Modeling LNG Pool Spreading and Vaporization

An ioMosaic Corporation Whitepaper

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MODELING LNG POOL SPREADING AND VAPORIZATION

Liquefied Natural Gas (LNG) vapor dispersion analysis is heavily influenced by the estimation of the source term: (a) the LNG (liquid) leak rate and duration, and (b) the pool spreading and vaporization. A sophisticated dispersion model will produce the wrong answer if the source term used is in error.

This paper discusses the validation of SuperChems™ Expert's dynamic liquid pool model for simultaneous spreading and vaporization. The model is capable of performing multi-component analysis to account for differences in LNG composition. LNG spills can be modeled on various surfaces including water.

SuperChems™ Expert's dynamic pool model is shown to accurately reproduce field data for LNG as well as other liquids.

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INTRODUCTION

Consequence analysis of LNG hazards requires modeling of liquid spills on land and water surfaces. The liquid spill duration, release rate, and rate of vaporization are important factors for the estimation of safe separation distances for flammable vapor dispersion and thermal radiation from pool fires. Dispersion distances calculated to ½ LFL are required for the siting of LNG facilities.

For an LNG spill, NFPA 59A (2001) requires facilities to have impoundments be sited such that the average concentration of methane in air does not exceed 50% of its lower flammability limit (LFL) beyond the property line[1]. The federal code of regulations for siting LNG facilities in 49 CFR Part 193 allows the use of both DEGADIS and FEM3A[2] for dispersion analysis. DEGADIS is a refined box model while FEM3A is a computational fluid dynamics (CFD) model. There is no defined model for calculating the source term.

LNG dispersion analysis is heavily influenced by the estimation of the source term: (a) the leak rate and duration, and (b) the pool spreading and vaporization. LNG vapors are heavier than air. They usually form low, pancake shaped clouds which spread due to their own density even in the absence of wind. Since the heavy gas dispersion behavior of LNG is different from buoyant clouds, numerous models have been proposed to mathematically represent heavy gas dispersion. The proliferation of dispersion models has resulted in several good dispersion models. DEGADIS and FEM3A are two such heavy gas dispersion computer programs recommended for calculating flammable vapor dispersion distances.

The applicability of a mathematical model generally depends on the degree to which important physical phenomenon are represented. In that regards, FEM3A is least limited by various approximations but at the same time needs significantly more computational time. FEM3A is free of surface geometry constraints and can treat obstacles.

However, in general, the quality of predictions of dispersion models is very similar, as demonstrated in Table 1 and Table 2. The selection of dispersion models does not appear to significantly affect the quality of results.

A sophisticated dispersion model will produce the wrong answer if the source term (vaporization rates and duration) used are in error. We need to establish realistic, accurate, and prudent estimates of the vaporization rates. Fortunately, and despite several factors that are difficult to quantify such as wave action for spills on water, we can use existing methods to establish safe estimates of pool spreading and dynamic vaporization rates.

This paper discusses the theoretical basis for SuperChems™' dynamic pool spreading model and details the performance of SuperChems™ against several field data sets for a wide variety of fluids including LNG.

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Table 1 – Comparison of Measured Field Peak Concentrations to Model Predictions[3]

	Maximum downwind extent of the LFL. (in meters)			
	Field Data	Germeles-Drake (Box)	SLAB (refined box)	FEM3 (3D)
Burro 3	255	126	215	199
Burro 7	200	150	264	210
Burro 8	420	661	418	630
Burro 9	325	235	315	330

Table 1 - Comparison of Measured Field Peak Concentrations to Model Predictions[4]

	Ratio of Predicted/Experimental Peak Concentrations			
	FEM3A (3D)	SuperChems™ (Box)	DEGADIS (Refined Box)	Gaussian
Falcon 4	0.7 – 1.35	N/A	N/A	N/A
Burro 8	0.6 – 1.14	1.1 – 1.8	0.63 – 2.55	1.14 – 2.65
Burro 9	1.16 – 1.34	0.8 – 1.84	0.8 – 3.54	0.9 – 1.45

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SUPERCHEMS™ OVERVIEW

SuperChems™ contains advanced software for the estimation of single and multi-phase flows, dispersion, chemical reaction systems, fire, and explosion dynamics. SuperChems™ was developed in 1988 by Arthur D. Little Inc. Its models have been the subject of many publications and validation studies with field and incident data. SuperChems™ is used by more than 250 users worldwide.

