A Predictive Model for Rollover in Stratified LNG Tanks

The incubation period preceding "rollover" within a stratified LNG tank involves intensive heat and mass transfers between layers. Numerical integration of equations describing these processes leads to predicted time-history and boil-off characteristics which are in excellent agreement with Sarsten's (1972) documentation of the LaSpezia rollover incident.

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SCOPE

Liquefied natural gas (LNG) is stored in tanks at temperatures of about 115 K and pressures slightly above 1 atm. Heat leaks, even in well-insulated tanks, cause a slow boil-off of the LNG, and this requires removal of some vapor. During this "weathering" process the composition of the LNG changes because the small amount of nitrogen present is much more volatile than the methane and the heavier hydrocarbons are effectively nonvolatile. Obviously the temperature and density of the LNG change as well.

Natural convection causes circulation of the LNG within the tank, maintaining a uniform liquid composition. The addition of new liquid, however, can result in the formation of strata of slightly different temperature and density. The energy and mass transfer between these strata (or cells), given sufficient time, will result in an unstable interface and rapid mixing of the cells. This is called rollover. When the lower, more dense cell is also at a higher temperature, rollover causes the vapor pressure at the top of the LNG to rise very rapidly, and a rapid evolution of a large quantity of vapor results. At best, such a situation results in a loss of valuable fuel. At worst, it could be dangerous.

In operating an LNG storage facility it would be helpful to have a reliable method for predicting the occurrence and severity of a rollover and for evaluation of countermeasures to prevent it. This in turn requires a good understanding of the energy and mass transfer between the cells and of the rate of boil-off. A mathematical (computer) model of the dynamics within the tank, with provision for addition and removal of LNG, would be a useful tool.

Only one rollover incident, at LaSpezia in Italy, has documentation sufficient for testing a computer model of the rollover process (Sarsten, 1972). Chatterjee and Geist (1972, 1976) and Germeles (1975) developed models which omitted the important contribution of nitrogen to the density and volatility of the LNG; they used the thermohaline equations of Turner (1965) and Huppert (1971); and introduced simplifications which required "adjustment" of the data supplied by Sarsten.

The present paper gives a more adequate theoretical framework for rollover analysis and presents quantitative computer results for the simulation of the LaSpezia rollover.

CONCLUSIONS AND SIGNIFICANCE

A model has been developed which closely simulates the LaSpezia incident details using only input data from Sarsten (1972). It contains only two adjustable constants. The first is the fraction of the heat leak into the vapor space which is transferred to the vaporizing film; changing this fraction from 0.95 to 0.85 has no sensible effect on the dynamics of vaporization and rollover. The second is the proportionality constant in the expression for the intercellular heat transfer coefficient. The rollover time is acutely sensitive to this constant. A +20% change of this constant leads to approximately a −15% change in predicted rollover time. Sarsten (1972) reported 31 hours for rollover time. Use of the McAdams (1954) heat transfer correlation leads to a predicted time of 33.1 hours, whereas use of the Globe and Dropkin (1959) correlation gives 28.4 hours. Predicted vapor evolution for the incubation period is either 10% low or in exact agreement, respectively. Total vapor evolution is within 14% of Sarsten's (1972) theoretical estimate for the entire rollover incident.

Material and energy balances for each species in each liquid cell and the vapor-space are formulated. The inclusion of nitrogen, methane, and three heavier hydrocarbons as separate species is necessary in the analysis in order to match the temperatures, densities, and vapor pressures of the LNG's considered in the LaSpezia case.

The thermohaline mass and heat transfer correlation of Turner (1965), used by most earlier workers for describing transfers between stratified LNG layers in tanks, is considered inapplicable. The thermohaline expressions do not allow sufficient mass transfer between cells to simulate the LaSpezia incident without an unreasonable adjustment of the stability of the interface or of the initial conditions of the cells. In place of this model, the heat and mass transfer coefficients are assumed to be related in the usual way for fully turbulent systems.

For accurate "weathering" analysis it is important to recognize that a thin film exists at the vapor-liquid interface. Evolved vapor is in thermodynamic equilibrium with the liquid in the film; material and energy exchange is accomplished by the "Rayleigh" circulation flow between the bulk liquid and the film; heat transfer from the vapor-space to the film is also significant.

This model will permit evaluation of strategies for rollover prevention and predictions of rollover severity. It may thereby increase the flexibility and safety of LNG terminal operations.

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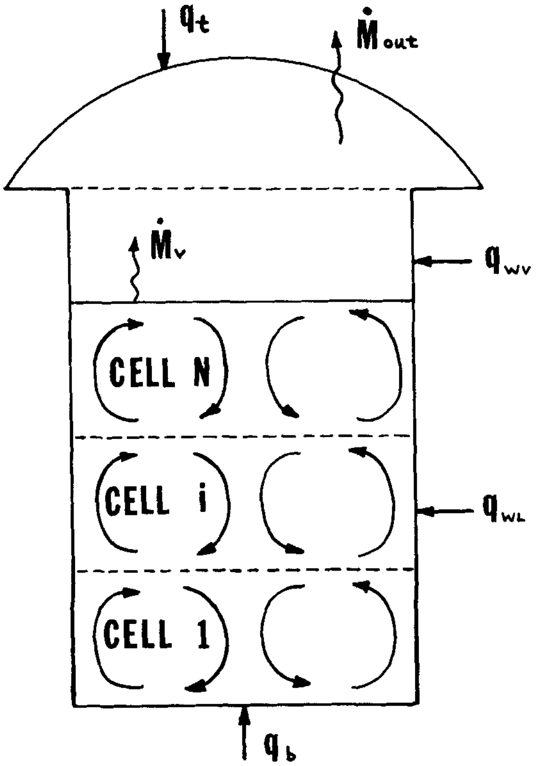

Figure 1. Stratified LNG tank showing cell numbering and the vaporization and heat flux quantities.

PROBLEM CONSIDERED

Stratification in an LNG storage tank, in its simplest form, can give rise to the situation shown schematically in Figure 1. The circulation patterns shown are produced by heat leak into the bottom and sides of the tank. The lower cell has a higher density than the upper one, and this can produce a surprisingly stable interface, even though the individual cells are sensibly homogeneous. The stability of the interface does not prevent heat and mass transfer between the cells, and this tends to equalize their compositions and temperatures. However, the presence and stability of the interface is hydrodynamic, not a question of miscibility.

As the densities of the two cells approach equality two considerations, both of which are important to the present problem, enter. The first of these is the hydrodynamic instability of the interface to a disturbance, cf. Lamb (1945); this indicates that interfacial waves will grow in amplitude. The second is that at some time the liquid flowing up the wall of the tank in the lower cell will become low enough in density so that it can join the fluid in the upper cell and continue to the top of the upper cell. These two considerations explain the rapidity of the mixing (or rollover) when the densities of adjacent cells become equal.

