Journal of Hazardous Materials, 5 (1981) 111—130
Elsevier Scientific Publishing Company, Amsterdam — Printed in The Netherlands

MODELS FOR CRYOGENIC LIQUID SPILL BEHAVIOR ON LAND AND WATER

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(Received March 15, 1981; accepted May 29, 1981)

Summary

Evaluation of the potential hazards arising from the accidental spills of cryogenic liquids requires calculation of their spread extent and rate of vaporization. In this paper, various spill scenarios are discussed and modelled. Expressions for the radius of spread, evaporation rate, and volume of liquid remaining at any time are indicated. Types of spills considered include instantaneous, semi-continuous and continuous. A criterion for classifying spills into instantaneous or continuous types is indicated. Spills on land are modelled with decreasing heat transfer rate with time, and spills on water are analyzed based on constant heat flux. A summary table of results is provided.

1. Introduction

Industrial gases, such as ammonia, propane, natural gas, oxygen and hydrogen are handled, stored, transported and used in large quantities in the form of cryogenic liquids. Releases of these liquids caused by on-site or transportation accidents result in potential hazards because of the toxic and/or flammable nature of the vapors, or the burning of the liquid in a pool. Evaluation of the extent of these potential hazards is becoming an important part of industrial operations that involve the handling of hazardous cryogenic fluids. Both government regulatory agencies and the chemical industry have initiated a number of research activities to understand better the behaviour of a variety of chemicals released accidentally into the environment. The information presented in this paper was developed over many years of participation by the author in a number of such research studies. Modelling the behavior of spills of cryogenic fluids in liquid form onto land or the surface of a large body of water is the subject matter of this paper.

The spectrum of cryogenic liquid spill scenarios is very wide. Spills can

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0304-3894/81/0000—0000/$ 02.50

be classified on the basis of the activity in which the spill occurs (from storage tanks, from processing, or during transportation), the environment into which the liquid is spilled (onto land or water surface), or on the basis of rate, quantity and duration of spill. The classification based on rate of release and duration includes (1) "instantaneous release" in which all of the spill occurs in a "very short time", (2) "semi-continuous spill" in which a given volume of liquid is spilled at a finite rate over a given duration of time, and (3) the "continuous spill" in which the spill continues at a finite rate for a "long time". The distinction between short time and long time depends on a number of factors including the size of spill, the properties of the liquid and the environmental conditions. For example, the rupture of a storage tank or the bursting of the tank on a truck by a road accident may be construed as "instantaneous" release, whereas the spill from a leaky pipe joint will be a continuous release.

When a liquid spill is ignited, the "pool fire" that develops causes potential hazards in the vicinity of the fire because of direct fire contact or thermal radiation. However, in the case of non-ignition and boil-off of the cryogenic liquid, the vapors generated are dispersed by atmospheric turbulence and cause toxic or flammability hazards in areas far removed from the scene of release. In either case, the hazard extent depends on the source strength of vapor, the pool size and the temporal behavior of the spilled liquid. These source parameters can be determined by using the models developed to determine the spill size, liquid evaporation rates and other aspects of spill behavior.

Cryogenic liquid boils or evaporates rapidly because of heat transfer from the ground or water onto which it is spilled. Also, in any flat terrain, the spilled liquid will spread as a result of gravitational effects. In a land spill, the land underneath the spreading pool of liquid will cool by the extraction of heat. The spreading system will lose mass through evaporation and sometimes by percolation into porous soils. Mass loss in a water spill occurs due to boiling of the liquid on water.

The purpose of this paper is to detail the models and their development and to summarize the results. The modelling effort is limited to the considerations of simple geometries and conditions. Only flat, smooth, impervious terrains are considered for land spills and calm water conditions are assumed for water spills.

2. Previous studies

Experimental data on the phenomena of cryogenic liquid spill, spread, and evaporation are very limited and do not cover all possible spill scenarios. Burgess et al. [1] report data from liquefied natural gas (LNG) spill tests on water in which the mean heat flux from water was calculated to be 90 kW/m^2 when the spread was constrained and an ice layer formed underneath the liquid. The liquid (radial) spread rate was found to be

0.38 m/s for an instantaneous spill in an unconfined situation. Because of the small quantity of LNG used in these tests, the accuracy of scaling the result to large spills is in doubt. Feldbauer et al. [2] conducted a series of LNG spill tests on the open ocean with spill volumes ranging from 0.84 m^3 (221 U.S. Gallons) to 10.2 m^3 (2700 gallons), and spill durations varying from 5.2 s to 35 s (for the 10 m^3 spill). It is reported that the spilled LNG spread radially as coherent pool up to a certain time and then broke up into smaller pools. The total evaporation rate, estimated from vapor concentration measurements, indicates an increase with the square of time. The maximum evaporation rate is reported to have occurred at the time of pool break up. The water-to-LNG heat flux calculated by this author, from the data presented by Feldbauer et al., indicates a value of 99 kW/m^2. This value is close to that reported by Burgess et al. Boyle and Kneebone [3] conducted tests with LNG spill onto water in a pond and concluded that the average water-to-LNG heat flux was 15 kW/m^2. This value is much lower than those observed by Feldbauer et al. and Burgess et al. The reason for this discrepancy is not readily apparent.

