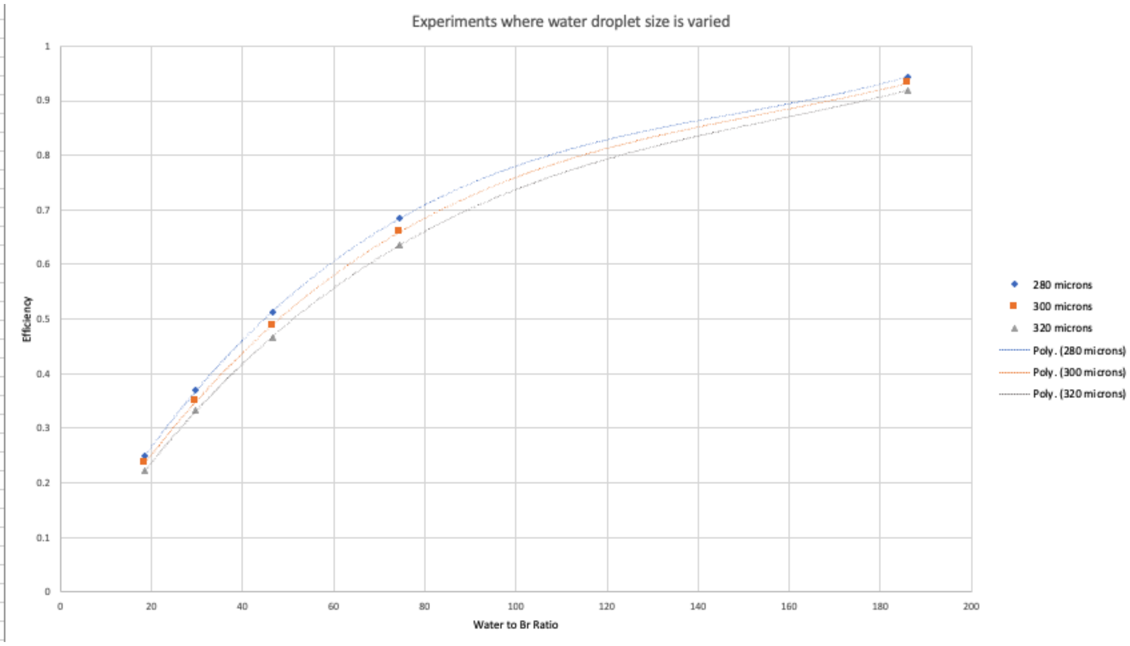


*Figure 7: Results of simulated experiments where the water droplet size was varied.*

<u>Safety:</u>

As bromine is an extremely hazardous chemical, potentially fatal if inhaled and able to cause severe skin burns and eye damage, proper safety precautions will need to be taken during experiments. Use of PPE including tight-fitting splash goggles, protective clothing, and butyl-rubber gloves is essential. Since aerosols will be generated during the experiments, a respirator is required as well. Bromine waste generated should not be mixed with other waste due to its reactivity and should not be released to the environment due to its acute toxicity. Though the scrubber as described above will mitigate a significant portion of the $Br_2$ release, a second scrubber, attached to a waste line, should be included in the experimental setup to prevent release of any bromine not mitigated. As always, $Br_2$'s SDS should be referred to for any clarification on what to do when working with it [15].

Discussion of simulated experiments:

The simulated experiments obtained from the model show some promising results for water mitigation of $Br_2$. Firstly, Figure 5 above shows that with larger water flow rates, higher absorption efficiencies can be achieved, especially when compared to figure A2 and A3 where 1 and 0.5 gpm is used respectively. This makes sense as the absorption efficiency for $Br_2$ increases with a higher water to $Br_2$ ratio. In order to obtain better scrubbing efficiencies, this initial set of simulated experiments shows that more water is required.

Another relatively promising result from the simulated experiments is the water droplet size. Figure 7 above shows that as the droplet size is decreased from 320 to 280 microns, the absorption efficiency increases. Looking at a water to $Br_2$ ratio of around 75, the difference in absorption efficiency between 280 and 320 microns is about 4.9%, which is fairly large. These preliminary results also match the ICHMAP experiments, which also found that the use of smaller drops increased absorption efficiency. [6]

When the flow rate of the released $Br_2$ was increased, the absorption efficiency dropped. This is due to the fact that the water to $Br_2$ ratio drops, resulting in lower absorption efficiencies. $Br_2$'s solubility in water is fairly low at about 3.3 wt.% of $Br_2$ in water [16], so increasing the volume of Br requires a large increase in the volume of water used to achieve the same efficiency.