The rapid mixing of the two cells, when the lower cell is at a higher temperature, gives rise to a rapid increase of vapor pressure of the top cell and a consequent rapid evolution of vapor which must be removed from the tank. It could be helpful to have a method of predicting, via a computer model of the tank behavior, the occurrence and severity of a rollover. The successful model will also permit evaluation of prevention strategies, e.g., mixing of the tank contents via external recirculation of liquid.

At this time only one rollover incident has been reported in the open literature with sufficient detail for testing a computer model. Sarsten (1972) carefully documented a rollover event at LaSpezia, Italy; the relevant data are presented in the Appendix, Table A1. These data represent the experiment against which any model must be tested. The successful model will match the experimentally observed rates of vapor evolution and the time from loading to the observed rollover event with the initial conditions given by Sarsten. The model will also successfully describe the "weathering" of tank contents.

EVALUATION OF PREVIOUS WORK

Previous models have been developed by Chatterjee and Geist (1972) and by Germeles (1975). Both of these models used the thermohaline experiments of Turner (1965) as a basis for treating the heat and mass transfer between cells. This method effectively obviates mass transfer between cells as a major factor until the interface becomes unstable. Both of the models simplify the problem to consideration of methane and a non-volatile heavy component. This latter simplification required "adjustment" of the LaSpezia initial conditions as described by Sarsten (1972) to match the temperatures and vapor pressures; unfortunately these adjustments, described in detail by Germeles (1975), have the effect of shortening the time to rollover in both models.

Further, when one notes that the presence of relatively small amounts of nitrogen increases both the vapor pressure and the density of the liquid, it is evident that both the previous models over-simplified the composition. However, when one considers a sufficient number of species (CH_4, C_2H_6, C_3H_8, n-C_4H_{10} and N_2) to match the temperatures, vapor pressures and densities given by Sarsten (1972), it becomes evident that the descriptions of the interfacial transfer of energy and mass obtained from the thermohaline studies simply do not allow sufficient mass transfer in the early stages to match the data.

The model of Chatterjee and Geist (1972) used equality of temperature and composition as a criterion for rollover. But, if one mixes two cells of the same temperature and composition, no change of vapor pressure would be expected. The only reason any increase in boil-off occurs with this model is that the model uses tolerances for equality of composition ($\Delta x(CH_4) < 0.002$) and temperature ($\Delta T < 0.0278$ K). Germeles (1975) has discussed other inconsistencies in this model.

Since the stability of the interface between the cells is an hydrodynamic phenomenon, there should be no net mass transfer across the interface. This is approximated by Chatterjee and Geist (1972) and in the present work by equimolar counter-diffusion. Germeles' model (1975) fixes the volumes of all cells except the top cell.

Both previous models used the Hashemi-Wesson (1971) description of boil-off rate as a basis for handling the vaporization from the top layer. Chaterjee and Geist (1972) assumed the film at the top of the tank was at the same temperature as the top cell. Germeles (1975) used the ideal solution law and the Clausius-Clapeyron equation for describing the vapor-liquid equilibrium. Both models give a normal boil-off from the LaSpezia tank which differs from the data by a factor of about two. This sort of difference affects the temperature and density history of the top cell because a major part of the energy for vaporization comes from the top cell. Again the presence of nitrogen in the liquid plays a critical role because the solutions containing nitrogen are nonideal.

Clearly, the previous models, while containing the general features required, are inadequate for prediction and development of rollover prevention strategies. Table 1 summarizes the principal features of previous rollover models as well as those in the proposed analysis of this paper.

BASIS OF THE PROPOSED ANALYSIS

Heat Fluxes through Tank Walls

The heat fluxes through the walls of the tank, q_b, q_{WL}, q_{WV} and q_t are sensibly fixed by the construction of the tank itself. The insulation of the tank is by far the controlling resistance, with q_b being somewhat larger owing to the fact that the bottom of the tank is often heated to prevent freezing of the ground under the footings. These fluxes are sensibly independent of the variations inside the tank itself during the period of a rollover development because the variation in the temperature driving force are quite insignificant. Accordingly, for the LaSpezia incident these fluxes are:

TABLE 1. COMPARISON OF PRINCIPAL FEATURES OF ROLLOVER MODELS

Model Features	Chatterjee and Geist (1972)	Chatterjee and Geist (1976)	Germeles (1975)	Present Work
Chemical Species Considered	CH_4 and non-volatile heavy	CH_4, C_2H_6 and N_2	CH_4 (solvent) and fictitious non-volatile solute	CH_4, C_2H_6, C_3H_8, n-C_4H_{10} and N_2
Rollover Criterion (or Criteria)	$(\Delta x)_{CH_4} < 0.002$ *and* $(\Delta T) < 0.0278$ K	Not stated	Equal cell densities	Equal cell densities
La Spezia Rollover Time after Start of the Cargo Transfer	151,200 s	Not Considered	122,400 seconds	109,800 s
Sarsten (1972): 111,600 s				
Normal Boil-Off Rate at La Spezia*	0.00869 kgmol CH_4 per s	Not considered	0.0764 kgmol/s	0.0176 kgmol/s
Sarsten (1972): 0.278 kg/s				
Peak Boil-Off Rate at La Spezia**	45.5 times their predicted normal rate	Not Considered	3 times his predicted normal rate	0.176 kgmol/s
Sarsten (1972): Speculative				
Layer Heights	Constant	Time-varying densities and depths	Constant, except top cell	Time-varying densities and depths
Tank Pressure	Given and constant	Given constant	Given constant	Given constant
Liquid Density As a Function of Temperature and Composition	Yes (but data base was not stated)	Not stated	Interpolation in tabulation of Boyle (1972)	Interpolation in tabulation of Boyle (1972)
Boil-Off Rate Expression	Hashemi-Wesson (1971)	Flash vaporization of bulk liquid of upper cell	Hashemi-Wesson (1971)	modified Hashemi-Wesson (1971)
Turner's (1965) Thermohaline Heat and Mass Transfer Rates	ACCEPTED with no change of heat transfer rates; mass transfer rates were doubled for Lewis number effect	ACCEPTED; used individual mass transfer coefficients	$R_c = 2$ ACCEPTED and Huppert's (1971) heat and mass transfer expressions	REJECTED in favor of the usual turbulent natural convection
Mass Transfer between Liquid Cells	Equimolar Counterdiffusion	Not stated, but presumably equimolar counterdiffusion	Diffusion handled on a mass basis	Equimolar Counterdiffusion
Saturation Condition of the Top Layer Temperature	Film temperature same as bulk temperature (a function of the bulk composition)	Used a detailed flash calculation	Determined by the bulk composition of top cell and the tank pressure	Film liquid and vapor at equilibrium at film temperature
Vapor-Liquid Equilibrium Model	Insufficient details given	Three-component mixture with (variable ?) K-values	Ideal solution; Clausius-Clapeyron equation used for methane	Prausnitz-Chueh (1968) procedure using Soave-Redlich-Kwong equation

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* Sarsten (1972) gave the normal LaSpezia vapor removal rate as 0.278 kg s^{-1} (or approximately 0.0167 kgmol s^{-1} if the average molecular weight of the vapor is taken at 16.6).