May and Perumal [4] have reviewed the pool spread data from all three of the above test series and have concluded that a simple gravitational spread model adequately predicts the observed pool spread behavior. In this model the radius of spread varies as the square root of time. In view of this result and the observation by Feldbauer et al. that the total evaporation

TABLE 1

Boiling parameters for different ground materials

Material	Nominal thermal conductivity, K (W/m K)	Substrate thermal property, S ($Ws^{1/2}/m^2$ K)
Soil		
Dry (1300—1800 kg/m^3) density	~6	1445
AGA test soil [7] (9.4% moisture)	~0.5	~2020
Other tests [6] at MIT	—	865—1440
Gaz de France test [7]	—	2890—4330
Sand (< 4% water)		~1445
Dry polyurethene (120 kg/m^3 density)	0.12	78
Insulating concretes		
Dycon K-23	0.22	136
K-25	0.24	188
Grace G-24	0.16	130
G-34	0.42	245

Source: Reid and Wang [6]

$\dot{M} = S t^{-1/2}$; for dimensional heat transfer $S = \sqrt{\frac{(K\rho C)_G}{\pi}}\,\Delta T$

rate of LNG was proportional to the square of time, it can be inferred that in the experiment by Feldbauer et al., the pool area averaged heat flux from water-to-LNG increased continuously with time. This may be a consequence of change over in the LNG boiling regime from film type to nucleate type, over increasing areas of the pool, with the progress of time. In fact, this may even explain the late annular ring type of spreading.

Reid and Smith [5] report heat flux results from the boiling of liquefied petroleum gas (LPG), propane, ethane and n-butane on water in an adiabatic calorimeter. The results indicate that the heat flux reduces as the inverse square root of time because an ice layer forms on the water surface. Reid and Wang [6] have presented the data for the rate of LNG boiling on many dike floor solid materials, obtained from laboratory tests. In these cases, also, the inverse square root time dependence of the boiling rates is evident. Table 1 shows modified results from Reid and Wang. No data are available for simultaneous spreading and evaporation of cryogens on solid substrates.

3. Analyses

The models presented below are derived by considering the hydrodynamics of spread, the heat transfer to the spreading liquid from the substrate, and the coupling between them. Spills on land and water are considered separately. Decrease in heat transfer rate with time is the characteristic of the land spills, whereas in water spills, the heat flux is assumed to be constant.

3.1 Liquid spills on land

In modeling spills on land, the following assumptions are made:

(1) Heat transfer rate can be obtained from quasi one-dimensional theory.

(2) The ground is perfectly flat and frictionless.

(3) The diameter of the spill jet is small compared to the size of spread of liquid. That is, the source is a point source on the ground.

(4) The thermal boundary layer in the ground grows laterally because of the liquid spread, and depthwise because of thermal propagation.

(5) Thermal boundary layer profiles are similar to one another at all times.

3.1.1 Continuous spill

The physical situation is shown schematically in Fig. 1. The cryogenic liquid released continuously in the form of a jet onto a warm ground spreads radially, uniformly, and evaporates as it spreads. The thermal boundary layer has zero thickness at the spread front.

If the liquid accumulation on the ground surface can be neglected in formulating the above model, then it can be shown that the spread extent at any given time is larger than when the liquid spread is determined by

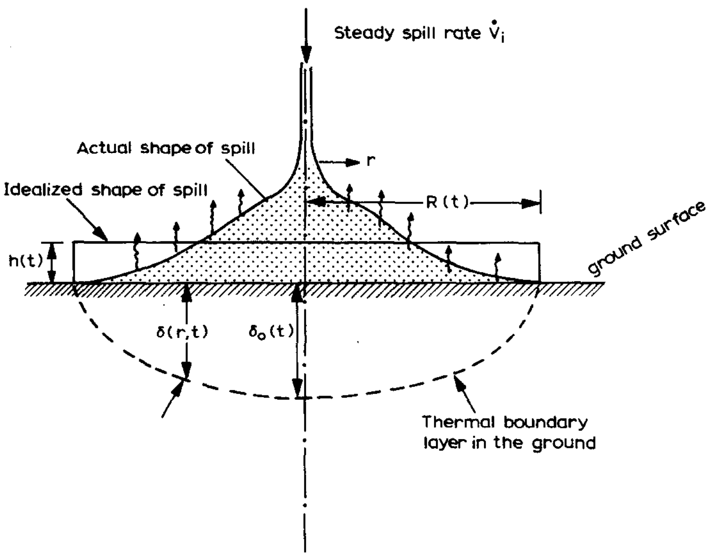

Fig. 1. Spreading of a continuously spilled cryogenic fluid on the surface of a flat ground.

taking into account both hydrodynamics and heat transfer. The model with the assumption of no liquid accumulation, will therefore give a conservative result for (i.e., overestimate of) spread radius at any time. This calculation is presented below. The model developed assumes that the total evaporation rate of the liquid from the spreading system is equal to the liquid spill rate. This assumption implies that there is no liquid accumulation on the ground. In such a case, the term "spread radius" has to be interpreted as the radius of a "wetting front" that is assumed to spread radially on the ground surface.