Lastly, when the distance from the release was decreased from 1 to 0.5m, the absorption efficiency decreased, as seen in Figure 6. A change in half a meter resulted in a drop of efficiency by roughly 26% when looking at a water to $Br_2$ ratio of 74. This could be due to the fact that with a shorter distance, less $Br_2$ will rain out, and more will remain in the air as a mist, decreasing the water:$Br_2$ ratio which evaluates airborne $Br_2$.

Although these simulation results show some promise for water mitigation, it is worth noting from comparing these graphs to Figure 2 that the water:Br ratio required to achieve efficiencies above 90% (~180) is 3-4 times that required for HF (~50). Ultimately, experiments must be conducted in order to more accurately determine how well water sprays work against $Br_2$. The experiments should also be used to further develop the model, and improve its functionality at calculating absorption efficiencies. Results from the experiments should be used to calculate both mass transfer coefficients, and validate the claim made earlier regarding which mathematical model for calculating the mass transfer coefficient can be better. Experimental results should also be used to calculate the constant $C_1$, as this value was determined through a series of estimations.

**Conclusion**

This report presents a newly developed model for water mitigation of $Br_2$ releases, building upon previous studies on HF releases. A rainout model has been developed in Excel that can tentatively estimate the percent of the release that will remain in liquid form without the need for water mitigation; this model still needs to be edited for removal of extraneous release components, as well as other equations that outline different molecular interactions that do not affect $Br_2$ . On top of this, a set of equations originally derived for the modeling of HF release has been adapted to model for $Br_2$. This release model was validated against HF experimental release data, using HF parameters as inputs. Once validated, several laboratory experiments could be designed and then modeled, where variables such as release flow rate, water flow rate, distance from the orifice, and water droplet size can be tested. Based on the model's predictions, water mitigation is a potentially effective way to capture released $Br_2$ and warrants further experimental investigation. High water flow rates, larger distances between the release and water curtain, and smaller water droplet sizes are all expected to contribute to maximizing the efficiency of water mitigation.

**Proposed steps forward**

It is recommended that EM further work on and develop both the rainout and absorption efficiency model in order to optimize them and more accurately predict values. Certain constants like $C_1$ in equation 15 need a better approximation. Further studies can obtain a more accurate value for that constant. It is also recommended to conduct experiments in order to fully determine the feasibility of water mitigation for a $Br_2$ loss of containment event, as well as to further develop the models to more accurately predict absorption efficiencies. The experiments that are proposed have been discussed above in the experimental section, where parameters like release flow rate, water flow rate, distance from the orifice, and water droplet size are varied.

## References


[1] Krambeck, F. Water Mitigation Model. *EMRE Process Engineering.* **2000**.

[2] Schotte, W. Fog Formation of Hydrogen Fluoride in Air. *Ind. Eng. Chem. Res.* **1987,** 26, pp. 300-306.

[3] Fthenakis, V. HGSPRAY: A Complete Model of Spraying Unconfined Gaseous Releases. *J. Loss Prev. Process Ind.* **1993,** 6(5), pp. 327-331.

[4] Davies, J. Turbulence Phenomena: An Introduction to the Eddy Transfer of Momentum, Mass, and Heat, Particularly at Interfaces. **1972**.

[5] Ricou, F.; Spalding, D. Measurements of Entrainment by Axisymmetrical Turbulent Jets. *Journal of Fluid Mechanics.* **1961,** 11(1), pp. 21-32.

[6] The Industry Cooperative HF Mitigation/Assessment Program, Water Spray Subcommittee. Effectiveness of Water Spray Mitigation Systems For Accidental Releases of Hydrogen Fluoride. **1989.**

[7] Muralidhar, R.; Durand, P.; Jersey, G. Small Scale HF/Additive Release Tests at MHF Design Conditions. Mobil Confidential Interoffice Correspondence. **1996**, pp. 151-328.

[8] National Library of Medicine. PubChem - Bromine. May 07, **2021**. https://pubchem.ncbi.nlm.nih.gov/compound/bromine

[9] Green, D.; Perry, R. Perry's Chemical Engineers' Handbook (8th Edition). **2007**.

