

Analysis of Available Data from Liquefied Natural Gas Rollover Incidents to Determine Critical Stability Ratios

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Liquefied natural gas (LNG) rollover refers to the sudden mixing of stratified LNG layers, which can cause the generation of significant amounts of boil-off gas. Such events are a significant safety concern in LNG storage but there are no reliable models for its description at industrial scales available in the open literature. In this article, the data and models for LNG rollover existing in the open literature are reviewed and a new framework for quantitatively analyzing the limited available data is presented. We extended the definition of the hydrostatic stability ratio for binary mixtures to allow its estimation for multicomponent mixtures, either from the reported LNG layer compositions or measurements of the LNG layer densities. By analyzing the graphical data of Bates and Morrison (*Int J. Heat Mass Transfer*, 1997;40:8) the critical value of the stability ratio, R_c , separating the diffusive phase of LNG rollover from the penetrative convection phase was estimated to be 3.8 ± 0.5 . This is significantly larger than the critical ratio of 2 reported for saline solutions and is also larger than the initial stability ratio of 1.7 estimated from the best documented LNG rollover incident at La Spezia in 1971. Lumped-parameter models for LNG rollover reported in the literature have successfully described the La Spezia incident by using the Reynolds analogy to estimate mass transfer rates from heat transfer correlations. However, these same models are unsuccessful when applied to other reported LNG rollover incidents, with the predicted rollover time being too short because the mass-transfer coefficient is overestimated. The results presented here suggest that these limitations could be overcome by using a smaller mass-transfer coefficient (estimated, e.g., from the Chilton-Colburn analogy) and by tracking the multicomponent system's stability ratio until the critical value is reached whereupon the mass transfer regime changes. © 2013 American Institute of Chemical Engineers *AIChE J.*, 60: 362–374, 2014
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Introduction

Liquefied natural gas (LNG) is a mixture predominately containing methane, with lower levels of other components such as ethane, propane, butane, and nitrogen, that is usually stored and transported in liquid form at pressures near atmospheric and temperatures near -162°C . The composition of LNG differs from region to region and plant to plant, based on the source raw gas composition, the type of processing, and the level of purification. At both shipping and receiving terminals, and during intercontinental sea transportation, LNG is usually stored in full containment cryogenic tanks. In all LNG storage applications, rollover is a major

concern in terms of safety and asset integrity, and the potential for its occurrence is avoided as carefully as possible.

Rollover is a phenomenon that can occur in systems containing stratified liquids. Some examples¹ include saline water layers in the ocean, water layers in volcanic lakes, and liquefied petroleum gas (LPG) or LNG layers in storage tanks loaded with different products. The rollover phenomenon was first studied by physical oceanographers. They tried to explain the reason water layers of different temperatures and salinities in deep oceans and volcanic lakes suddenly invert their positions.^{1,2} In general terms, rollover is a sudden mixing of the existing stratified layers of liquid. The stratified layers are characterized by different values of temperature and composition, which lead to different densities. Originally the layers were in mechanical (hydrostatic) equilibrium ($\rho_L > \rho_U$, where ρ_L is the mass density of the lower layer and ρ_U is the mass density of the upper layer). Over time, these densities can alter through changes in

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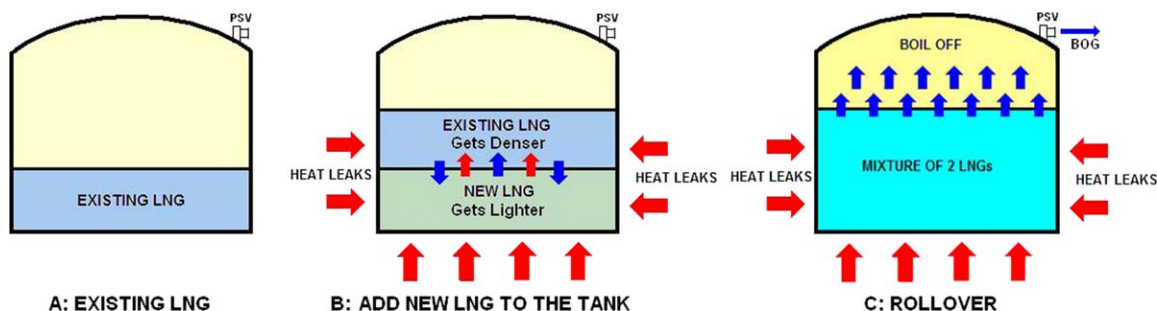


Figure 1. Schematic showing the stages of rollover in an LNG storage tank.

Blue arrows represent the mass transfer and red arrows represent the heat transfer. Upon rollover the additional BOG generated is vented through the pressure safety valves. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

temperature and composition, driven by heat and mass exchanges between the layers. If the layer densities evolve in such a way that the density difference $\rho_L - \rho_U \rightarrow 0$, but the temperature difference remains finite, the system can reach a point of hydrostatic instability, causing the liquid layers to mix rapidly.

Rollover in LNG storage tanks is a phenomenon that is not widely understood nor discussed thoroughly in the open literature. Such LNG rollover events are usually caused by inter-layer heat and mass transfer, as well as a net heat flow into the cryogenic storage tank. While at the moment of rollover the densities of the LNG layers have equalized, invariably their temperatures have not, which leads to the release of an abnormal amount of vapor into the storage tank, which must be handled and/or vented safely by the boil-off gas (BOG) handling system. Rollover can also occur in other multicomponent liquid hydrocarbon systems such as LPG but due to the higher design pressure of LPG storage tanks compared with those used for LNG (LNG storage tanks are atmospheric) the effect of rollover in LPG systems is usually not as severe as rollover occurrences in LNG storage. Furthermore, the cryogenic nature of LNG storage means that heat transfer from the environment provides a driving force toward stratification and hence the potential for rollover. A significant amount of research on LNG rollover has been conducted over several decades yet because of the commercial value of the results produced there is only a limited amount of data available in the open literature for scrutiny or analysis.