The development of flow models in SuperChems™ is overseen by a Technical Steering Committee of the American Institute of Chemical Engineers[1]. In July 2002, the American Institute of Chemical Engineers (AIChE) Design Institute for Emergency Relief Systems Users Group (DIERS) adopted SuperChems™ to replace DIERS' existing software for designing emergency relief systems. AIChE currently markets its own version of SuperChems™, called SuperChems™ for DIERS which is a subset of SuperChems™ Expert that is primarily focused on single and multiphase flow and relief systems dynamics.

As part of the New Jersey Toxic Catastrophe Prevention Act (TCPA) program, the New Jersey Bureau of Release Prevention determined that SuperChems™ constitutes a set of models which meet the TCPA regulations in complying with risk assessment requirements.

SuperChems™ has also received favorable reviews and acceptances from several local and regional regulatory agencies in California. SuperChems™ Expert is currently used by the California South Coast Air Quality Management District. SuperChems™ is also used by agencies internationally known such as Transport Canada, and most of the leading Universities in the United States and Canada with active process safety programs in Chemical Engineering.

Details of SuperChems™' Dynamic Pool Spreading and Vaporization Model

SuperChems™' dynamic pool model is based on numerical solutions of the conservation equations for a liquid pool[5], as illustrated in Figure 1, for a liquid pool of radius "r" and thickness "z". A mass balance is written for the ith component in the liquid pool mixture such that:

$$Accumulation = Input \ - \ Evaporation \ - \ Percolation/Dissolution$$

$$\frac{dn_i}{dt} = \frac{dn_{i,in}}{dt} \ - \ \frac{dN_{i,out}}{dt} \ - \ \frac{dn_{i,out}}{dt}$$

$$\frac{dN_{i,out}}{dt} = \pi \ r^2 \ w_i$$

Where n is the liquid number of moles (kmol), N is the vapor number of moles (kmol), and w is the liquid regression rate (vaporization rate) in kmol/m2/s. Usually, measured evaporation/ vaporization data is reported as liquid regression rate. The liquid regression rate is a function of composition, the spill surface type, the spill surface thermal properties, and time.

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[1] http://www.iomosaic.com/iomosaic/products/software/superchems_user_group.html

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Figure 1 - Liquid Pool Representation Used in SuperChems™
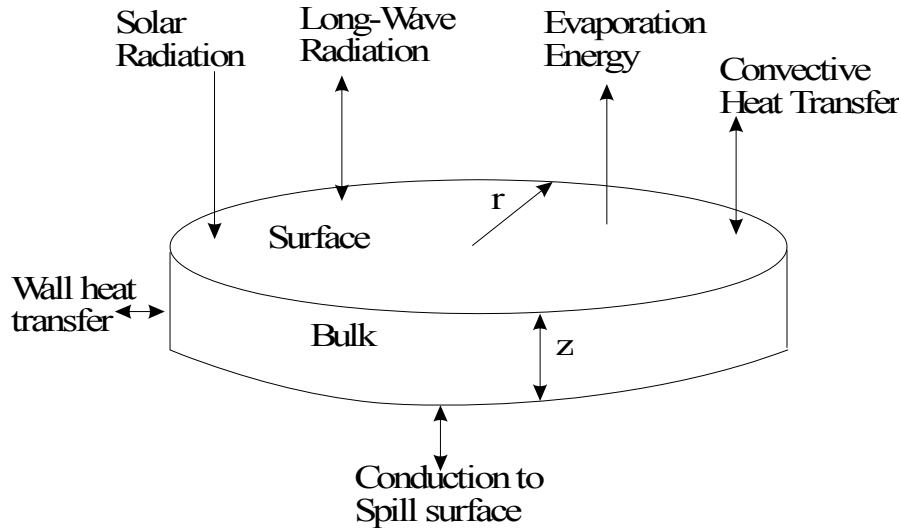
SuperChems™ uses two energy balances to dynamically solve (as a function of time) for the liquid pool surface temperature, bulk liquid temperature, and the underlying surface temperature. All excess energy is converted into boiling energy when the bulk liquid temperature reaches the composition-averaged bubble point of the liquid pool mixture. Note that the bubble point and liquid pool composition are changing with time as light ends are depleted, i.e. vaporize first. The energy balances account for all possible modes of heat transfer for a liquid pool. For cryogens, conductive heat transfer from the substrate usually dominates. SuperChems™ uses a spill / spill surface correction factor, ϕ^2 , to account for surface irregularities for spills on land, and for interfacial distortions leading to increased surface area for spills on water. ϕ is determined based on field data for a variety of spill surfaces including water. A porous dry soil will have a higher effective heat transfer area than highly compacted soil or moist soil.