** Information given by Sarsten leads to values for peak vapor removal rate in the range 0.417 to 1.67 kgmol s^{-1}.

$$q_b = 20.82\ \text{W·m}^{-2}$$

$$q_{WL} = 6.94\ \text{W·m}^{-2}$$

$$q_{WV} = 6.94\ \text{W·m}^{-2}$$

$$q_t = 15.77\ \text{W·m}^{-2}$$

Composition

An examination of the initial conditions for the LaSpezia incident shows that temperature differences of the order of 5 K and liquid density differences of less than 0.7% are important. Thus, any approximation to the actual composition must permit matching of temperature and densities with an accuracy consistent with these data. For accurate modeling of the effects of boil-off on the composition good estimates of the vapor pressures are also required. Finally, even though nitrogen is a minor component of most LNG's, its effect on the vapor pressure and density is significant. Therefore, any approximation to the actual composition must include enough species to match liquid densities and vapor pressures at specified temperatures, and heats of vaporization whether or not nitrogen is present. It was found that this can be accomplished by using C_1 through C_4 normal hydrocarbons and nitrogen. A comparison of the computed initial conditions with those given by Sarsten (1972) for the LaSpezia incident is shown in Tables A-I and A-II.

Intercell Transfer

The thermohaline models of interfacial energy and mass transfer of Turner (1965) and Huppert (1971), for the initial conditions specified by Sarsten (1972) for LaSpezia, show that mass transfer is sensibly negligible until the densities are nearly equal. That is, the time required for equalization of the densities is mainly dependent on heat transfer between the cells. An analysis of the heat transfer estimated from the thermohaline model shows that the time to rollover for the LaSpezia case would be about three times that reported. This discrepancy is far too great to be attributable to errors in the data. The only sensible conclusion is that the thermohaline model is not applicable. Significant mass transfer must take place at an early stage.

In the present model it was assumed that the transfer from either cell to the interface is for fully turbulent conditions, i.e., $h_i/(k_i\hat{C}_L) = 1$. There are, thus, two turbulent convection films at each interface, one from each cell, and the motion is characterized by the Grashof number,

$$N_{Gr} = \left(\frac{gL^3\Delta\rho}{\nu^2\bar{\rho}}\right).$$

If the compositions are uniform, this expression reduces to the usual heat transfer Grashof number. If the interface has a density intermediate between the two cells, then the overall transfer coefficient at an interface will be $(2)^{-4/3}$ the value for a single heated plate facing upward (or cooled plate facing downward). McAdams (1954) gives a correlation for this case, based on data for air:

$$hL/k = 0.14(N_{Pr})^{1/3}(N_{Gr})^{1/3}$$
$$= 0.1243(N_{Gr})^{1/3}$$

since the Prandtl number for air is 0.7. It is believed that the Prandtl number plays no role in the circulatory flow heat transfer in the LNG system. The heat transfer coefficient predicted for the interfacial heat transfer (cell to cell) from the McAdams correlation

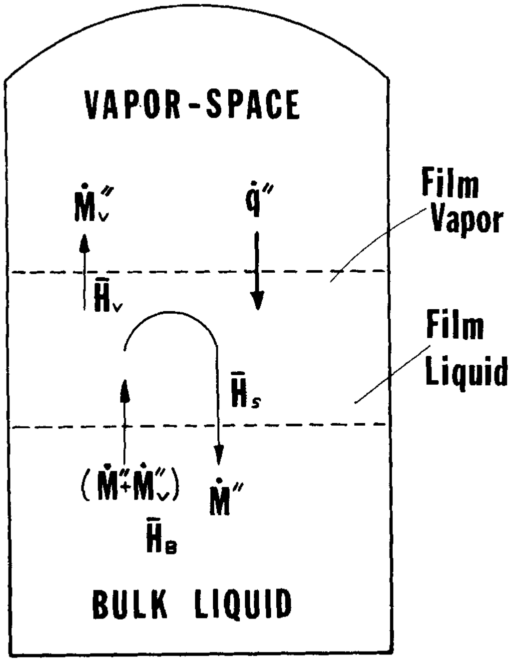

Figure 2. Boil-off from the interfacial film showing the circulatory Rayleigh flow.

is

$$h = 0.0493\,k\left(\frac{g\Delta\rho}{\nu^2\bar{\rho}}\right)^{1/3} \tag{1}$$

An alternative expression for intercellular heat transfer coefficient is provided by the correlation of Globe and Dropkin (1959) for transfer through the fluid placed between two horizontal plates and heated from below. Here the two convective films are already accounted by the correlation:

$$hL/k = 0.069(N_{Pr})^{0.407}\,(N_{Gr})^{1/3}$$
$$= 0.0597\,(N_{Gr})^{1/3}$$

The predicted heat transfer coefficient is then

$$h = 0.0597\,k\left(\frac{g\Delta\rho}{\nu^2\bar{\rho}}\right)^{1/3} \tag{2}$$

Vaporization

In order to maintain a proper accounting of the composition and temperature of the top cell and to describe "weathering" of the stored LNG, an accurate model of the composition and rate of evolution of the vapor is needed. For the present work a modified Hashemi-Wesson (1971) model was chosen as applicable to the larger tanks of interest.

It is assumed that the vapor evolved is in thermodynamic equilibrium with an arbitrarily thin film of liquid on the surface of the top cell. Energy is transmitted to this film from the vapor space above at rate $\dot{q}''$ and energy and mass are exchanged between the film and the liquid below it. The concept is shown schematically in Figure 2. The appropriate energy and material balances are:

$$(\dot{M}'' + \dot{M}''_V)\bar{H}_B - \dot{M}''\,\bar{H}_S - \dot{M}''_V\bar{H}_V + \dot{q}'' = 0 \tag{3}$$

$$(\dot{M}'' + \dot{M}''_V)x_B(j) - \dot{M}''x_S(j) - \dot{M}''_V y_S(j) = 0 \quad (j = 1,2,\ldots,5) \tag{4}$$

$\dot{M}''$ is the "Rayleigh flow," mass interchange between the bulk liquid and the film; there is no mass or energy accumulation in the film.

In addition to Eqs. 3 and 4, the equilibrium between the surface liquid and the evolved vapor relates $\bar{H}_V$ and $y_S(j)$ to $\bar{H}_S$ and $x_S(j)$ and the temperature of the film must be such that the vapor pressure matches the tank pressure. The rate of vapor evolution is, then,

$$\dot{M}''_V = \left[\frac{\dot{M}''(\bar{H}_B - \bar{H}_S) + \dot{q}''}{(\bar{H}_V - \bar{H}_B)}\right] \tag{5}$$

Note: This analysis is not valid for condensation from the vapor which would obtain should the Eq. 5 give a negative value of $\dot{M}''_V$.