[10] The Engineering ToolBox. Gases - Specific Heats and Individual Gas Constants. **2003**. https://www.engineeringtoolbox.com/specific-heat-capacity-gases-d_159.html

[11] Muralidhar, R.; Jersey, G.; Krambeck, F.; Sundaresan, S. A Two-Phase Release Model For Quantifying Risk Reduction For Modified HF Alkylation Catalysts. *Journal of Hazardous Materials*. **1995,** 44, pp. 141-183.

[12] Noulty, R.; Leaist, D. Diffusion of Aqueous Hydrofluoric Acid and Aqueous Potassium Fluoride. *Electrochimica Acta*. **1985**, 30(8), pp. 1095-1099.

[13] National Library of Medicine. PubChem - Hydrofluoric Acid. October 14, **2021**. https://pubchem.ncbi.nlm.nih.gov/compound/Hydrofluoric-acid#section=lnChl

[14] Muralidhar, R. Progress Report on HF/Additive Release Model - Program User's Manual. Mobil Confidential Interoffice Correspondence. **1995,** pp. 1-9.

[15] *Bromine extra pure*. CAS RN 7726-95-6; 035-001-00-5; Version 9.1. EMD Millipore Corporation, 400 Summit Drive, Burlington MA. July 25, **2021.**

[16] Rhodes, F.; Bascom, C. Vapor-Composition Relationships in the System Bromine-Water. *Industrial and Engineering Chemistry.* **1927,** 19(4), pp. 480-481.

## Appendix

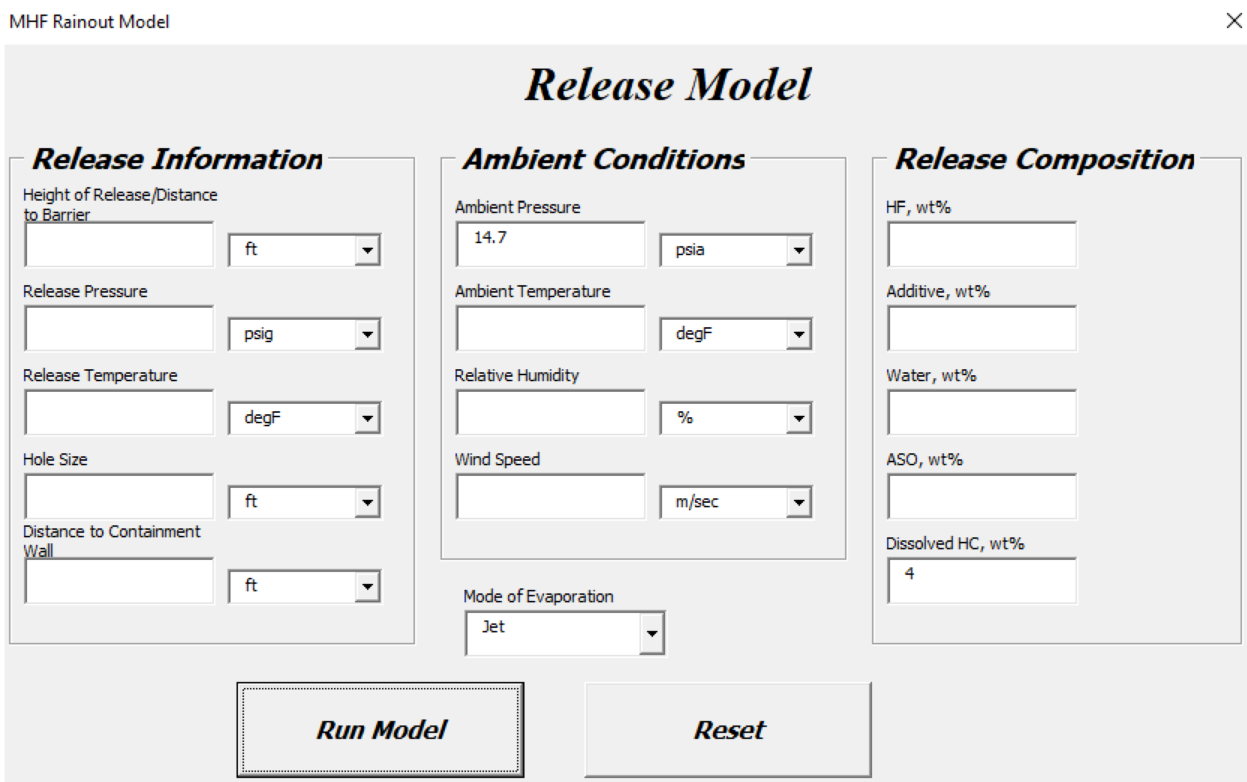


Figure A1: Input screen for rainout model. Note in the Release Composition box, for the Br model "HF, wt%" refers to $Br_2$ and should be set as high as possible (~99.6) while the other components should be set as low as possible (~0.1).