Consider an annular ring of wetted area of radius r_1 and width dr_1 at the instant of time t. The spill occurs when time t is zero. The radius of the wet front is R. Then, assuming that the heat transfer is limited by the conduction through the ground, the rate of heat transfer through the annular area is given by:

$$d\dot{Q} = \frac{K_G \Delta T}{\sqrt{\pi \alpha_G (t - t_1)}} \; 2\pi r_1 \, dr_1 \ , \tag{1}$$

for $t > t_1$.

The denominator in the above equation represents the thickness of the boundary layer at position r_1, growing from zero thickness at time t_1 to the present thickness at time t. In this span of time, the wet front radius will have increased from r_1 to R. Equating the spill rate to total evaporation rate, we have

$$\dot{V}_L = \frac{\dot{Q}}{\lambda\rho_L} = \frac{\pi K_G \Delta T}{\lambda\rho_L\sqrt{\pi\alpha_G t}} \int_{r_1=0}^{R(t)} \frac{2r_1 \mathrm{d}r_1}{\left(\sqrt{1-\frac{t_1}{t}}\right)} \tag{2}$$

If we assume that the thermal boundary layer profiles in the ground are similar to one another at all times, the above equation can easily be solved [8]. This results in the following equation for the radius of spread as a function of time:

$$R(t) = \left[\frac{2\lambda\rho_L \dot{V}_L}{\pi^2 S \Delta T}\right]^{1/2} t^{1/4} \tag{3}$$

where

$$S = \sqrt{\frac{(K\rho C)_G}{\pi}} = \text{thermal property of substrate.}$$

In dimensionless form, eqn. (3) is

$$\xi = \tau^{1/4} \tag{4}$$

where

$$\xi = R/L\ ;\ \tau = t/t_{ch} \tag{5}$$

The parameters L and t_{ch} are, respectively, the characteristic length and time scales in the system. They cannot be determined independently, but are connected by the equation

$$L = \left[\frac{2\lambda\rho_L \dot{V}_L}{\pi^2 S \Delta T}\right]^{1/2} t_{ch}^{1/4} \tag{6}$$

Physically, L represents a characteristic radius over which the evaporation rate is exactly equal to the spill rate at time t_{ch}.

It can be shown that for the integral in eqn. (2) to be of finite value, the thermal boundary layer variation has to be given by the modified elliptic profile

$$\left[\frac{\delta(r)}{\delta_0}\right]^2 + \left[\frac{r}{R}\right]^4 = 1 \tag{7}$$

where

$\delta_0 = \sqrt{\pi\alpha_G t}$ = Depth of penetration of thermal boundary layer underneath the spill point (8)

Also, the heat transfer mean boundary layer thickness can be shown to be

$$\delta_m = (2/\pi)\delta_0 \tag{9}$$

where δ_m is defined by

$$\dot{V}_L = \frac{\pi R^2 K_G \Delta T}{\lambda \rho_L \delta_m} = \frac{\pi R^2 S \Delta T}{\left(\frac{2}{\pi}\right) \lambda \rho_L \sqrt{t}} \qquad (10)$$

Equation(3) represents the relationship between duration of spread and radius of spread. In a real spill situation, the actual spread radius, at a specified time, will be smaller than that predicted by eqn. (3) because of accumulation of liquid in the spreading system as well as non-uniformities on the ground surface. However, the developed result is useful in evaluating the time of spread of a cryogenic spill in a given dike configuration. If the time to spread is substantially longer than the duration of spill, the above analysis can no longer be used. This situation is discussed in the following section.

3.1.2 Continuous spill: finite duration of spill

An assessment of the hazard extent based on the assumption that the boiling rate is equal to the spill rate may be overconservative in many situations. It is uncertain whether such an assumption can be made for less volatile liquids or for liquids whose boiling points are close to the ambient temperature. In addition, when a finite quantity of liquid is spilled at a constant rate over a definite duration, the liquid spreads to a maximum radius before completely evaporating. The analysis presented below evaluates the maximum spread radius and time for complete evaporation, taking into consideration the hydrodynamics of liquid spread.

The physical situation is identical to that depicted schematically in Fig. 1. A given volume of liquid V_L is released uniformly and continuously at the constant rate $\dot{V}_L$ over a period of time t_s.

The following assumptions are made in addition to the ones stated earlier

(1) The liquid film thickness is uniform at all instants of time.

(2) The rate of spread is proportional to the square root of the mean liquid thickness.

Using the results in eqns. (8)—(10), the volume balance equation becomes for the two periods in the problem,

$$V(t) + \frac{\pi^2 S \Delta T}{2\lambda \rho_L} \int_{t=0}^{t} \frac{R^2}{\sqrt{t}} \, dt = \begin{cases} \dot{V}_L t & \text{for } t \leqslant t_s \qquad (11a) \\ \dot{V}_L t_s = V_L & \text{for } t > t_s \qquad (11b) \end{cases}$$

The first term on the left side is the volume of liquid in the spreading system at time t. The second term represents the total volume evaporated due to heat transfer from the ground over time duration t. The terms on the right-hand side indicate the total volume spilled up to time t, when t is less than spill time t_s; and the total volume spilled if t is greater than t_s.