After Hashemi and Wesson (1971) the Rayleigh flow is taken

$$\dot{M}'' = 0.3276\,\frac{k}{\hat{C}_{L,\mathrm{BULK}}}\left(\frac{g|\Delta\rho|}{\nu\kappa\bar{\rho}}\right)^{1/3} \tag{6}$$

where the absolute value of the density difference rather than the temperature difference has been used; the numerical coefficient is that given by Hashemi and Wesson (1971).

The value of $\dot{q}''$ in Eq. 5 is of some importance and difficult to estimate from first principles owing to the hydrodynamic stability of the mass in the vapor space, the venting of the vapor, and the transpiration of vapor from the surface of the liquid. The value of $\dot{q}''$ is not negligible, however, because the energy required for the normal boil-off rate is greater than the heat flux through the wetted side walls and the bottom of the tank. An energy balance on the vapor space, employing the heat fluxes q_t and q_{WV} (given above) and the normal boil-off rate, indicates that unless about 95% of the heat transmitted to the vapor space is transferred to the liquid phase, the computed temperature of the vapor space becomes unreasonably high. Accordingly, it is assumed in the present model that 95% of the heat transmitted to the vapor space of the tank is transmitted to the liquid film of the top cell.

The dynamics of the rollover are sensibly unaffected by a reduction of the percentage of vapor-space heat flux transferred to the film to 85%. This is the only consideration in the present program which is dependent on knowledge of actual LNG tank operations.

The Model

The model is based on material and energy balances on the N cells (liquid strata) and the vapor space, the number indices beginning at the bottom. These balances include cargo transfer and liquid recirculation.

Cell 1

$$\frac{d}{dt}\,[C_1L_1x_1(j)] = (\dot{M}_{CG,1}/A)x_{CG,1}(j) - (\dot{M}_{R,1}/A)x_1(j) + k_1[x_2(j) - x_1(j)] \tag{7}$$

$$\frac{d}{dt}\,[C_1L_1\hat{C}_{L,1}(T_1 - T_0] = (\dot{M}_{CG,1}/A)\hat{C}_{L,CG,1}(T_{GC,1} - T_0) + q_b + \left(\frac{q_{WL}\pi DL_1}{A}\right) + h_1(T_2 - T_1) \tag{8}$$

Cells i = 2 to N − 1

$$\frac{d}{dt}\,[C_iL_ix_i(j)] = k_{i-1}[x_{i-1}(j) - x_i(j)] + k_i[x_{i+1}(j) - x_i(j)] \tag{9}$$

$$\frac{d}{dt}\,[C_iL_i\hat{C}_{L,i}(T_i - T_0)] = \left(\frac{q_{WL}\pi DL_i}{A}\right) + h_{i-1}(T_{i-1} - T_i) + h_i(T_{i+1} - T_i) \tag{10}$$

Cell N (Top Cell)

$$\frac{d}{dt}\,[C_NL_Nx_N(j)] = (\dot{M}_{CG,N}x_{CG,N}(j)/A) - \dot{M}''_V y_S(j) + (\dot{M}_{R,N}x_{R,N}(j)/A) + k_{N-1}[x_{N-1}(j) - x_N(j)] \tag{11}$$

$$\frac{d}{dt}\,[C_NL_N\hat{C}_{L,N}(T_N - T_0)] = \left(\frac{q_{WL}\pi DL_N}{A}\right) + h_{N-1}(T_{N-1} - T_N) + f_Q\left(\frac{Q}{A}\right) - \dot{M}''_V\bar{H}_V + (\dot{M}_{CG,N}/A)\hat{C}_{L,CG,N}(T_{CG,N} - T_0) \tag{12}$$

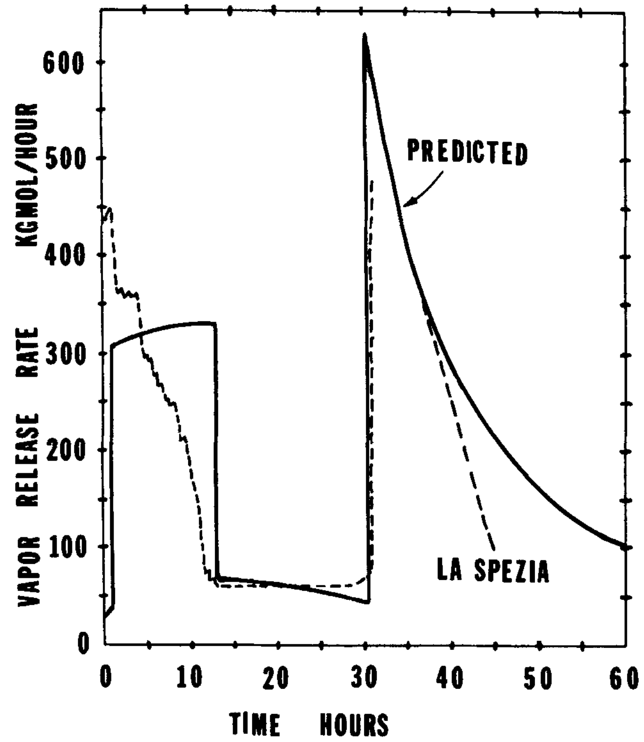

Figure 3. Predicted vapor release rate for the LaSpezia rollover compared with Sarsten's reported data.

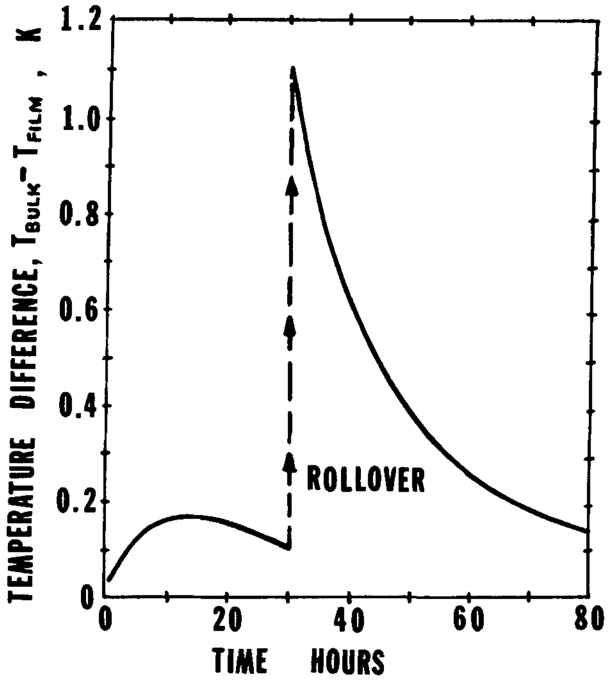

Figure 5. Predicted temperature difference between the bulk liquid and vaporizing film as a function of time (LaSpezia).

where

$$Q = q_t A + q_{WV} \pi D L_{VS} \tag{13}$$

and $\overline{H}_V$ is the specific enthalpy of the material added to the vapor-space from the vaporizing film, relative to liquid of the same composition at temperature T_0. The methods for treating liquid recirculation are, for reasons of brevity, not included in the present paper. They are, however, a part of the program and included with the supplementary material deposited.