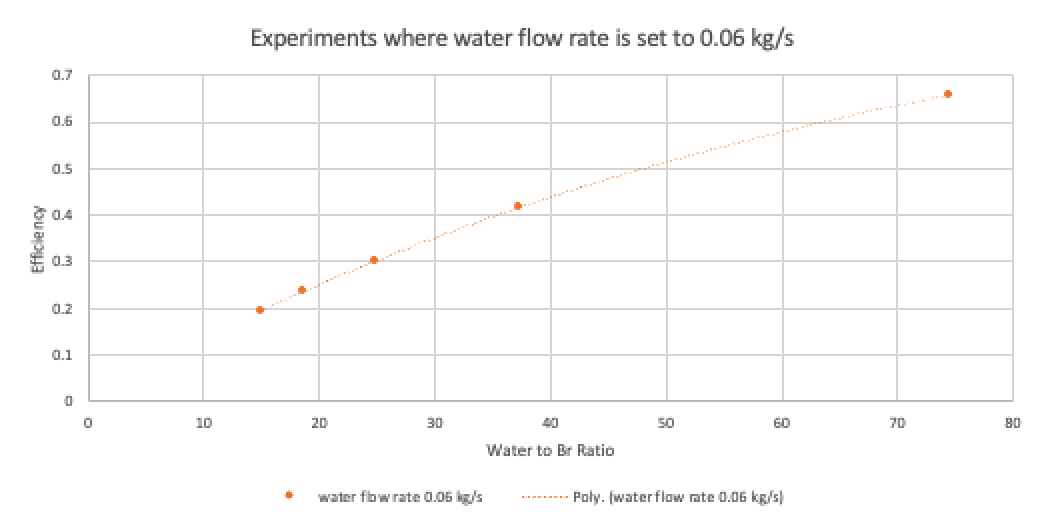


Figure A2: *Results of simulated experiments when 1 gpm (0.06 kg/s) of water is used.*

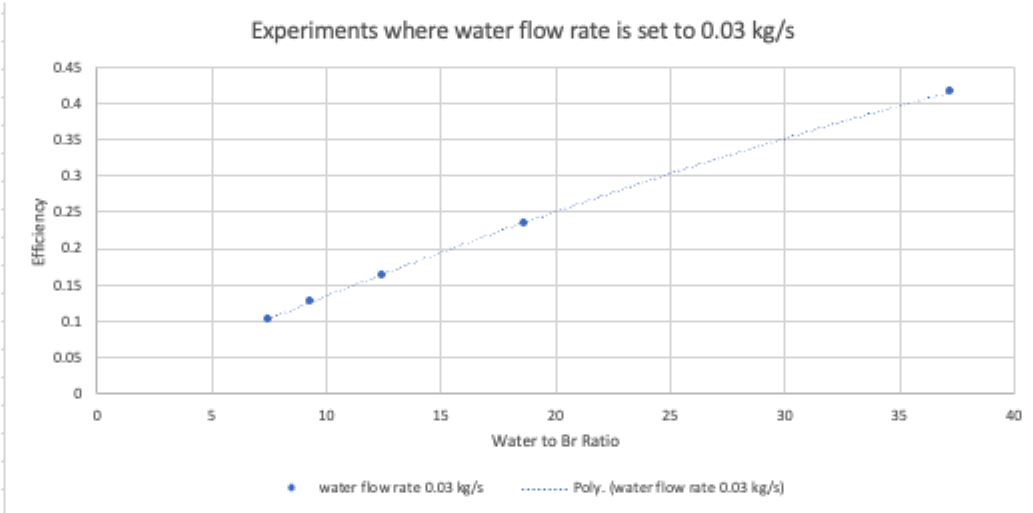


*Figure A3: Results of simulated experiments when 0.5 gpm (0.03 kg/s) of water is used.*