The extent of spreading of a liquid pool is a key factor which affects the overall emission rate. Larger pools yield higher emission rates. The spreading of liquid pool in SuperChems™ is described using numerical solution of mass and momentum conservation equations based on Weber's[6] formulation of the shallow water equations. For a liquid spill spreading symmetrically on a flat surface, Weber simplified and integrated shallow water equations to describe the bulk properties of liquid pool as follows:

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[2] A heat transfer area enhancement factor

$$\frac{dn}{dt} = \frac{dn_{in}}{dt} - \frac{dN_{out}}{dt} - \frac{dn_{out}}{dt}$$

$$\frac{du}{dt} = \frac{4\Delta(1-s)z}{r} - F$$

$$\frac{dr}{dt} = u$$

where

u – liquid radial spreading velocity

F – viscous effects resistance

$\Delta = g = $ acceleration due to gravity due to spills on land

$\Delta = g\left[1 - \dfrac{\rho_1}{\rho_w}\right] = $ acceleration due to gravity reduced

by the relative density differecne for spills on water

As the liquid pool spreads three flow regimes are recognized:

1. Gravity – inertia
2. Gravity – viscous
3. Surface tension – viscous

In regime 1, the gravity force and liquid inertia are dominant. In regime 2, the viscous drag becomes important and must be taken into account. In regime 3, the surface tension replaces gravity as the driving force. Cryogenic liquids spills rarely reach the second regime because they vaporize quickly. The third regime is important for spills of heavy hydrocarbons on water.

The dynamic simultaneous liquid pool spreading and vaporization equations are solved for every time step leading to concentric annular rings of the spilled liquid to be in contact with the substrate for different periods. For cryogenic spills, the heat exchanged between the bulk liquid and the substrate results in cooler surface temperatures and consequently reduced vaporization rates. Furthermore, SuperChems™ accounts for the film boiling and the transition from film to nucleate/pool boiling.

SuperChems™ successfully captures the underlying physics involved in pool spreading and vaporization for cryogenic and non-cryogenic spills alike. Technical details of the pool model equations can be found in the SuperChems™ reference manual[5].

Model Validation

The following sections detail the performance of SuperChems™ against several field data sets including a wide variety of liquids as well as LNG.

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1. <u>Drake and Reid's LNG Experiments[7]</u>

Drake and Reid conducted an experimental program to study the effect of soil type, moisture content, and LNG composition on boiling rates of LNG. A cylindrical well, 0.18 m in diameter and 0.22 m deep, was cut into a 0.31 m Styrofoam cube. Soil samples were packed to a depth of 0.05 – 0.06 m at the bottom of the well. Approximately 0.27 – 0.4 kg of cryogen was spilled in 2 – 3 seconds. The experiments were performed with the following cryogens:

1. Liquid nitrogen
2. Liquid methane
3. A mixture of 93 % methane and 7 % ethane

The entire test apparatus was mounted on a load cell to monitor changes in the system mass. The boiling rate of cryogens appears to increase with lower moisture content because when water freezes it plugs the pores thereby reducing the surface area available for heat transfer. Reduced boiling rates were observed when a plastic barrier was used to prevent percolation in the soil. The boiling rates observed for LNG were higher than pure methane. Figure 2 and Figure 3 provide a comparison of experimental and predicted data for liquid methane and LNG spills respectively.
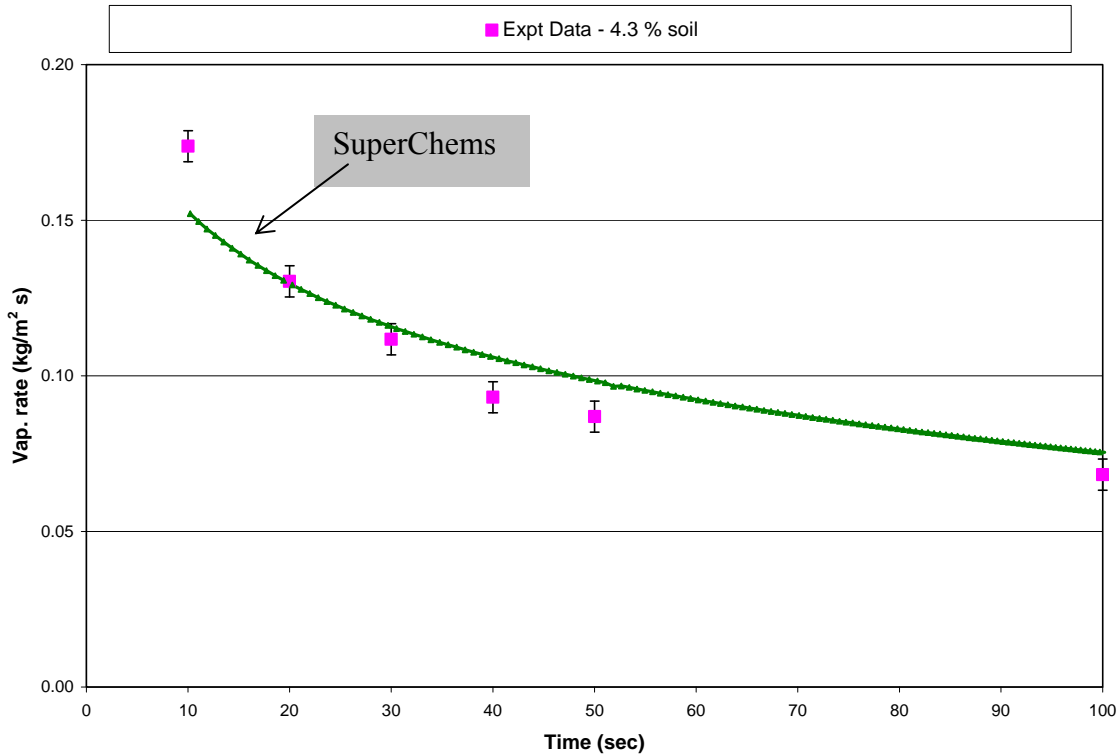
Figure 2 - Liquid Methane Vaporization Data