Also, we have

$$V_L = \dot{V}_L t_s \tag{12}$$

$$V(t) = \pi R^2 h = \text{volume of liquid in the system} \ , \tag{13}$$

and

$$\frac{dR}{dt} = c\sqrt{gh} = \text{spread rate} \ . \tag{14}$$

Substituting for h from eqn. (14) in eqn. (13) and substituting the result for V in eqn. (11), an integral differential equation is obtained for the spread radius R as a function of time t. This resulting equation can be expressed in the following dimensionless form:

$$A^2 \left[\xi \frac{d\xi}{d\tau}\right]^2 + \int_{\tau=0}^{\tau} \frac{\xi^2}{\sqrt{\tau}} d\tau \quad \begin{cases} = \tau & \text{for } \tau \leqslant 1 \quad (15a) \\ = 1 & \text{for } \tau > 1 \quad (15b) \end{cases}$$

with initial conditions

$$\xi(0) = \left(\frac{d\xi}{d\tau}\right)_{\tau=0} = 0 \tag{16}$$

where

$$\tau = t/t_s \ ; \ \xi = R/L \tag{5}$$

$$A = \frac{\dfrac{2}{\pi} \dfrac{\lambda \rho_L (V_L/t_s)^{1/2}}{\sqrt{(K\rho C)_G} \Delta T}}{c\sqrt{g t_s^2}} = \left[\frac{\pi L^4/V_L}{c^2 g t_s^2}\right]^{1/2} =$$

$$= \frac{\text{Evaporation length scale}}{\text{Hydrodynamic spread length scale}} \tag{17}$$

The characteristic length scale L is related to the time scale t_s by eqn. (6) in which t_{ch} is replaced by t_s.

The parameter A represents the relative importance of evaporation compared with hydrodynamics in the spreading process. It is noted from eqn. (17) (and also from eqn. (6)) that for a given spill rate and duration, the greater the heat transfer rate from the ground, the smaller the evaporation length scale. Similarly, if a given mass is spilled over a long duration, the heat transfer effect dominates and the hydrodynamic effect can be ignored because of the relatively small thickness of the spreading liquid. That means that when the value of A is small compared to unity, the heat transfer effect dominates, and when A is large relative to unity, the hydrodynamic spread due to gravity is important.

Asymptotic solutions to eqn. (15) can be obtained for values of A substantially different from unity. It can be shown that these results are:

(1) for $A = 0$; *Heat Transfer Dominating*

$$\xi^2 = \tau^{1/2} \tag{18}$$

This result is the same (in dimensionless terms) as the result in eqn. (3). We also note that the maximum radius of spread is $\xi = 1$ and occurs at $\tau = 1$; that is, at the end of the spill time t_s.

(2) for $A \gg 1$; *Gravitational Spread Dominating*

$$\xi^2 = \frac{4}{3A} \tau^{3/2} \tag{19}$$

Note, however, that despite the low heat transfer rate inferred by $A \gg 1$ all of the liquid spilled will evaporate eventually. An estimate of the time to evaporate can be obtained by first assuming that no evaporation occurs until all the liquid is spilled, and subsequently that liquid spreads with a constant radial velocity equal to its value at $\tau = 1$. It can then be shown that the total evaporation time is obtained by solving the cubic equation

$$x^3 - x = 3A/4 \ ; \ x = \sqrt{\tau_e} \tag{20}$$

where τ_e = dimensionless evaporation time.

The solution to the above equation is shown graphically in Fig. 2 for a range of values of A. It can also be shown that this result gives the lowest value for the evaporation time.

The maximum radius of spread and the time for complete evaporation can be obtained by solving eqn. (15) numerically, using the 4th order Runge—Kutta method for the 2nd degree differential equation. The final spread radius obtained from such a numerical solution is also shown plotted in Fig. 2 in dimensionless terms.

3.1.3 Instantaneous spill

When a given mass of cryogenic liquid is spilled in a very short time ("instantaneously"), it tends to spread because of gravitational force. The spreading is opposed by the inertia of the liquid in the system. Evaporation occurs because of heat transfer from the ground during the spreading phase. This phenomenon is modeled below subject to the following *assumptions*:

(1) The ground is smooth and frictionless.
(2) All the evaporation occurs in the gravity—inertia phase of liquid spread.
(3) The heat transfer from the ground can be modelled using a quasi one-dimensional approach.

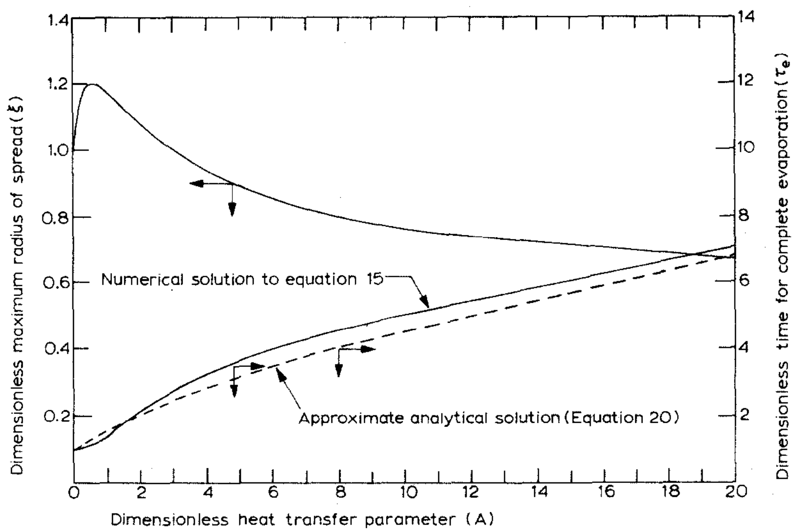

Fig. 2. Maximum spread radius and spread time vs. heat transfer parameter for continuous release of a finite mass of cryogenic liquid on land.