Vapor-liquid equilibrium in the system is treated by the method of Prausnitz and Chueh (1968) as amplified by Zudkevitch and Joffe (1970), Joffe et al. (1970), Soave (1972), Hirata et al. (1975), Kato et al. (1976), and Valencia-Chávez (1978). The Soave-Redlich-Kwong equation of state is used.

Liquid densities are computed by interpolation within the tabulations of density, composition and temperature prepared by Boyle (1972).

A computer program (ROLLO) has been written to integrate these equations from the specified initial conditions. A fourth order Runge-Kutta numerical integration is used. The necessary values

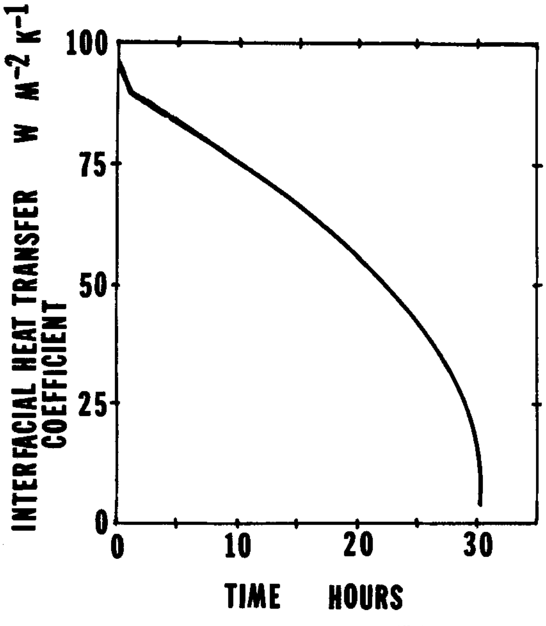

Figure 4. Predicted interfacial heat transfer coefficient prior to rollover (LaSpezia).

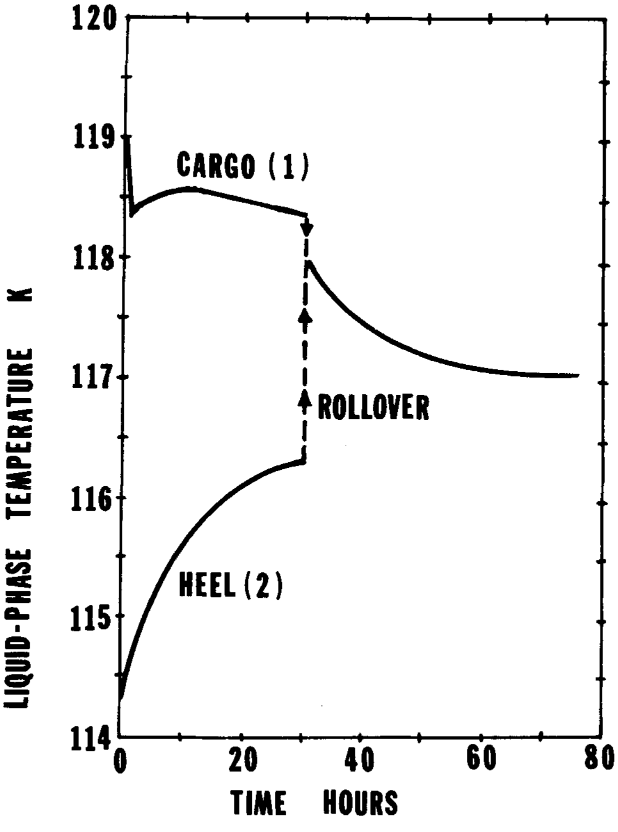

Figure 6. Predicted bulk temperatures of the cargo and heel cells as functions of time (LaSpezia).

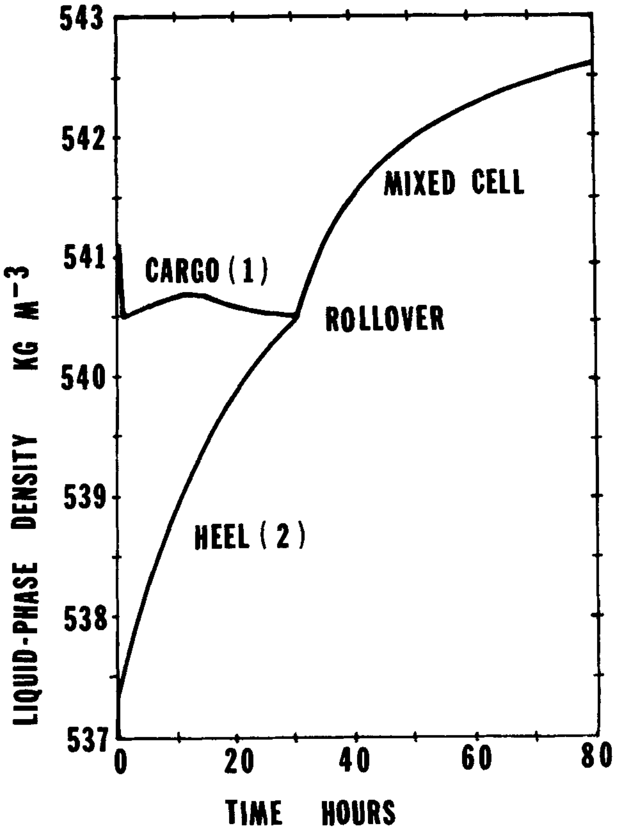

Figure 7. Predicted bulk densities of the cargo and heel cells as functions of time (LaSpezia).

of temperature, density, composition, boil-off rate, transfer coefficients, etc. are computed at the start of each time increment.

RESULTS

The initial conditions used for simulation of the LaSpezia incident are given in the Appendix, Table A2, and the program print-out is Supplement Table S1; the 43,200 seconds of cargo transfer is included in the computation. Two cells, cargo and heel, were considered. The computed results are shown in Figures 3 to 8. All of these Figures are drawn up from the results calculated with the program ROLLO using the equation $N_{Nu} = 0.0425\,(N_{Ra})^{1/3}$ to evaluate the intercellular heat transfer coefficient. This equation differs slightly from $N_{Nu} = 0.0553\,(N_{Gr})^{1/3}$, which comes about if the Prandtl number of LNG is put equal to 2.2 (exactly). In fact, the Prandtl number is composition dependent; this variation has not been properly handled in arriving at the latter equation. The major difference is approximately 1% difference in the predicted rollover time.