<u>Simulation details</u>: Spill rate – 0.04 kg/s; Spill duration – 10 sec.; Spill area – 0.025 m²; Spill composition – Liq. Methane

![ioMosaic logo]
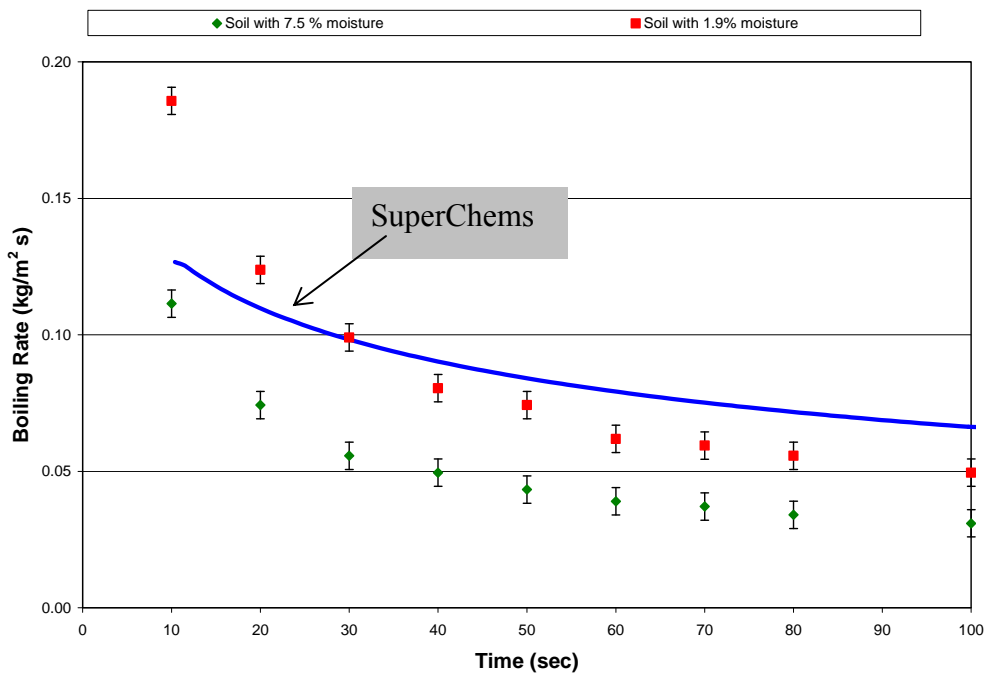
Figure 3 - LNG (93 % methane, 7 % ethane) Vaporization Data

Simulation details: Spill rate – 0.04 kg/s; Spill duration – 10 sec.; Spill area – 0.0254 m2; Spill composition – 93% Methane, 7 % ethane.