For LNG, rollover is most likely to occur following the loading of two or more LNGs from different sources/cargos, each with a different temperature and composition, into the same storage tank as shown in Stage A and B of Figure 1. The potential for LNG rollover increases if the richer composition layer with higher mass density but also higher temperature is on the bottom, and the lighter but colder layer on top. With time, the LNG layers absorb heat from the surrounding tank walls and the bottom base plate as shown in Figure 1, Stage B. The amount of heat entering through the tank bottom is greater than through the tank wall and so the temperature of the lower layer increases faster than the upper layer. As a result the thermal expansion of the lower layer will decrease its density at a faster rate than that of the upper layer. As the lower layer's temperature rises so does its vapor pressure but it does not boil because of the static pressure head from the upper layer. Although the temperature of the upper layer is increasing, its mass density can either increase or decrease depending on the effects of mass transfer between the two layers caused by their different compos-

tions. If the mass density of the upper layer increases in spite of its temperature increase, then the system's stability decreases and there is a potential for rollover. When rollover occurs, the hotter, more volatile liquid from the bottom is brought rapidly to the upper surface. The removal of the previously existing hydrostatic head (≈ 30 kPa) results in a "flash" and a large amount of boil-off, as shown in Figure 1 Stage C. This boil-off may be too large for the storage tank's pressure safety valves to handle.

Clearly, the procedure of loading new LNG cargos into a tank with an existing LNG is very important and must be done carefully to avoid the potential for rollover occurrence. Ensuring any loaded cargo is well mixed is obviously a strategy to mitigate rollover, and this is commonly practiced; however, excessive mixing also leads to the undesirable production of additional BOG. It is a common practice in modern LNG tankfarms to load the new cargo on top or below the existing LNG (based on their respective densities) to reduce the rate of BOG generation. Research into optimized methods of LNG tank loading is ongoing. For example, Koyama et al.³ conducted a computational fluid dynamics (CFD) simulation of the loading and unloading of a LNG tank to improve safety and reduce costs. They studied the process of filling the tank with different-density LNGs using numerical models and compared the model predictions with some limited operational measurements of temperature, density, and pressure in a small tank. They considered the BOG generation and its effect on rollover and concluded that the initial density difference, the initial LNG depth, and the filling rate were the most sensitive factors in the loading procedure that could lead to potential stratification.

The potential for LNG rollover can also arise after loading because stratified liquid layers can potentially evolve through the boil-off of lighter components driven by heat leaks to the cryogenic storage tank; this process is often called LNG weathering. Hashemi and Wesson⁴ provided a correlation for estimating the rate of evaporation of LNG in a storage tank as a function of the difference in temperature between the bulk liquid and the liquid surface. However, for liquid layer stratification to be predicted, information about the composition of the BOG is also needed. In particular, the amount of nitrogen in the LNG cargo is crucial and there is some evidence that excessive N_2 concentrations are related to the phenomenon of rollover.^{5,6} Nitrogen is the most volatile component of LNG, which boils off preferentially leading to an increase in the remaining liquid's bubble point temperature but also a reduction in its mass density (The molar masses of N_2 and CH_4 are 28 and 16, respectively).

Nitrogen-induced stratification (also known as auto-stratification) can occur if a sufficient quantity of nitrogen is present initially. Generally, the engineering specifications of allowed N_2 content in LNG are very low (about 1%^{6–8}) primarily because the exact details about nitrogen-induced rollover phenomenon are not well known. In general, the removal of N_2 from LNG feed streams is a difficult and expensive process, so a better understanding of exactly how N_2 content in the LNG leads to auto-stratification would be very valuable.^{9–11}

Actual industrial incidents of rollover, whether they have been caused by LNG weathering or loading, are rarely documented in the open literature. Acton and van Meerbeeke¹² reviewed the incidence of LNG rollover in the early stages of the LNG industry and found that over the 13 year period from 1970 to 1982, 41 incidents occurred in 22 plants. Over half the incidents were attributed to loading a new LNG to a storage tank with an existing inventory, and four were attributed to N_2 -induced auto-stratification. The most thoroughly documented occurrences of LNG rollover in the open literature are the La Spezia incident, as reported by Sarsten,¹³ and the Partington incident reported by Baker and Creed.¹⁴ Bates and Morrison¹⁵ also presented some limited data from measurements conducted at a facility in Nantes, France. In 2013, Lukaszewski et al.¹⁶ presented some information from instrumented LNG storage tanks about a rollover incident that occurred in the USA during 2007.

The majority of efforts to simulate industrial incidents of LNG rollover have benchmarked their simulations against the data reported by Sarsten¹³ for the La Spezia incident. Heestand et al.¹⁷ were the first to develop a model that matched adequately the observations of the La Spezia incident.¹³ Recently, Deshpande et al.¹⁸ described a model similar to that of Heestand et al.,¹⁷ implemented in modern software, and tested its predictions against the data reported for both La Spezia and Partington incidents.¹⁴ Deshpande et al.¹⁸ demonstrated the sensitivities of time to rollover predictions on the various parameters used in such models. Furthermore, while they could replicate the results reported from the La Spezia incident, they found a large discrepancy between the predicted and observed rollover times in the case of the Partington incident. Deshpande et al.¹⁸ identified that correctly describing heat and mass transfer between the layers was crucial to the prediction of any rollover models. Accordingly they extracted values of effective heat and mass-transfer coefficients by monitoring level-temperature-density data from instrumented LNG storage tanks and then regressing the model parameters to force agreement between the predicted and observed data. However, the results of Deshpande et al.¹⁸ indicate that the generality of current rollover models appears to be effectively limited to the description of the La Spezia incident.¹³

The objectives of this article are to explain this apparent limitation and, by suggesting the use of a more appropriate heat-mass transfer analogy, increase the generality of rollover models. To achieve this, the hydrostatic stability analysis developed originally by Turner² for binary saline solutions is extended to multicomponent LNG mixtures and is then used to estimate from available literature data the condition after which diffusion is no longer the dominant mass-transfer mechanism during LNG rollover.