The computed vaporization rate is compared with that reported by Sarsten (1972) in Figure 3. The predicted time to rollover, 109,800 seconds, is close to the reported value, 111,600 seconds. The computed boil-off rate in the period between the end of cargo transfer and the onset of rollover is also satisfactory. Obviously the cargo transfer and rollover processes will not be modeled accurately with the assumption of completely steady operation for the former and instantaneous mixing for the latter. Nonetheless, the agreement is striking. Figure 4 illustrates the strong variations of intercellular heat transfer coefficient that result. Figure 5 shows the difference between the bulk temperature of the top cell and the computed temperature of the liquid film from which the vaporization takes place. The computed difference is in agreement with that reported by Huntley (1957) for nitrogen. The density differences are shown in Figure 8. That these small differences can account for the necessary energy transfer is important and perhaps surprising. The composition of the film is not greatly different from the bulk. The difference for the nitrogen is important; the effect on the rate of nitrogen evolution is significant, especially for LNG's with higher nitrogen content and for computation of the "weathering."

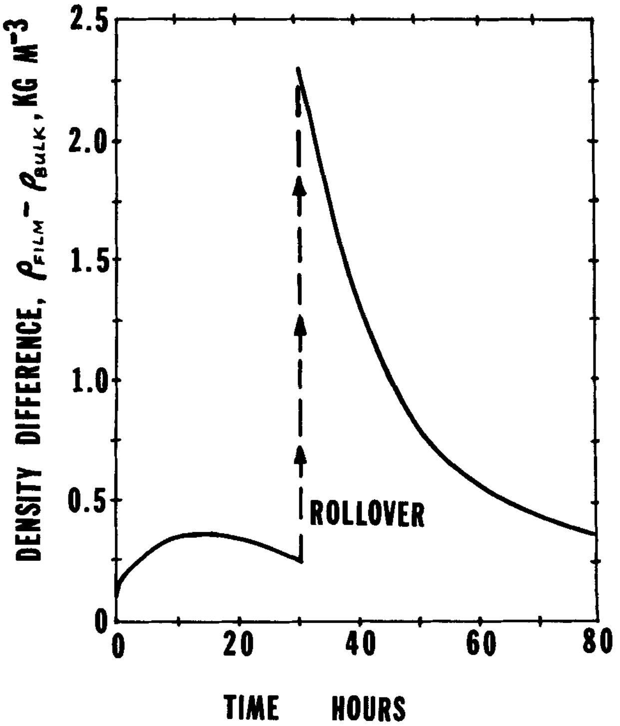

Figure 8. Predicted liquid density difference between the vaporizing film and the bulk liquid as a function of time (LaSpezia).

The temperatures and densities of the two cells as functions of time are shown in Figures 6 and 7. It is significant that about 2 K difference in temperature at rollover can give rise to a several-fold increase in vaporization rate. This emphasizes the need for the accurate modeling of compositions used in the present model.

Table 2 provides comparisons of predicted rollover times, average boil-off rates after cargo transfer and before rollover, and peak boil-off rates after rollover for several candidate expressions for the intercellular Nusselt number. The calculations show that retention of a Prandtl number effect, such as the McAdams (1954) or Globe and Dropkin (1959) correlations, leads to incubation periods which are significantly too short and boil-off rates too large during incubation. If it is assumed these correlations are valid for air ($N_{Pr} = 0.7$) and LNG ($N_{Pr} = 2.2$, approximately), and if the Prandtl number influence is removed from the correlations, one obtains equations of the form

$$N_{Nu} = (\text{constant})(N_{Gr})^{1/3}$$

The modified correlations have multiplicative constants of 0.0493 and 0.0597, respectively. An arithmetic average constant, 0.0545, provides predictions of rollover time and boil-off characteristics with surprising fidelity to the data of Sarsten (1972).

SUMMARY OF TECHNICAL CONCEPTS

1. The temperature-density-vapor pressure characteristics of LNG can be described adequately by a five component mixture of methane, ethane, propane, n-butane and nitrogen.
2. Vapor-liquid equilibrium can be simulated by the Prausnitz-Chueh (1968) method, using the Soave-Redlich-Kwong (1972) equation of state for the species.
3. Stratified, stable layers can exist in LNG storage tanks. Such nearly homogeneous layers can have developed within them essentially turbulent circulatory motions from density variations much less than those involved in the stratification.

TABLE 2. ROLLOVER TIME, AVERAGE BOIL-OFF RATE AFTER CARGO TRANSFER AND BEFORE ROLLOVER, AND PEAK BOIL-OFF RATE AT ROLLOVER. VALUES ARE CALCULATED BY ROLLO FOR SEVERAL ALTERNATIVE EXPRESSIONS FOR THE INTERCELLULAR HEAT TRANSFER COEFFICIENT

Eq. for Intercellular Heat Transfer Coefficient	Rollover Time, s (h)	Avg. Boil-Off Rate after Cargo Transfer and before Rollover, kgmol/h	Peak Boil-Off Rate after Rollover, kgmol/h
$N_{Nu} = 0.0731\,(N_{Ra})^{1/3}$ (Globe and Dropkin, 1959, with Prandtl No. Effect Retained)	73,400 (20.4)	79.0	618.0
$N_{Nu} = 0.0556\,(N_{Ra})^{1/3}$ (McAdams, 1954, with Prandtl No. Effect Retained)	89,200 (24.8)	68.0	625.0
$N_{Nu} = 0.0597\,(N_{Gr})^{1/3}$ (Globe and Dropkin, 1959, with Prandtl No. Effect Removed)	102,200 (28.4)	60.0	631.0
$N_{Nu} = 0.0493\,(N_{Gr})^{1/3}$ (McAdams, 1954, with Prandtl No. Effect Removed)	119,200 (33.1)	54.0	639.0
$N_{Nu} = 0.0425\,(N_{Ra})^{1/3}$ (Case for Which Figures 3-8 Were Drawn)	109,800 (30.5)	57.0	634.0
$N_{Nu} = 0.0553\,(N_{Gr})^{1/3}$ (Case Corresponding to Figs. 3-8 if Prandtl No. Effect Removed)	108,700 (30.2)	57.0	634.0

4. Mass and heat transfers between stratified cells in an LNG storage tank are described by transfer equations appropriate to fully turbulent exchange processes. They are *not* described by the thermohaline transfer equations proposed by Turner (1965) and Huppert (1971) for salt-sugar solutions. The heat transfer coefficient is described by a turbulent natural convection equation of the form

$$h_i = (\text{constant})k\left(\frac{g\Delta\rho}{\nu^2\bar{\rho}}\right)^{1/3}$$

where $\Delta\rho$ is the *total* density difference between the bulk phases which are interacting. The multiplicative constant is intermediate to the coefficients associated with the McAdams (1954) and Globe and Dropkin (1959) correlations, after removal of the Prandtl number effects. The mass transfer rate of each species across an interface is described by the product of a common mass transfer coefficient, $k_i = h_i/\hat{C}_L$, and the difference in mol fractions of the species in the two cells.