2. MIT LNG Research Center Data[8]

Boiling rates of LNG and liquid methane on various dike floors were measured at the MIT LNG research center for GRI study. In this report, tests 38 and 40 are chosen for data validation, and details of the tests are summarized below. A comparison of predicted and experimental data is shown in Figure 4 and Figure 5.

| Test no.	Test 40	**Test 38**
Spill mass (kg)	**0.663**	0.875
Spill composition (mol %)	**99 % methane, 1 % ethane**	99 % methane, 1 % ethane
Spill area (m^2)	**0.1**	0.1
Substrate	**Low compact soil**	Sand

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Figure 4 - Test 40

<u>Note</u>: There is an inconsistency among the reported experimental data since the reported vaporized mass is greater than the reported spill mass.
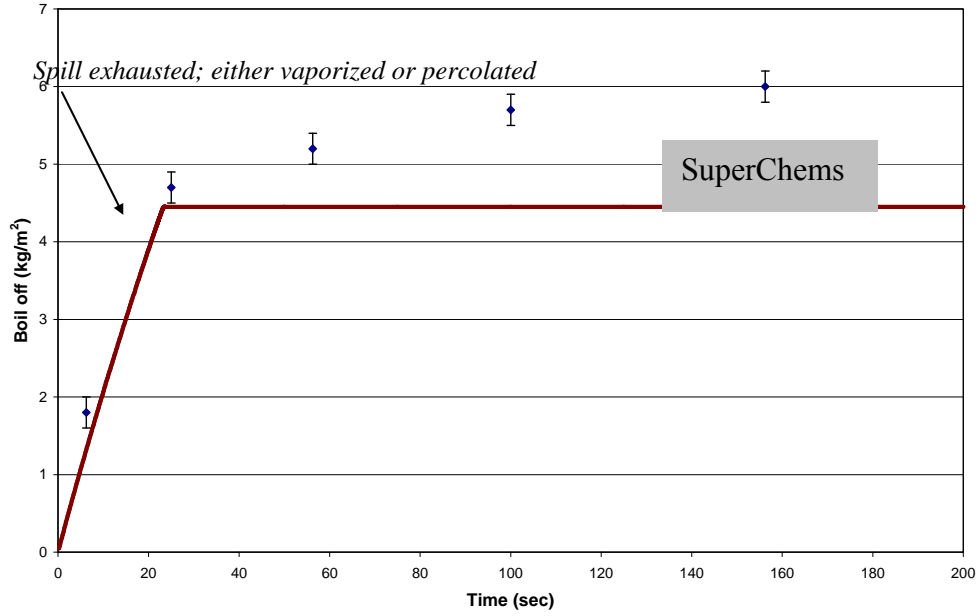
Figure 5 - Test 38

<u>Note</u>: Although sand was used, rates similar to soil were obtained. Soil heat transfer properties were used during simulation. There is an inconsistency among the reported experimental data since the reported vaporized mass is greater than the reported spill mass.
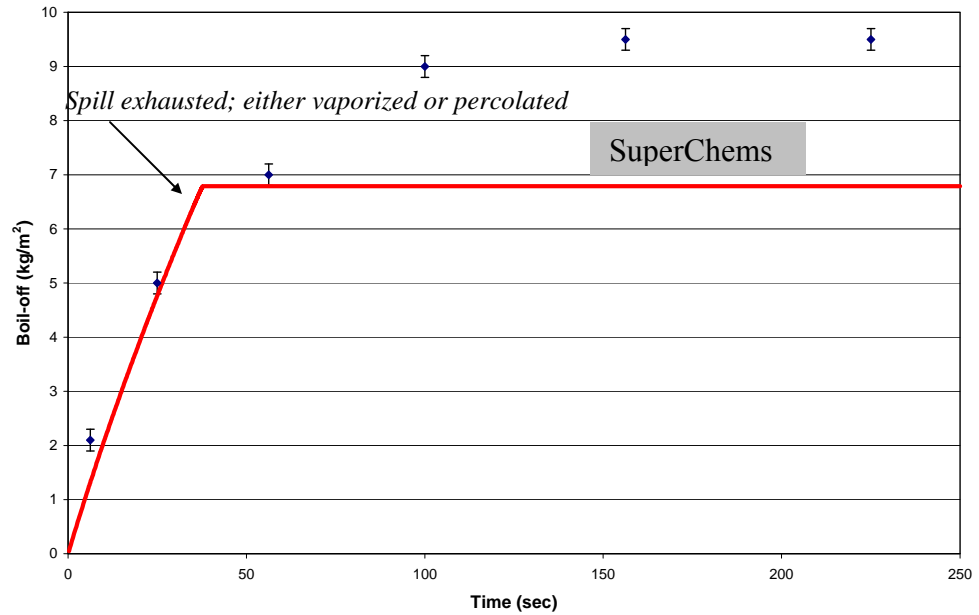
3. Bureau of Mines LNG Spills on Water[9]

The U.S. Bureau of Mines conducted 13 LNG spills onto water in strip mine lake near Florence, PA. For measuring vaporization rates, up to 2×10^{-3} m^3 of LNG was poured from a height of 0.46 m (1.5 ft) into a bucket containing 22.7 m^3 of water. Based on the weight loss and a heat of vaporization value of 577.4 kJ/kg, a 20-second average vaporization rate of 0.155 kg/m^2 s is reported.