The volume (or mass) conservation equation for the above physical situation is

$$V(t) = V_L - \int_0^t \pi R^2(t)\dot{y}(t)\,dt \tag{21a}$$

with

$$R(0) = 0 \tag{21b}$$

The volume remaining in the liquid system at any time is represented by V, the left hand side of the above equation. The initial volume V_L is the first term on the right hand side. The second term on the right hand side represents the total volume of liquid evaporated over time t. The spread radius at the instant of time t is R.

Using the results in eqn. (10) we have

$$\dot{y} = \frac{S\Delta T}{\left(\frac{2}{\pi}\right)\lambda\rho_L\sqrt{t}} = \text{time dependent liquid regression rate} \tag{22}$$

By equating the spreading gravitational force with the inertial resistance, Raj and Kalelkar [9] have shown that the spread law is given by

$$R\,\frac{d^2R}{dt^2} = -\,\frac{gh}{P}\;;\; P \simeq 0.754 \tag{23}$$

where P represents the ratio of the inertia of the liquid system to the inertia if all of the liquid were moving at the acceleration of the spread front. By comparing the above spread law to the rigorous solution of the spread problem in the absence of evaporation, the value of P has been deduced [9] to be 0.754. The mean liquid film thickness is represented by h.

The geometric relationship is represented by

$$V = \pi R^2 h \tag{24}$$

Equations (21), (23) and (24), together with the result in (22), constitute three coupled equations for the unknowns, R, h and V. The solution for the radius R, expressed in dimensionless form, has been shown to be [9]

$$\xi^2 = \frac{16}{15} \frac{B}{P} \tau^{5/2} + 1.3\,\tau \tag{25}$$

$$\kappa = 1 - \frac{16}{45} \frac{B^2}{P} \tau^3 - \frac{2.6}{3} B \tau^{3/2} \tag{26}$$

where

$$\xi = R/L \;;\; \tau = t/t_{ch} \tag{27a}$$

$$\kappa = V/V_L = \text{dimensionless volume of liquid remaining} \tag{27b}$$

$$L = V_L^{1/3} = \text{characteristic length scale} \tag{27c}$$

$$t_{ch} = \sqrt{L/g} = \text{characteristic time scale} \tag{27d}$$

$$\dot{y}_{ch} = \frac{S \Delta T}{\left(\frac{2}{\pi}\right) \lambda \rho_L \sqrt{t_{ch}}} = \text{characteristic regression rate} \tag{27e}$$

$$B = \frac{\dot{y}_{ch}}{\sqrt{gL}} = \frac{\text{characteristic evaporation velocity}}{\text{characteristic spread velocity}} \tag{27f}$$

The parameter B represents, physically, the relative importance of evaporation compared to the gravitational spreading effect. From eqns. (25) and (26), it can be shown that the maximum spread radius and total evaporation time (after substituting the value for P) are given by

$$\xi_e = \frac{1.4507}{B^{1/3}} = \text{final spread radius} \tag{28}$$

$$\tau_e = \frac{0.864}{B^{2/3}} = \text{total evaporation time} \tag{29}$$

3.2 Liquid spills on water

The models presented below are applicable only to lighter than water, im miscible, cryogenic liquids. In most cases, the behavior of a cryogenic liquid spill on water can be modelled in a manner similar to that of a spill on land except for two important differences. The gravitational spread action on water is due to the buoyancy force; hence, the effective gravitational acceleration is used instead of actual gravity. The second difference lies in the rate of heat transfer from the water to the liquid. Small scale experiments have indicated a constant heat flux; this is used in the modelling.

The following assumptions are made in the derivations given below:

(1) The dynamic interaction due to the penetration of liquid jet into water is unimportant.
(2) The effects of wave action, if any, are small.
(3) The cryogenic liquid is lighter than water and is immiscible with water.
(4) Liquid spreading is radial and contiguous.

3.2.1 Continuous spill: Constant heat flux

Consider the spill of a cryogenic liquid onto the water surface at a volumetric rate of $\dot{V}_L$. Because of the constant heat flux from the water, the boiling rate (or the liquid regression rate $\dot{y}$) is a constant. For a long duration spill, the liquid spreads to that radius at which the total evaporation rate is equal to the spill rate. That is

$$R_{max} = \left[\frac{\dot{V}_L}{\pi \dot{y}}\right]^{1/2} \qquad (30)$$

where R_{max} is the final maximum radius of spill and $\dot{y}$ is the constant regression rate. For a given cryogenic liquid, we assume that the value of $\dot{y}$ is known, say, from experimental measurements.