Overview of Rollover Models

All rollover models require the solution of a set of equations describing the heat and mass transfer in the liquid and

vapor phases over time. There are two different approaches for modeling the heat and mass transfer in and between the (three) phases: lumped parameter (LP) models and distributed numerical models. For LP models, it is assumed that there are always distinguishable liquid and vapor layers in the system, which are separated by sharp interfaces. Heat and mass are exchanged across these interfaces. The liquid layers exchange components initially through diffusion in a direction governed by the difference in molar concentration of each component. One advantage of these LP models is that they can readily incorporate the effects of vaporization on the upper liquid layer. Such effects are very important but are much harder to replicate currently with distributed numerical models that are solved generally using CFD techniques. However, lumped-parameter models have an inherent limitation that can be avoided by using CFD; as the point of rollover is approached the boundaries between the stratified liquid layers become dynamic and less well defined. Table 1 presents a summary of the LP and CFD models for LNG rollover that have been described in the open literature.

In 1993, Shi et al.⁵ were one of the first groups to apply numerical modeling of fluid dynamics to the study of mixing between stratified liquid layers of liquid nitrogen and liquid oxygen mixtures. They also conducted ambient temperature experiments with liquid Freon mixtures, applying flow visualization techniques. The use of Freon meant that boil-off rates could not be measured reliably during their experiments and thus the experiments focused only on the liquid phase motions. Their results showed that the mixing of the two stratified layers involves two stages in sequence: migration of the interface followed by rapid mixing between the remaining liquids. These observations were consistent with the numerical simulations which used a free convective flow regime to model the mixing in rectangular tanks. A key conclusion of their work was that the ratio of the base to side heat flux into the tank is a major factor in determining the mode and intensity of the subsequent rollover event. This heat flux ratio determines the entrainment rates on the two sides of the (initial) interface, and helps determine when it starts to migrate. The longer the period prior to migration, the greater the rollover severity in terms layer mixing and boil-off generation. Shi et al.⁵ pointed out that that of the incidents reviewed by Acton and Van Meerbeke,¹² the amount of BOG produced was quite variable and that their model was only applicable to the most dramatic (end-) stages of the rollover. The ability to describe the comparatively long periods of time prior to interface migration is an essential feature of a comprehensive model for LNG rollover in industrial scenarios.

Zimmerman et al.¹⁹ further extended the numerical approach of investigating the rollover hydrodynamic instability and its dependence on diffusion. They used hydrodynamic and heat and mass transport equations to study the stability characteristics of rollover. They conducted a linear stability analysis of the system in a transient hydrodynamic state and concluded that the transition from a “corner eddy” mode spinning down to spinning up is the driver for the rollover instability. In building the numerical model, Zimmerman et al.¹⁹ identified and used time and length scales to convert the equations into relations between dimensionless quantities and groups. They identified that the indicative time scale for describing the rollover in the systems they simulated was the conductive time scale. However, if this time scale were to be applied to LNG storage tanks of

Table 1. Summary of the Lumped Parameter (LP) and CFD Models for LNG Rollover Described in the Open Literature

Year	Reference	Model type	Source of h	Source of k	Comparison	$\frac{t_{\text{rollover}}^{(\text{predicted})}}{t_{\text{rollover}}^{(\text{observed})}}$	Comment
1971	Chatterjee and Geist ⁷	LP-Pred	Correlation (flat-plate)	Saline analogy ²	La Spezia (1971) ¹³	1.35	(T, x) equalization as rollover criterion
1975	Germes ⁸	LP-Pred	Correlation (flat-plate)	Adapted saline analogy ²	La Spezia (1971) ¹³	1.10	Density equalization as rollover criterion
1983	Heestand et al. ¹⁷	LP-Pred	Correlation ²³	Reynolds	La Spezia (1971) ¹³	0.98	Abandoned saline analogy for Reynolds analogy to match La Spezia data
1993	Shi et al. ⁵	CFD	Not used. Replaced by thermal diffusivity + convection	Not used. Replaced by mass diffusivity + convection	Freon experiments		Predicted circulation & entrainment confirmed by visualization experiments
1997	Bates and Morrison ¹⁵	LP (diffusive Phase 1) & Parametric (convective Phase 2)	Assumed constant (diffusive phase)	Saline analogy (diffusive phase) ²	Nantes (1987–89)		Identified diffusive and convective phases in LNG rollover
2007	Zimmerman et al. ¹⁹	CFD	Not used. Replaced by thermal diffusivity + convection	Not used. Replaced by mass diffusivity + convection			Transition of corner eddy mode drives interface instability
2011	Deshpande et al. ¹⁸	LP-Pred LP-Pred LP-Inv (from Ref. 16) LP-Inv	Correlation ²² Correlation ²² Calculated from tank data Calculated from tank data	Reynolds Reynolds Calculated from tank data Calculated from tank data	La Spezia (1971) ¹³ Partington (1993) ¹⁴ USA (2007) ¹⁶ USA (2007) ¹⁶	1.01 0.01 1.12 0.90	Improved description of vaporization Showed Reynolds analogy not generally appropriate Optimization method (regression) Normal equations method

The LP models are classed as predictive (Pred) or inverse (Inv) depending on whether the heat (h) and mass (k) transfer coefficients were predicted or derived from tank data. For models that were compared with rollover incidents the ratio of the predicted to observed rollover time (t_{rollover}) is listed.

industrial dimensions, the characteristic rollover times would be of order 100 years.

A likely reason for the inapplicability of the results obtained by Zimmerman et al.¹⁹ to industrial-sized tanks was the choice of model boundary conditions selected for the nominal vapor–liquid interface in the CFD model. Zimmerman et al. investigated four different boundary conditions but all of them related to variations in the heat transfer at the interface with no mass transfer permitted at the vapor–liquid boundary: the absence of a significant vaporization rate in the CFD model means that the dominant boundary effects were not included. The effect on the CFD simulation of using any of the four thermal boundary conditions was found to be small, which further suggests that the heat loss due to vaporization and the change in composition of the upper liquid layer due to the preferential boil-off of more volatile components are the more important phenomena that need to be captured in any model of LNG rollover. To simulate rollover in LNG storage tanks, it is clear that CFD models need to account properly for boil-off at the vapor–liquid interface and the convective Rayleigh flow that drives this boil-off. However, as Zimmerman and coworkers point out in a subsequent article,¹⁸ extending CFD simulations to realistic LNG storage scenarios is problematic because of the need to develop appropriate Reynolds-averaged Navier-Stokes equations. Incorporating such a realistic boundary condition remains a significant challenge for future, improved CFD models of LNG rollover.