5. Vaporization rates of LNG can be described by a *modified* Hashemi-Wesson (1971) equation which includes implicitly the influence of composition as well as temperature variations. A thin film of vaporizing material is assumed to exist at the vapor-liquid interface. It is in communication by mass and heat transfer with the bulk liquid below it through the "Rayleigh circulation flow," and it receives heat from the vapor-space above. The evolved vapor is in thermodynamic equilibrium with the film liquid.

6. The program ROLLO provides a predictive tool to examine the likelihood of rollover in stratified LNG storage tanks. The incubation period boil-off and the intensity of such a rollover can be studied. "Weathering" characteristics of LNG stored at constant tank pressure can also be examined.

TABLE A1. INITIAL CONDITIONS FOR LASPEZIA ROLLOVER

Components	Initial Heel	Esso Brega Cargo
Methane	63.62 mol%	62.26 mol%
Ethane	24.16	21.85
Propane	9.36	12.66
n-Butane	1.45	1.94
iso-Butane	0.90	1.20
n-Pentane	0.05	0.01
iso-Pentane	0.11	0.06
Nitrogen	0.35	0.02
	100.00	100.00
Temperature (K)	114.356	118.994
Liquid Depth (m)	5.029	17.831
Density (kg/m^3)	541.742	545.586
Vapor Pressure (N/m^2)	3923.0	16,280.
Vapor Space Height after Filling		3.962 m

TABLE A2. FACTORS USED FOR ROLLO

Components	Initial Heel	Esso Brega Cargo
Methane	63.62 mol%	62.26 mol%
Ethane	24.16	21.85
Propane	9.36	12.66
n-Butane	2.51	3.21
Nitrogen	0.35	0.02
	100.00	100.00
Temperature (K)	114.355	118.997
Density (kg/m)	537.316 (Calculated)	541.118 (Calculated)
Liquid Depth (m)	5.029	
Vapor-Space Temperature	122.039 K	
Vapor-Space Height	20.422 m	(95.0 mol% CH_4 and 5.0 mol% N_2)

Heat-Leak Rates	Location of Heat-Leak	Initial Total Heat Flux
$q_b = 20.82\ \text{W·m}^{-2}$	Tank Bottom	39,390 W
$q_{WL} = 6.94\ \text{W·m}^{-2}$	Tank Walls to Liquid	19,080 W (Cargo) 5,390 W (Heel)
$q_{WV} = 6.94\ \text{W·m}^{-2}$	Tank Walls to Vapor	4,250 W
$q_t = 15.77\ \text{W·m}^{-2}$	Vapor Dome	29,840 W
		Total = 97,950 W

APPENDIX: THE LaSPEZIA ROLLOVER

The initial conditions for the LaSpezia rollover were given by Sarsten (1972). Briefly, they are as shown in Table A1.

Initial heel and cargo depths, temperatures, densities, compositions and heat-leak rates used in ROLLO for the LaSpezia case are given in Table A2.

NOTATION

A = cross-sectional area of LNG tank, m^2
A = constant in vapor pressure equation (Table 1)
B = constant vapor pressure equation (Table 1)
$\bar{C}$ = molar liquid concentration (averaged between two neighboring cells, kgmol·m^{-3}
C_i = molar concentration of cell i liquid, kgmol·m^{-3}
$\hat{C}_L$ = molar liquid heat capacity (taken to be a function of composition but independent of temperature), J·kgmol^{-1}·K^{-1}

$\hat{C}_L(j)$ = molar liquid heat capacity of species j, J·kgmol^{-1}·K^{-1}

$\hat{C}_{L,\mathrm{BULK}}$ = molar heat capacity of bulk liquid in uppermost cell, J·kgmol^{-1}·K^{-1}

$\hat{C}_{L,CG,i}$ = molar heat capacity of cargo transfer liquid to cell i, J·kgmol^{-1}·K^{-1}

$\hat{C}_{L,F}$ = average molar heat capacity of a liquid having the same composition as the flash vapor, J·kgmol^{-1}·K^{-1}

$\hat{C}_{L,i}$ = molar heat capacity of cell i liquid, J·kgmol^{-1}·K^{-1}

$\hat{C}_{L,R}$ = average molar heat capacity of the residue liquid from flashing, J·kgmol^{-1}·K^{-1}

C_p = mass heat capacity at constant pressure, J·kg^{-1}K^{-1}

$\hat{C}_V(j)$ = molar vapor heat capacity of species j, J·kgmol^{-1}·K^{-1}

$\hat{C}_{V,F}$ = average molar heat capacity of flash vapor, J·kgmol^{-1}·K^{-1}

$\hat{C}_{V,S}$ = average molar heat capacity of vaporizing material, J·kgmol^{-1}·K^{-1}

$\hat{C}_{V,VS}$ = average molar heat capacity of vapor-space material, J·kgmol^{-1}·K^{-1}

D = Diffusion coefficient, m^2·s^{-1}

f_Q = fraction of total heat transfer to the vapor-space which is passed along to the vaporizing film, dimensionless

f_V = fraction of the feed liquid which flashes, dimensionless

$f(\;)$ = function of the quantity within the parentheses

g = acceleration of gravity, 9.80665 m·s^{-2}

h = turbulent natural convection heat transfer coefficient (heat transfer through fluid confined between two parallel plates held at different temperatures and with heat flow upwards), W·m^{-2}·K^{-1}

h_i = heat transfer coefficient across the interface between cell i and cell $(i + 1)$ liquids, W·m^{-2}·K^{-1}

h_{SP} = heat transfer coefficient for turbulent natural convection between two horizontal flat plates, W·m^{-2}·K^{-1}

$\overline{H}$ = specific enthalpy of liquid or vapor, J·kgmol^{-1}

$\overline{H}_V$ = enthalpy of vapor evolved from the vaporizing film, J·kgmol^{-1}

i = index used to identify cell numbers (cells are numbered upwards beginning from the bottom of the tank: $i = 1,2,\ldots,N$)

j = index used to identify species: $j = 1,2,\ldots,5$

1 = methane 4 = n-butane

2 = ethane 5 = nitrogen

3 =propane

k = thermal conductivity of LNG, 0.185 W·m^{-1}·K^{-1}

k_i = turbulent mass transfer coefficient for all species across the interface between cell i and cell $(i + 1)$, kgmol·m^{-2}·s^{-1} Δ(mol fraction)$^{-1}$

k_x = turbulent mass transfer coefficient for all species, kgmol·m^{-2}·s^{-1} Δ(mol fraction)$^{-1}$

L = height, m

L_i = height of cell i liquid, m

L_{TANK} = overall height of tank, m

$\dot{L}$ = molar flow-rate of recirculating liquid or cargo transfer to be flashed in the vapor-space, kgmol·s^{-1}