The time taken to reach the maximum radius can be evaluated by solving the spread equation given in eqn. (14). That is,

$$\frac{dR}{dt} = c\sqrt{g'h} \qquad (14)$$

where h is the mean thickness of liquid layer and g' is the effective gravitational acceleration given by

$$g' = g(1 - \rho_L/\rho_w) \qquad (31)$$

The volume conservation equation is given by

$$\frac{dV}{dt} = \dot{V}_L - \pi R^2 \dot{y} \; ; \quad V(0) = 0 \qquad (32)$$

where V is the volume of liquid in the spreading system and R is the spread radius at the instant of time t. Equation (14) is solved together with eqn. (32) and the geometric relationship (24) to obtain radius of spread as a function of time. Because the velocity at the spread front is related to the mean thickness (eqn. (14)) rather than to the thickness at the spreading front, the solution will indicate the continuation of spread when the maximum radius (calculated from eqn. (30)) has been reached. To this extent, the solution is approximate, as will be the spread time indicated.

Equations (14), (24) and (32) are expressed in dimensionless form by defining the following scaling parameters:

$$\xi = R/R_{\max} = \text{dimensionless radius} \tag{33a}$$

$$\eta = h/h_{\text{ch}} = \text{dimensionless mean liquid thickness} \tag{33b}$$

$$\kappa = V/V_{\text{ch}} = \xi^2\eta = \text{dimensionless volume} \tag{33c}$$

$$\tau = t/t_{\text{ch}} = \text{dimensionless time} \tag{33d}$$

$$h_{\text{ch}} = R_{\max}\left[\frac{\dot{y}}{c\sqrt{g'R_{\max}}}\right]^{2/3} = \text{thickness scale} \tag{33e}$$

$$t_{\text{ch}} = \frac{R_{\max}}{c\sqrt{g'h_{\text{ch}}}} = \frac{R_{\max}}{[c^2g'R_{\max}\dot{y}]^{1/3}} = \text{time scale} \tag{33f}$$

$$V_{\text{ch}} = \dot{V}_{\text{L}}t_{\text{ch}} = \text{volume scale} \tag{33g}$$

Solving the differential eqn. (32), we get

$$\kappa = (\tfrac{3}{4})^{2/3}\xi^{4/3}(1-\xi^2/2)^{2/3} \tag{34}$$

and

$$\eta = (\tfrac{3}{4})^{2/3}\xi^{-2/3}(1-\xi^2/2)^{2/3} \tag{35}$$

Expressing eqn. (14) in dimensionless form and rearranging, it can be shown that the solution for τ as a function ξ becomes

$$\tau = \int_{x=0}^{\xi} (\tfrac{4}{3})^{1/3}x^{1/3}\left(1-\frac{x^2}{2}\right)^{-1/3}\mathrm{d}x \tag{36a}$$

$$\tau = (\tfrac{2}{3})^{1/3}\beta(\tfrac{2}{3},\tfrac{2}{3})I_{\xi^2/2}(\tfrac{2}{3},\tfrac{2}{3}) \tag{36b}$$

where β is the complete Beta function and I is the incomplete Beta function [10]. The time to spread to the maximum radius ($\xi = 1$), is given by

$$\tau_{\text{e}} = 0.897 \tag{37}$$

If the duration of the constant rate and continuous spill exceeds the time for spill to spread to the maximum radius, the hazard radius of spill is given by eqn. (30). If, on the other hand, the spill is terminated within the time given by eqn. (37), the maximum radius is not reached at all before all the liquid evaporates.

3.2.2 Instantaneous spill: Constant heat flux

The model for the simultaneous spreading and evaporation in the case of cryogenic liquid spill on water is developed by equating the gravitational spreading force to the inertial resistance and accounting for the loss of mass continuously during the process. In this model, also, the interaction, if any, between the liquid and water due to the sinking of the liquid into the water during release is neglected. All other assumptions indicated earlier are also applicable to this situation.

As indicated in eqn. (23), the law of spread can be written as

$$R \frac{d^2 R}{dt^2} = - \frac{g'h}{P} \; ; \; P \simeq 0.754 \qquad (38)$$

where P has the same meaning as in eqn. (23), g' is the effective gravity (eqn. (31)), and h and R are the mean liquid thickness and spread radius at any instant, respectively.

The volume conservation equation is

$$V(t) = V_{\mathrm{L}} - \int_{t=0}^{t} \pi R^2(t)\dot{y}\,dt \; ; \; R(0) = 0 \qquad (39)$$

in which $\dot{y}$ the liquid regression rate is a given constant. Equations (38), (39) and the geometric equation (24) together constitute a set of integro-differential equations. This set of equations has been solved (Raj and Kalelkar [9]) analytically, and the solutions are indicated below.

The definitions for the characteristic parameters and dimensionless parameters are the same as indicated in eqns. (27a)—(27f) in which g is replaced by g' and $\dot{y}_{\mathrm{ch}}$ is replaced by $\dot{y}$, the given liquid regression rate. Also, we define the following characteristic parameter

$$D = \frac{\dot{y}}{\sqrt{g'L}} \qquad (40)$$

Then the solutions to the set of eqns. (24), (38) and (39) are

$$\xi = [1.3\tau + 0.4422D\tau^3]^{1/2} \qquad (41)$$

$$\kappa = 1 - 2.04D\tau^2 - 0.3473D^2\tau^4 \qquad (42)$$

From eqn. (42), the total time for complete evaporation is obtained by equating κ to zero. Also, the maximum radius of spread is obtained from eqn. (41).