Zimmerman et al.¹⁹ also identified that the hydrodynamically interesting features of the rollover process were proceeded by a long-period dominated by diffusive mass transfer between the liquid layers, which is consistent with observations and industrial records of LNG rollover incidents. It is apparent that while numerical CFD models offer insight into rollover, they are not yet able to fully describe events that occur in industrial LNG storage and that significant advances in multiphase CFD modeling will be required to achieve this. Thus, LP models offer the only current prospect of analyzing and/or predicting LNG rollover incidents and, in particular, the conditions and slow evolution of the system prior to the brief period of hydrodynamic activity that can be described by CFD models.

Figure 2 shows a conceptual schematic similar to that used by Heestand et al.¹⁷ and Deshpande et al.¹⁸ to model the La Spezia LNG rollover incident with a lumped-parameter approach. Essentially, lumped-parameter models solve the coupled differential equations describing the material and energy balance of each layer in the stratified system, including the vapor phase. The general forms of these equations are as follows

$$\frac{d(n_{\text{tot}}x_i)}{dt} = k_i A \Delta x_i - F_{R,i} x_i \quad (1)$$

$$n_{\text{tot}} C_P \frac{dT}{dt} = h A \Delta T + q_{\text{out}} \quad (2)$$

Here, n_{tot} is the total number of moles in the layer, C_P is the molar isobaric heat capacity of the layer, h and k_i are heat and component mass-transfer coefficients, q_{out} is the total amount of heat transferred to the layer either from outside the tank and/or from the vapor (i.e., it includes the important contribution of the heat of vaporization), T is the layer's temperature, ΔT is the temperature difference of the

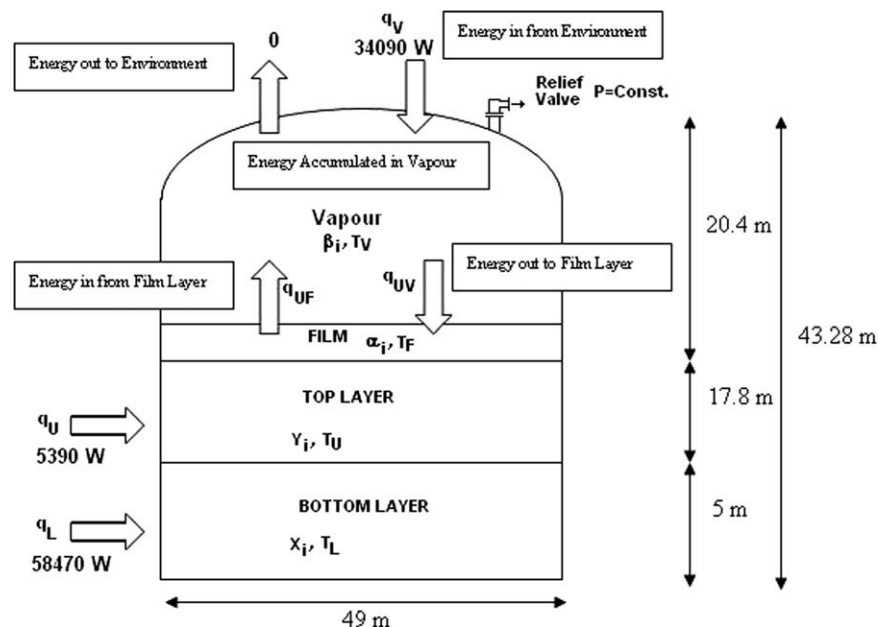


Figure 2. Schematic of the model used by Heestand et al.¹⁷ to simulate the La Spezia incident reported by Sarsten.

layers, x_i are the component mole fractions in the layer, Δx_i are the differences in component mole fractions between the layers, F_R is any molar flow leaving the layer (e.g., boil-off, convective circulation, or filling/emptying/draining) and A is the tank cross section. The (SI) units of k_i as defined in Eq. 1 are $\text{mole} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$ because a mole fraction scale is used to quantify the concentration difference between the two layers. If another concentration scale (e.g., molar or molal) were used, the units of k_i would change accordingly; however, the mole fraction scale is the one used conventionally to model LNG rollover. For further details about the specifics of the equations used for each layer in Figure 2, the reader is referred to, for example, Refs. 17, 20 or 18.

Since the solution to these differential equations for the layer composition and temperatures as a function of time is relatively straightforward, within the domain of the lumped-parameter model's validity (e.g., stable interfaces), the accuracy of the simulation depends critically on the validity of values used for the other quantities in the equations. Reliable models for the thermophysical properties of the layers as a function of temperature and composition are crucial; modern equations of state (EOS) for LNG mixtures, such as the GERG-2004 EOS²¹ should be used in place of cubic EOS given the poor density predictions of the latter model.²⁰ Accurate information about the external heat fluxes into the tank is of course also vital to the predicted time to rollover. Nevertheless, the accurate calculation of fluid properties and external heat fluxes into the tank are in general relatively straightforward in comparison with the principal challenges associated with the lumped-parameter approach, namely the estimation of the heat- and mass-transfer coefficients.

The prediction of the heat-transfer coefficient, h , is usually done using empirical correlations linking the Nusselt number, $\text{Nu} \propto h$, to the Rayleigh (or Grashof) number of the system at the interface between the two liquid layers. Heestand et al. and Deshpande et al. tested the correlations of Globe and Dropkin²² and McAdams²³ in their simulations of the La Spezia incident; these two correlations (which were developed from liquids very different to LNG) have the

same functional forms but differ in the numerical value of a proportionality constant. Both Heestand et al.¹⁷ and Deshpande et al.¹⁸ found that the choice of the proportionality constant used in the correlation for h caused the predicted time to rollover for the La Spezia incident to range from 20 h to 40 h.

Prediction of the mass-transfer coefficient(s) to be used in the solution of the material balance equations is even more problematic because k is usually calculated from h using a heat-to-mass transfer analogy. Thus, the accuracy of the mass-transfer coefficient depends both on the accuracy of heat-transfer coefficient and the validity of the heat-to-mass transfer analogy used. The lumped-parameter simulations of LNG rollover reported in the past have taken one of two approaches for selecting this analogy.