Table 2 - Liquid Regression Rates for LNG Spills on Water[4]

| Surface	Regression rate (m/s)
Water	4.34×10^{-4}
Water	3.72×10^{-4}
Aluminum	1.74×10^{-4}
Water	4.68×10^{-4}
Water	0.57×10^{-4}
Water	4.68×10^{-4}

SuperChems™ predicts a 20 second average vaporization rate of 0.155 ± 0.016 (2 σ) kg/m^2 s. The model predicts a steady state mass flux of around 0.1 kg/m^{2}s, which is consistent with literature values.

SuperChems™ predicts an average regression rate of 3×10^{-4} m/s and a maximum regression rate of 6.3×10^{-4} m/s for the Bureau of Mines tests. This is in agreement with the reported values in Table 2, which summarizes regression rates for LNG spills on water from different experiments.

1. Welker[10] LPG Data

Welker conducted numerous experiments to quantify the vaporization rate of propane pools. In test P-15, ~ 18.2 kg of propane was spilled into a 0.47 m² (5 ft²) perlite concrete pit in 15 seconds. Ambient wind speed was 5.1 m/s. Figure 6 presents a comparison of the mass of propane remaining in the pit as a function of time.

**Figure 6 - Weight of Propane Remaining in the Pit**
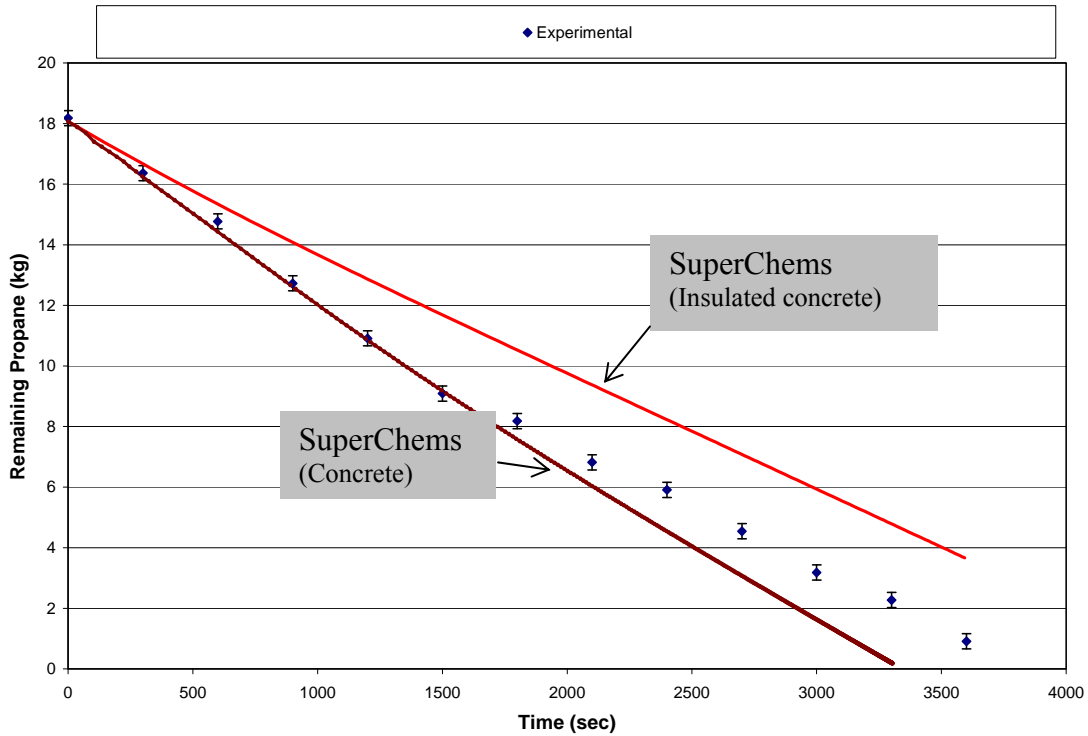
1. **Mikesell et al[11]Ammonia-Water Non-Ideal System**

2240 grams of 28.8 % by weight aqueous ammonia was poured into a 18.8 x 28.8 x 4.76 cm plastic pan. The ambient temperature was 25 °C, with a prevailing wind of 1.59 m/s and 59 % relative humidity. Figure 7 compares the predicted values for ammonia weight fraction in the pool and the total amount of ammonia evaporated from the pool as a function of time to experimentally measured values. SuperChems™ also successfully predicts the bulk and surface temperatures measured for the pool as shown in Figure 8.