It can be shown then that

$$\tau_{\mathrm{e}} = \frac{0.6743}{D^{1/2}} = \text{maximum time of spread} \qquad (43)$$

$$\xi_e = \frac{1}{D^{1/4}} = \text{maximum radius of spread} \quad (44)$$

These results can be expressed in dimensional terms as:

$$t_e = 0.6743 \left[\frac{V_L}{g' \dot{y}^2}\right]^{1/4} \quad (45)$$

$$R_{max} = \left[\frac{V_L{}^3 g'}{\dot{y}^2}\right]^{1/8} \quad (46)$$

The results obtained in Sections 3.1 and 3.2 are summarized in Table 2.

4. Discussion

The models presented in this paper are applicable to the spill of cryogenic liquids that generally boil and evaporate on contact with the warm ground or water. The key concept used in the development of the models is the loss of mass from the spreading system. Therefore, the same models can also be utilized for determining the spread extent of other liquids that may not evaporate, but which may be "lost" because of percolation in the ground or mixing with water. The results of the models indicated in this paper can also be utilized for determining the total volume of the chemical spilled, knowing from field measurements the extent of spread. This may be particularly useful in establishing the quantity of chemical spilled in, say, a hazardous material storage dump once the extent of the chemical's migration on the surface and the percolation characteristics of the soil are established.

The analyses presented in this paper are based on the premise that for spills on land, the rate of heat transfer to the liquid decreases with time (inverse square root relationship) and for spills on water, the heat flux is a constant. It should be noted that such classification is intended only as a matter of convenience. For example, if an ice layer forms between the cryogenic liquid and water, in the case of a spill on water, the results developed for spills on land can be utilized. This is possible because with the formation and growth of the ice layer, the rate of heat transfer to the liquid decreases as the inverse square root of time. Similarly, the results from water spill with constant heat flux can be used to evaluate the spreading characteristics of noncryogenic liquid spills on land in which there is a constant rate of percolation of liquid into the soil.

The criteria by which a given spill situation can be categorized as 'continuous' or 'instantaneous' are difficult to establish. Comparison can be made only between the rapid release of a given volume and the release of the same volume of liquid relatively slowly. One criterion for classification is the maximum radius of spread. That is, for the given situation, the maximum radii of spread are calculated using both instantaneous and continu-

TABLE 2

Summary of results

Spill environment	Spill characterization and details	Scaling parameters: length (L)	Scaling parameters: time (t_{ch})	Characteristic parameter
Land spill	Continuous spill at volumetric rate $\dot{V}_L$	$L = \left[\frac{2}{\pi^{3/2}} \frac{\lambda \rho_L \dot{V}_L}{\sqrt{(K\rho C)_G} \Delta T}\right]^{1/2} t_{ch}^{1/4}$	t_{ch} can be chosen arbitrarily	—
	Continuous spill for finite duration V_L, volume spilled over period t_s $\dot{V}_L = V_L/t_s$	$L = \left[\frac{2}{\pi^{3/2}} \frac{\lambda \rho_L \dot{V}_L}{\sqrt{(K\rho C)_G} \Delta T}\right]^{1/2} t_s^{1/4}$	$t_{ch} = t_s$	$A = \left[\frac{\pi L^4}{V_L c^2 g t_s^2}\right]^{1/2}$
	Instantaneous spill of volume V_L	$L = V_L^{1/3}$	$t_{ch} = \sqrt{\frac{L}{g}}$	$B = \left[\frac{\sqrt{\pi}}{2} \frac{\sqrt{(K\rho C)_G} \Delta T}{\lambda \rho_L \sqrt{t_{ch} g L}}\right]$
Water spill	Continuous spill at volumetric rate $\dot{V}_L$	$L = R_{max} = \left[\frac{\dot{V}_L}{\pi \dot{y}}\right]^{1/2}$	$t_{ch} = \frac{L}{[c^2 g' L \dot{y}]^{1/3}}$	—
	Instantaneous spill of volume V_L	$L = V_L^{1/3}$	$t_{ch} = \sqrt{\frac{L}{g'}}$	$D = \frac{\dot{y}}{\sqrt{g' L}}$

Spill environment	Spread radius vs. time relationship	Maximum spread radius	Maximum time for total evaporation	Remarks
Land spill	$\xi = \tau^{1/4}$	—	—	In the land spill, the heat transfer rate varies with inverse square root of time
	Approximate solutions given in eqns (18) and (19) exact solution has to be obtained numerically	See Fig. 1		$\xi = \frac{R}{L}$ $\tau = \frac{t}{t_{ch}}$
	$\xi = [1.3\tau + 1.415\tau^{5/2}]^{1/2}$ $\kappa = [1 - 0.867B\tau^{3/2} - 0.472B^2\tau^3]$	$\xi_e = \frac{1.4507}{B^{1/3}}$	$\tau_e = \frac{0.864}{B^{2/3}}$	$\kappa = \frac{V}{V_L}$ $1 \leqslant c \leqslant \sqrt{2}$
Water spill	$\tau = 1.7938 I_{\xi^2}/2(\frac{2}{3},\frac{2}{3})$ $\kappa = (\frac{3}{4})^{2/3}\xi^{4/3}\left[1 - \frac{\xi^2}{2}\right]^{2/3}$	$\xi_e = 1$	$\tau_e = 0.897$	For spill on water, the heat flux is assumed to be a constant $g' = g\left(1 - \frac{\rho_L}{\rho_w}\right)$
	$\xi = [1.3\tau + 0.442\tau^3 D]^{1/2}$ $\kappa = 1 - 2.04D\tau^2 - 0.3473D^2\tau^4$	$\xi_e = \frac{1}{D^{1/4}}$	$\tau_e = \frac{0.6743}{D^{1/2}}$	$I_\kappa(y,z)$ is the incomplete beta function