The first analogy used was based on the observations of Turner² who investigated and quantified the relationship linking the heat and mass transfer between layers of salt solutions at various concentrations and temperatures. By measuring the change in salinity and temperatures of the solutions over time, Turner calculated the heat and mass fluxes between the layers as a function of time, and related them to the evolution of a parameter characterizing the hydrostatic stability of the system, known as the stability ratio, R_s (definitions for which are given below in Eqs. 6 and 9). Turner observed that for values of R_s greater than a critical value R_c , heat transfer was dominant over mass transfer, with the ratio of k/h being small and varying slowly with changes in R_s (see Figure 5 of Ref. 2). For $R_s < R_c \approx 2$ for the salt solutions studied by Turner, the slope of k/h with R_s increased and mass transfer rapidly became dominant as the limit of hydrostatic stability (at $R_s = 1$) was approached.

The first attempt to simulate LNG rollover by Chatterjee and Geist⁷ used the observations of Turner² to estimate the mass-transfer coefficient between two LNG layers from a heat-transfer coefficient estimated using a flat-plate heat flux correlation. When the model of Chatterjee and Geist⁷ was applied to the simulation of the La Spezia incident, the

predicted time to rollover was about 35% longer than reported by Sarsten.¹³ Subsequently, Germeles⁸ improved upon the model of Chatterjee and Geist⁷ by adopting layer density equalization as the criterion for rollover and by adapting the use of Turner's salt solution data to LNG systems so as to better estimate the mass-transfer coefficient from the heat-transfer coefficient. The agreement between the rollover times predicted with Germeles' model and the La Spezia observations in Sarsten's report improved but remained larger by about 10%, which implied that the mass transfer rates being used in the model were too small to describe the data available from that incident.

To address this deficiency, Heestand et al.¹⁷ introduced an alternative approach for estimating the mass-transfer coefficient from the heat-transfer coefficient in LNG rollover simulations. Heestand et al.¹⁷ abandoned the use of Turner's observations and instead utilized the Reynolds analogy, $\frac{kC_p}{h} = 1$ (for a mass-transfer coefficient defined in terms of a mole fraction scale for concentration differences). They found that the time to rollover in the La Spezia incident could be correctly simulated with this approach by using a heat-transfer coefficient correlation that was essentially the average of the Globe and Dropkin correlation²² and that of McAdams.²³ However, despite its apparent success in describing the La Spezia incident, the model of Heestand et al.¹⁷ contains several deficiencies which suggest that the model's agreement with the data reported by Sarsten¹³ may have been fortunate. For example, Heestand et al.¹⁷ stated that they modeled the vapor phase as being in thermodynamic equilibrium with a film on top of the upper-liquid layer but subsequently stated that the initial vapor composition was simply 0.95 CH₄ + 0.05 N₂, which is inconsistent with a flash calculation of the upper liquid layer using the SRK EOS.

In 2011, Deshpande et al.¹⁸ reported a model for LNG rollover that followed the approach of Heestand et al.¹⁷ but which addressed several of its deficiencies. They used the Antoine equation to more accurately calculate the composition of the BOG from the saturation pressures of the various species. They also used the Klosek-McKinley correlations of Boyle²⁴ and Medici²⁵ to calculate the densities and heat capacities of the LNGs. They used this model to investigate the sensitivity of the predicted rollover times on the choice of the empirical heat-transfer coefficient correlation, which was significant. Importantly though, Deshpande et al.¹⁸ retained the use of the Reynolds analogy to estimate the mass-transfer coefficient. As a result, while their model was able to simulate correctly the rollover time observed in the La Spezia incident, when it was applied to the 1993 LNG rollover incident at Partington the model severely underpredicted the time to rollover (18 h vs 68 days). Deshpande et al.¹⁸ identified that the prediction of rapid layer density equalization reflected that the model's heat- and mass-transfer coefficients were inaccurate, and developed a method of deriving them in near real-time (several minutes) from an adequately instrumented LNG storage tank. This inverse method involved optimization (regression) of the LP model's predictions to match the level, temperature and density (LTD) data from the storage tank by adjusting the values of the heat- and mass-transfer coefficients used in the model.

Subsequently, Lukaszewski et al.¹⁶ reported an alternative inverse modeling approach in which the normal equations method was used to extract the heat- and mass-transfer coef-

ficients from tank LTD data. The normal equations method is more computationally efficient than the optimization method of Deshpande et al.¹⁸ and can be solved in seconds with average desktop computers. Lukaszewski et al.¹⁶ then compared these two inverse LP models against an LNG rollover incident that occurred somewhere in the USA in 2007 for which LTD data were recorded. The observed time to rollover was 69 h, which was about 10% longer than predicted by the inverse LP model of Lukaszewski et al.¹⁶ and 12% shorter than determined by the inverse LP model of Deshpande et al.¹⁸

The primary function of lumped-parameter models is prediction and thus a means of robustly estimating the mass-transfer coefficients to be used in these models is essential; determining the k_i from well-instrumented LNG storage tanks is of limited use unless the results obtained can be generalized and applied to other storage tanks (with less instrumentation). The failure of the model of Deshpande et al.¹⁸ to describe the Partington incident data¹⁴ is likely to be caused by the use of the Reynolds analogy, which is justified only in the case of fully turbulent systems and it implies accordingly large mass transfer rates that would lead to a relatively rapid equalization of layer mass densities. Such an analogy is inconsistent with the double-diffusive phenomenon known to govern the early stages of rollover in saline aqueous solutions.^{2,6,8} The observations reported by Bates and Morrison¹⁵ suggest that double diffusion also governs the initial stages of LNG rollover, and that accordingly the Reynolds analogy should not be used prematurely when simulating LNG rollover.