Figure 7 - Ammonia Weight Fraction in Pool and Total Mass Evaporated
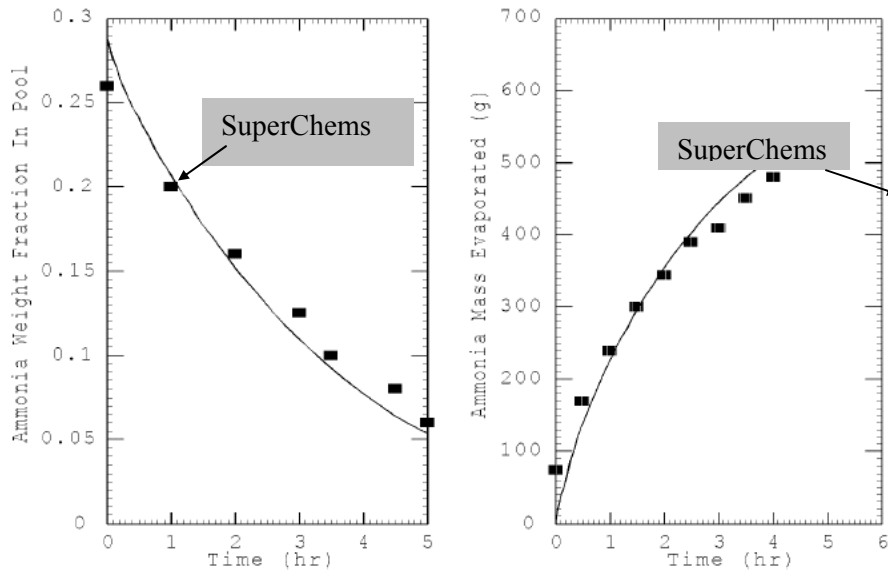

Figure 8 - Liquid Pool Temperature Histories

![ioMosaic]
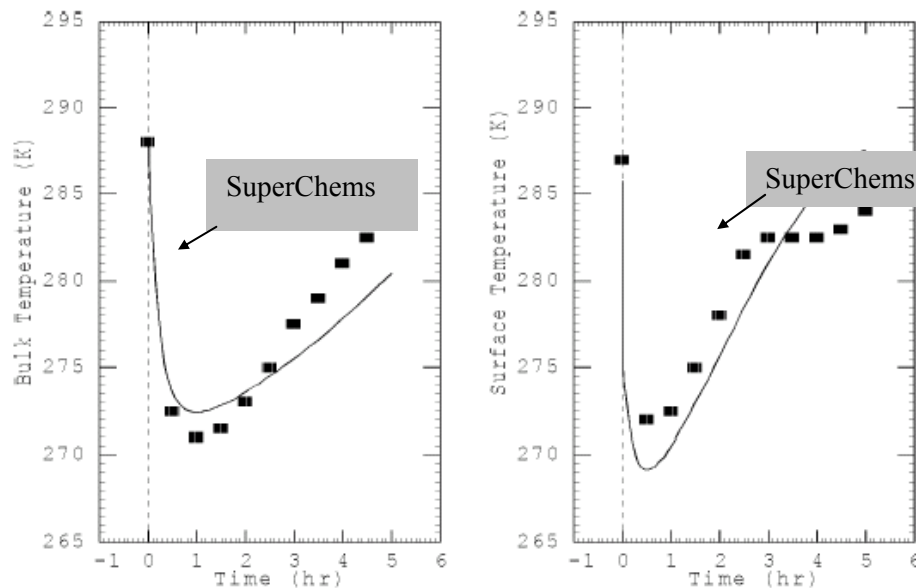
1. Merck[12] Organic Solvents (Methanol, Acetonitrile, and Toluene)

A glass cylinder 5 cm in diameter and 1.8 cm deep was used for the Merck study. The cylinder was placed in a chamber to control temperature and humidity. The effect of wind speed was studied by changing the fan speed in the chamber. The predicted results are in excellent agreement with test data as shown in Figure 9.