ous models, and the spill is classified into the category that gives the smaller of the two spread extents. Raj [11] has performed an analysis for water spills with the above criterion and shown that for a spill of volume V_L spilled over time t_s to be classified as a continuous spill, the following criterion has to be satisfied:

$$\frac{t_s \dot{y}}{V_L^{1/3}} > \frac{\sqrt{D}}{\pi} \tag{47}$$

No such simple explicit criterion has been developed for spills on land.

In the development of models presented in this paper, several simplifying assumptions have been made. The appropriateness of these assumptions cannot be easily evaluated because of lack of experimental data for each of the situations considered. For example, it has been assumed that there are no hydraulic jumps in the liquid system for continuous spills on land, similarly, the ground friction is also neglected. While friction is certainly present, hydraulic jumps may also occur depending on release velocities. The effects on the final radius and time of spread of these two phenomena are difficult to estimate. We have also neglected the effect of the initial liquid—liquid interactions underneath the spill jet for the case of liquid spills on water. It is entirely likely that when the temperature difference between water and the liquid is large (as in the case of liquefied natural gas), violent boiling may ensue, resulting in the liquid particles being thrown into the air. Clearly, in such cases the models presented do not represent the realistic spread conditions. Finally, we have assumed that the heat transfer from the ground can be estimated by a quasi one-dimensional theory, using self-similar profiles for the thermal boundary layer. The correctness of this assumption cannot be ascertained except by experiments or by performing extensive numerical solutions to the three dimensional heat conduction equations. However, the approach used here is similar to the common practice in heat transfer and fluid mechanics literature wherein the global conditions are satisfied without satisfying the exact differential equations. Therefore, the solutions presented are accurate only up to a constant factor. The exact value of the constant in each case has to be determined from experiments.

The results presented are all based on theoretical analyses. However, very limited data exist for spills of LNG on water [1—3] which seem to confirm the pool spread model developed in Section 3.2.2. Based on the review of these experimental data, May and Perumal [4] indicate a correlation in which the maximum diameter of pool spread, for LNG spilled instantaneously, is proportional to 0.35 power of spill volume. The model presented in Section 3.2.2 indicates this dependence to be with 0.375 power (eqn. [46]) Considering the uncertainties in the experimental measurements, this agreement may be considered to be a validation of the model. There are, however, no test data with which other models developed in this paper can be verified. Therefore, from the point of view of making better estimates of potential hazards from liquid spills, scaled experiments have to be conducted. These tests will, at the same time, verify the models developed in this paper and provide the data necessary for determining the values of the constants in the equations. Until such time as experimental data become available, the present models may provide sufficiently accurate results for engineering purposes. The models may also be useful for designing appropriate experiments.

Acknowledgments

The author wishes to thank all the sponsors, both in industry and Government, as a part of whose projects many of the models presented in this paper were developed. Also, the assistance provided by Arthur D. Little, Inc. in having the draft of the paper typed is gratefully acknowledged.

List of symbols

- A Dimensionless parameter for continuous spills indicating the relative importance of evaporation and gravitational spread
- B Dimensionless parameter for instantaneous spills
- c Gravitational spread velocity coefficient
- C Specific heat (J/kg K)
- D Ratio of evaporation velocity to characteristic gravitational spread velocity for spill on water
- g Acceleration due to gravity (m/s^2)
- g' Effective gravity for liquid spill on water (m/s^2)
- h Mean liquid thickness (m)
- K_G Effective thermal conductivity of ground (W/m K)
- L Characteristic length scale (m)
- M_s Total mass of liquid spilled (kg)
- $\dot{Q}$ Total heat transfer rate from ground (W)
- R Radius of spread of liquid at any time (m)
- S Ground thermal parameter = $\sqrt{(K\rho C)_G/\pi}$ (W s$^{1/2}$/m^2 K)
- t Time (s)
- t_s Spill time (s)
- T Temperature (K)
- ΔT Temperature difference between the soil and the boiling liquid (K)
- $\dot{V}_L$ Volume rate of spill (m^3/s)
- V_L Total volume of liquid spilled (m^3)
- $\dot{y}$ Liquid regression rate (m/s)
- α_G Thermal diffusivity (effective) of ground (m^2/s)
- ξ Dimensionless spread radius
- ξ_e Dimensionless final spread radius
- δ Boundary layer thickness (m)

λ	Heat of vaporization of the cryogenic liquid (J/kg)
τ	Dimensionless time
τ_e	Dimensionless evaporation time
ρ	Density (kg/m^3)
κ	Dimensionless volume of liquid remaining
η	Dimensionless mean thickness of liquid film

Subscripts

c	Continuous
ch	Characteristic parameter
e	End of spread
G	Ground
I	Instantaneous
L	Liquid
0	Center of spill
s	Spill
w	Water

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