In 1997, Bates and Morrison¹⁵ presented some graphical data (Figure 2 of Ref. 15) acquired at the Gaz de France LNG testing facility in Nantes. From this data set, Bates and Morrison identified that the rollover occurred in two phases, during which the mass transfer regimes are significantly different. During the long-lasting Phase 1 (about 48 h), the data of Bates and Morrison¹⁵ showed the system remained stratified with double diffusive convection being the principal mass transfer mechanism. Data from temperature and density sensors located at three levels within the tank were presented, with the lowest sensors being 4.5 m below the uppermost sensors, and the middle sensors being only 1 m below the upper sensors. The densities of the two layers converged slowly during Phase 1 primarily because of heat transfer from outside the tank, which caused the temperature of the bottom layer to increase steadily. During Phase 1, the lower and middle temperature sensors tracked one another indicating that the interface between the layers was within the 1-m interval between the middle and upper sensors. There was only modest heat transfer between the layers, which resulted in a reduced rate of temperature increase for the upper layer. The density of the bottom layer decreased with time as its temperature increased. Most of the mass transfer occurred subsequently during what they called Phase 2 of the rollover process, which was about half as long as Phase 1 in duration. However, although Phase 2 lasted 24 h in total, the temperature recorded by the middle sensor changed by 1 K in the first 2 h, decreasing from the temperature of the lower sensor to that of the upper sensor, suggesting that the interface shifted by more than a meter in this time. Accordingly, in contrast with the double diffusive convection, Bates and Morrison characterized the mass transfer in Phase 2 as being driven by penetrative convection, where plumes from one

layer enter and entrain fluid from another layer before they return under their own weight. The time and length scales of this convection are significantly faster and longer than in double diffusive convection and result in the appearance of a migrating interface. As the scale of the plumes increases, the interface between the two layers moves perceptibly and the density difference between them decreases until the rollover begins. The onset of this new mass-transfer mechanism coincided with a significant increase in the boil-off rate.

Bates and Morrison¹⁵ used a lumped-parameter model to describe the data from Phase 1 when the liquid layer interface was stationary, which they then extended on a parametric basis to describe Phase 2 when the liquid layer interface was moving. Unfortunately, many of the specific details about their model were not reported. Importantly though, as a result of the existence of Phase 2, large mass-transfer coefficients were not required in the LP model of Phase 1, so it was unnecessary to utilize the Reynolds analogy. Bates and Morrison¹⁵ stated that they varied h and k according to Turner's observations for salt-solutions and, during Phase 1, they held the ratio of the fluxes constant at 0.15. Furthermore, they also drew upon the observations of Turner for salt solutions by identifying a criterion for the transition from Phase 1 to Phase 2 based upon the value of the hydrostatic stability ratio, R_s , in comparison with a critical value R_c . Unfortunately, Bates and Morrison did not specify what the value of R_c for LNG systems was, although they did state that the predicted rollover times were very sensitive to the value it was assigned in the model. In contrast to the results obtained by Heestand et al. and Deshpande et al. for models utilizing the Reynolds analogy, Bates and Morrison stated that the results of their simulation for Phase 1 were insensitive to the specific values of the heat-transfer coefficient used in the model.

The work of Bates and Morrison¹⁵ on LNG rollover is seminal in its identification of the two different phases and the transition from one to the other at a critical value of the stability ratio, in a fashion similar to that observed by Turner for salt solutions. However, to utilize these observations in an improved lumped-parameter model of LNG rollover, it is necessary to have a numerical value for the critical stability ratio R_c , which was not provided by Bates and Morrison. Turner's data suggest that for saline solutions $R_c = 2$ but it would be surprising if the critical stability ratio for LNG systems was the same given the very different nature of the solvent and solutes. Furthermore, LNG is a multicomponent mixture whereas the salt solutions contained only a single solute.

In the following section, we provide a framework for calculating the stability ratio of a multicomponent LNG mixture and, by applying this framework, to estimate a value of R_c for LNG mixtures based on the graphical data presented by Bates and Morrison for LNG rollover. Obtaining this value will greatly improve the capacity to describe and predict rollover in LNG systems; for $R_s > R_c$, a LP model should adequately describe the system as it evolves through Phase 1. The values of the mass-transfer coefficients used in such models could be estimated through more appropriate heat-to-mass transfer analogies, such as the Chilton-Colburn analogy,²⁶ for which k is much smaller than if calculated using the fully turbulent Reynolds analogy. To model the second phase of rollover, where $R_s < R_c$, several approaches may be viable, including simply using the same lumped-parameter model but with the Reynolds analogy to obtain higher effective values of k . More rigorous models that account for the motion of the interface during Phase 2 would be preferable

and could perhaps be developed using CFD if the challenge of describing turbulent flows and boil-off can be overcome.

Hydrostatic Stability Ratios for Multicomponent LNG Mixtures

To establish the framework needed to estimate value of the hydrostatic stability parameter R_s for a multicomponent LNG mixture, it is helpful to start by reviewing the stability analysis for two liquid solutions containing a single solute with density differences caused by differences in temperature, T , and solute concentration, S . The relation for establishing hydrostatic stability can be derived by considering the force balance on a parcel of liquid as a function of depth. The parcel, which has an initial density of ρ_1 , is displaced rapidly through a small vertical distance δz . This causes its density to change to $\rho'_1 = \rho_1 + \left(\frac{\partial \rho}{\partial z}\right)_{Q=0} \delta z$, where the partial derivative is evaluated for an adiabatic pathway (no heat or mass transfer but the parcel can do work on the surrounding fluid). The parcel's hydrostatic stability is determined by comparing ρ'_1 with the density of the surrounding fluid, $\rho_2 = \rho_1 + \left(\frac{d\rho}{dz}\right) \delta z$. Hesselberg²⁷ defined the stability parameter E , as the ratio of the vertical acceleration of a displaced liquid parcel, a_z , to the acceleration due to gravity, g , or equivalently the ratio of the buoyancy force to the gravity force

$$E = \frac{-a_z}{g} = -\left(\frac{\rho_2}{\rho'_1} - 1\right) = \frac{\rho'_1 - \rho_2}{\rho'_1} \quad (3)$$