M_{VS} = total mols of vapor in the LNG tank vapor-space, kgmol

$\dot{M}_{CG,i}$ = cargo transfer flow-rate to cell i, kgmol·s^{-1}

$\dot{M}_F$ = molar rate of addition of flash vapor to vapor-space, kgmol·s^{-1}

$\dot{M}_{OUT}$ = molar venting rate from the vapor-space, kgmol·s^{-1}

$\dot{M}_{R,1}$ = recirculation liquid flow-rate from cell 1, kgmol·s^{-1}

$\dot{M}_{R,N}$ = recirculation liquid flow-rate to cell N, kgmol·s^{-1}

$\dot{M}_V$ = molar vaporization rate from the vaporizing film, kgmol·s^{-1}

$\dot{M}''$ = Rayleigh flow-rate (circulation current between the vaporizing film and the bulk liquid in uppermost cell), kgmol·m^{-2}·s^{-1}

$\dot{M}_V''$ = vaporization rate at the vapor-liquid interface, kgmol·m^{-2}·s^{-1}

N = total number of stratified liquid cells in LNG tank (also designates the top liquid cell in tank), dimensionless

N_{Le} = Lewis number ($N_{Le} = N_{Sc}/N_{Pr}$), dimensionless

N_{Nu} = Nusselt number ($N_{Nu} = hL/k$), dimensionless

N_{Pr} = Prandtl number ($N_{Pr} = C_p\mu/k$), dimensionless

N_{Ra} = Rayleigh number ($N_{Ra} = \beta\Delta TgL^3/\nu\kappa$), dimenless

N_{Sc} = Schmidt number ($N_{Sc} = \mu/\rho D$), dimensionless

P^o = vapor pressure, N·m^{-2}

q_b = heat leak rate into bottom of LNG tank, W·m^{-2}

q_{WL} = heat leak rate into liquid side-wall of LNG tank, W·m^{-2}

q_{WV} = heat leak rate into vapor side-wall of LNG tank, W·m^{-2}

q_t = heat leak rate into vapor dome of LNG tank, W·m^{-2}

$\dot{q}''$ = rate of heat transfer from vapor-space to vaporizing film, W·m^{-2}

Q = total heat transfer rate to vapor-space from surroundings, W

R = Stability parameter, $R = (\alpha\Delta S/\beta\Delta T)$, the ratio of the stabilizing influence of a difference in salinity, ΔS, to the destabilizing influence of a temperature difference, ΔT, dimensionless

R_c = critical value of the stability parameter

t = time, s or h

T = temperature, K

T_{BULK} = bulk liquid temperature of uppermost cell, K

$T_{CG,i}$ = temperature of cargo transfer liquid fed to cell i, K

T_F = temperature of flash vapor added to vapor space, K

T_{FILM}, T_S = interfacial temperature between uppermost cell and vapor-space, K

T_i = Temperature of liquid in cell i, K

T_o = reference temperature for zero liquid-phase enthalpy for all species, 99.82 K

T_{VS} = vapor-space temperature, K

U_{BL} = boundary layer velocity, m^{-1}

x = liquid-phase mol fractions, dimensionless

$x_B(j)$; $x_N(j)$ = mol fraction of species j in the bulk liquid of the uppermost cell, dimensionless

$x_{CG,i}(j)$ = mol fraction of species j in liquid cargo transfer to cell i, dimensionless

$x_i(j)$ = liquid phase mol fraction of species j in cell i, dimensionless

$x_R(j)$ = mol fraction of species j in the residue liquid from flashing, dimensionless

$x_{R,1}(j)$ = mol fraction of species j in the recirculation flow from cell 1, dimensionless

$x_{R,N}(j)$ = mol fraction of species j in the recirculation flow to cell N, dimensionless

$x_S(j)$ = mol fraction in liquid-phase of species j in vaporizing film, dimensionless

y = vapor-phase mol fractions, dimensionless

$y_F(j)$ = mol fraction of species j in the flash vapor, dimensionless

$y_S(j)$ = mol fraction in vapor-phase of species j in vaporizing film, dimensionless

$y_{VS}(j)$ = mol fraction of species j in the vapor-space, dimensionless

Greek Letters

α = fractional density increase per unit salinity difference, m^3·kg^{-1}

β = thermal expansion coefficient for liquid-phase (a function of temperature and composition), K^{-1}

$$\beta = -\frac{1}{\rho}\left(\frac{\partial \rho}{\partial T}\right)_x$$

ΔS = salinity difference, kg·m^{-3}
ΔT = temperature difference between two neighboring cells or between bulk and film, K
Δx = difference of liquid-phase mol fractions, dimensionless
$\Delta \rho$ = difference of liquid density for two neighboring cells or between bulk and film, kg·m^{-3}
κ = thermal diffusivity of LNG ($\kappa = k/\overline{C}\hat{C}_L$), 1.267 × 10^{-7}m^2·s^{-1}
λ_F = molar latent heat of vaporization of flash vapor, J·kgmol^{-1}
$\lambda(j)$ = latent heat of vaporization of species j at 99.82 K, J·kg^{-1}
μ = viscosity of LNG, kg·m^{-1}·s^{-1}
ν = kinematic viscosity of LNG, 2.787 × 10^{-7} m^2·s^{-1}
ρ_i = density of cell i liquid, kg·m^{-3}
$\overline{\rho}$ = averaged liquid density between two neighboring cells or between uppermost cell and the film, kg·m^{-3} [e.g., $\overline{\rho} = \frac{1}{2}(\rho_i + \rho_{i+1})$]
ρ_{BULK} = density of bulk liquid of the uppermost cell, kg·m^{-3}
ρ_{FILM} = density of liquid in the vaporizing film, kg·m^{-3}

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Characteristics of a Transferred-Arc Plasma

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The basic characteristics of a transferred arc argon plasma were determined using a cathode assembly suitable for transferring the electric arc to a molten metal bath or to a cooled anode. They indicated that the sustained voltage depended strongly on the arc length and much less on current. The inlet gas velocity past the cathode tip was determined to be an important operating parameter, rather than the volumetric gas flowrate.

The measurement of the axial and radial profiles of temperature was effected with ±8% accuracy by a novel diagnostic technique. Temperatures up to 18,500 K were observed on the axis of the plasma column, near the cathode tip, and decayed in both radial and axial directions. A sweeping microprobe was used to measure the axial and radial profiles of velocity. Velocities up to 190 m/s were recorded. The presence of a relatively colder flow surrounding the plasma column was detected. Mass and energy balances performed by taking this flow into account agreed with the measured input rates.

SCOPE

The application of plasma technology to chemical and metallurgical processes has been receiving increasing attention in the last two decades. Not only does a thermal plasma as a heat source permit greatly increased rates of reaction in most processes of industrial interest, but it frequently allows reactions to occur which would not be feasible at the lower temperature

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