Figure 9 - SuperChems™ Predicted Vaporization Data for Organic Solvents

<u>Note</u>: The solid lines represent results from SuperChems™.
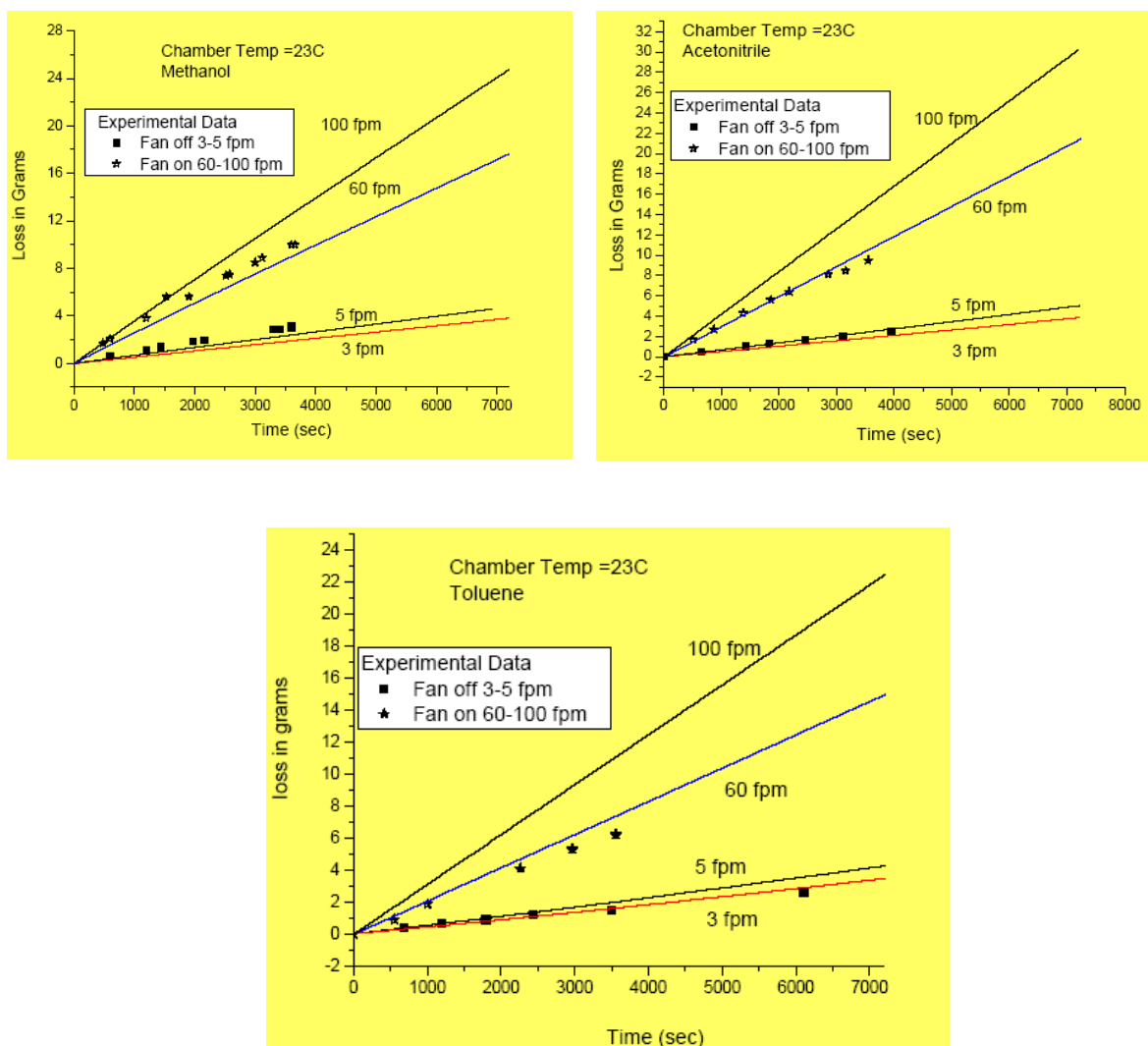
CONCLUSIONS

A prudent estimation of hazard zones requires a validated pool spreading and vaporization model. The SuperChems™ dynamic simultaneous spreading and vaporization liquid pool model represents all significant liquid pool heat and mass transfer mechanisms, vapor-liquid equilibrium, and the radial spreading of the liquid. It successfully captures the underlying physics involved in pool spreading and vaporization as evident by its performance against measured data for a wide variety of fluids. The pool model can be used to study liquid spills on different surfaces including water. The SuperChems™ model has been successfully validated against experimental data for cryogens and non-cryogens, and is commercially available through ioMosaic Corporation.

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