By this definition, if $E > 0$ then the liquid parcel will return to its original position and the system is stable. If $E < 0$, the parcel will accelerate away from its original position and the system is unstable. The full density derivative $d\rho/dz$ can be expanded in terms of the partial density derivatives with respect to pressure, temperature and solute concentrations and the vertical gradients of these quantities. Since $(dP/dz) = -\rho g$, by writing $\kappa_T \equiv \frac{1}{\rho} \left(\frac{\partial \rho}{\partial P}\right)_T$, $\kappa_Q \equiv \frac{1}{\rho} \left(\frac{\partial \rho}{\partial P}\right)_{Q=0}$, $\Delta\kappa = \kappa_T - \kappa_Q$, $\alpha \equiv (1/\rho)(\partial\rho/\partial T)$, and $\beta \equiv (1/\rho)(\partial\rho/\partial S)$, the stability criterion can be rewritten as

$$E = \frac{(\Delta\kappa \rho g - \alpha \frac{dT}{dz} - \beta \frac{dS}{dz}) \delta z}{1 - \kappa_Q \rho g \delta z} = 0 \quad (4)$$

where the substitution $\rho_1 \rightarrow \rho$ has been made. The term in brackets in the above equation determines whether the system is hydrostatically stable. The difference between the isothermal and adiabatic compressibilities $\Delta\kappa$ in pure fluids determines the net buoyant force on the (rapidly) upwards moving parcel, and thus sets the minimum temperature gradient required for convection. For mixtures this effect is very small in comparison with that due to the concentration difference and can be ignored. Thus the criterion for stability can be written in terms the thermal expansion coefficient, α , and the solute concentration expansion coefficient, β

$$-\alpha \frac{dT}{dz} - \beta \frac{dS}{dz} = 0 \Rightarrow -\alpha \frac{\Delta T}{\Delta z} - \beta \frac{\Delta S}{\Delta z} \cong 0 \quad (5)$$

The second equality in Eq. 5 corresponds to the case where over a finite vertical separation, Δz , the system transitions from one layer to another with ΔS being the difference in solute concentration and ΔT the difference in temperature between layers. This equation leads to Turner's definition of the stability ratio, R_s as

Table 2. Effects of a $\delta S_i = 0.01$ mol/kg Change in the Initial Concentration of Each Solute in the La Spezia LNGs on the Mole Fraction Compositions and the Densities of the Two LNG Mixtures, as Well as the Calculations of Difference in that Component's Concentration, ΔS_i , between the Layers

Component being varied (solute):	Nitrogen		Ethane		Propane		Butane		Pentane	
	New mole fractions		New mole fractions		New mole fractions		New mole fractions		New mole fractions	
	Bottom	Top	Bottom	Top	Bottom	Top	Bottom	Top	Bottom	Top
Methane (solvent)	0.62254	0.63614	0.62254	0.63614	0.62254	0.63614	0.62254	0.63614	0.62254	0.63614
Nitrogen	0.00030	0.00360	0.00020	0.00350	0.00020	0.00350	0.00020	0.00350	0.00020	0.00350
Ethane	0.21848	0.24158	0.21858	0.24168	0.21848	0.24158	0.21848	0.24158	0.21848	0.24158
Propane	0.12659	0.09359	0.12659	0.09359	0.12669	0.09369	0.12659	0.09359	0.12659	0.09359
Butanes	0.03140	0.02350	0.03140	0.02350	0.03140	0.02350	0.03150	0.02360	0.03140	0.02350
Pentanes	0.00069	0.00159	0.00069	0.00159	0.00069	0.00159	0.00069	0.00159	0.00079	0.00170
Calculated LNG properties										
Number of moles total	100.126	97.986	100.126	97.986	100.126	97.986	100.126	97.986	100.126	97.986
T (K)	118.997	114.355	118.997	114.355	118.997	114.355	118.997	114.355	118.997	114.355
P (MPa)	0.15	0.131	0.15	0.131	0.15	0.131	0.15	0.131	0.15	0.131
ρ (kg/m ³)	541.046	536.968	541.041	536.963	541.057	536.979	541.071	536.994	541.074	536.997
$\delta\rho$ (kg/m ³)	0.0144	0.0164	0.0096	0.0111	0.0249	0.0274	0.0393	0.0425	0.0421	0.0453
$\delta\rho/\rho$	0.00003	0.00003	0.00002	0.00002	0.00005	0.00005	0.00007	0.00008	0.00008	0.00008
$\beta_i = (1/\delta S_i)(\delta\rho/\rho)$ (kg/mol)	0.0026	0.0030	0.0017	0.0020	0.0046	0.0050	0.0072	0.0078	0.0077	0.0083
Average β_i (kg/mol)	0.0028		0.0019		0.0048		0.0075		0.0080	
ΔS_i [mol/kg]	0.3228		1.7956		-3.5041		-0.8412		0.0866	
$\beta_i \Delta S_i$	0.0009		0.0034		-0.0169		-0.0063		0.0007	

$$R_s \equiv \frac{\beta \Delta S}{(-\alpha \Delta T)} \quad (6)$$

A layered liquid system with R_s equal to 1 will be at the limit of hydrostatic stability. Often the absolute value of R_s is all that is considered when estimating whether a stratified layer is stable.² Nevertheless, as demonstrated below, there is significant information content in the sign of Eq. 6 which it is often useful to retain.

To extend this analysis to LNG,²⁰ it is helpful to draw an analogy between saline solutions and LNG by taking methane as the solvent and treating the heavier components as solutes of concentration S_i . However, to reliably evaluate the hydrostatic stability of a multicomponent mixture like LNG, the individual effect of each solute component on the mixture's density must be considered. Such an extension begins by defining a concentration expansion coefficient for each solute

$$\beta_i \equiv \frac{1}{\rho} \left(\frac{\partial \rho}{\partial S_i} \right) \rightarrow \beta_i \cong \frac{1}{\rho} \left(\frac{\Delta \rho}{\Delta S_i} \right) \quad (7)$$

The solute specific β_i quantify the fractional change in the mixture's mass density caused by a small change in that solute's concentration. The total effect of solute concentration on the mixture density is then the sum of the contributions of each specie. The implication of this extension on the requirement for hydrostatic stability is given by the following modification to the general stability equation

$$E = \Delta \kappa \rho g - \alpha \frac{\Delta T}{\Delta Z} - \sum_i \beta_i \frac{\Delta S_i}{\Delta Z} = 0 \quad (8)$$

Thus for an arbitrary length scale, the stability ratio for a multicomponent system becomes

$$R_s = \frac{\sum_i \beta_i \Delta S_i}{(-\alpha \Delta T)} = \sum_i R_{s,i} \quad (9)$$

In the above equations, the index refers only to solute species (not methane), and in Eq. 9 we introduce the component

specific stability ratio, $R_{s,i}$. The values of the volume expansivities, $-\alpha$, and the β_i can be estimated for LNG mixtures using, for example, the GERG-2004 EOS.²¹ For the La Spezia LNGs at their initial conditions of temperature and composition, the volume expansivities were $2.34 \times 10^{-3} \text{ K}^{-1}$ and $2.31 \times 10^{-3} \text{ K}^{-1}$, for the upper and lower layers, respectively. (For comparison, the value $-\alpha$ for pure liquid methane at approximately the La Spezia temperature and pressure is $3.5 \times 10^{-3} \text{ K}^{-1}$). For the purpose of calculating R_s , the average value of α for the two layers should be used. The initial product of $-\alpha \Delta T$ for the La Spezia system was 0.0108. Values for the β_i calculated using the GERG-2004 EOS for the La Spezia LNGs at their initial conditions are listed in Table 2, using a molal scale for the solute concentrations.

A state map for the stability parameter of a multicomponent mixture defined in Eq. 9 is shown in Figure 3 and broken into five regions of interest corresponding to various combinations of the values of $(-\alpha \Delta T)$ and $\sum \beta_i \Delta S_i$. In Region 1, where $R_s < 0$, the system is stable with no potential for rollover. In Region 2, the system is unstable because the upper layer is denser than the lower layer. The unstable region is wherever $\sum \beta_i \Delta S_i$ is more positive than $(-\alpha) \Delta T$; the numerical values of R_s have no physical meaning beyond the boundary between these two regions where $R_s = 1$. In Region 3, where $R_s > 0$ and $|R_s| > 1$, the system is stable but has the potential for rollover, which would result in the production of a boil-off vapor because the lower layer is at a higher temperature than the upper layer. In Region 4, where $R_s > 0$ but $|R_s| < 1$, the system is stable and has also the potential for rollover, which would result in condensation because the temperature of the lower layer is below that of the upper layer. Such a rollover would be the opposite of that normally considered in LNG scenarios; however it could in principle arise if the lower LNG were very lean but sufficiently cool so that its initial density was greater than the warmer, richer LNG above it. The effects of such an inverse rollover could potentially generate a partial vacuum in the storage tank that could cause problems with the containment and/or BOG handling systems. In Region 5, the system is nearly

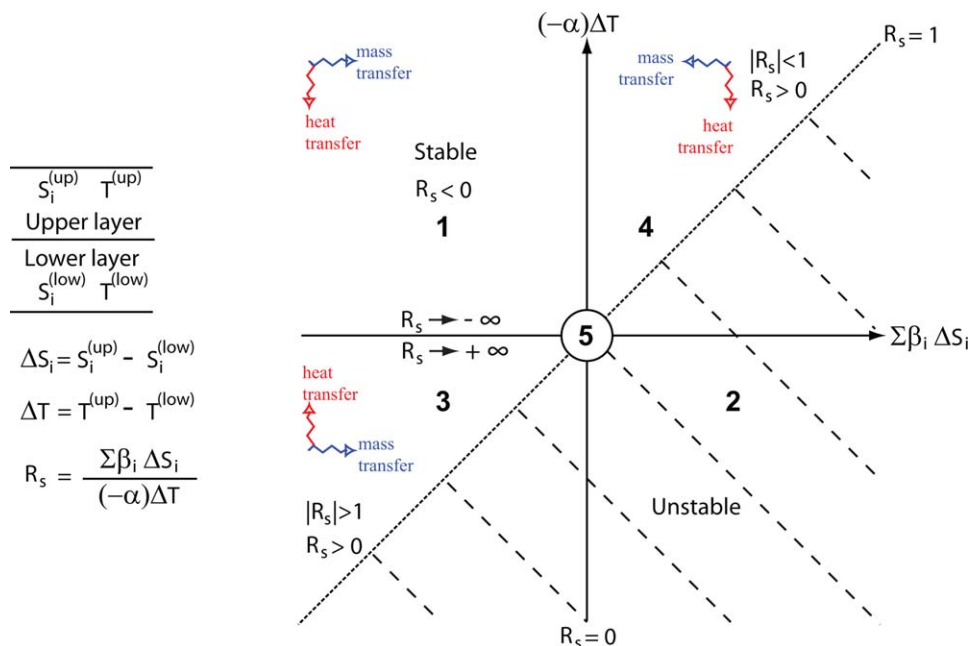


Figure 3. State map for the generalized stability ratio, R_s , in a multicomponent system.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

homogeneous with any gradients being too small for significant global effects. Similarly, the mathematical divergence of R_s to infinity along the abscissa between Regions 1 and 3 simply reflects a thermally uniform system with $\Delta T = 0$. Arrows indicating the effects of heat and mass transfer on an isolated system are shown in each of the stable regions. For Regions 3 and 4, it is the relative magnitudes of interlayer heat and mass transfer, combined with any heat leak into the system from the external environment, that governs whether the system evolves toward stability in Region 1 or a rollover event at $R_s = 1$.

The stability ratio presented here for multicomponent LNGs follows from the approach of Turner² and makes use of the key quantities of temperature and concentration measurable during an experiment. However, other approaches for quantifying the stability of the system can be used, for example, by making use of appropriate dimensionless groups that may be more convenient for scaling CFD simulations or describing systems where the interface between layers is not well defined. For example, Zimmerman et al.¹⁹ defined a stability parameter, S , in terms of the Lewis number and two Rayleigh numbers based on concentration or temperature, defined as follows

$$S = Ra_T Pr - Le Ra_C \quad (10)$$

where the Lewis number, Le , was taken to be the ratio of concentration to thermal diffusivities (proportional to k/h for diffusive systems), and the temperature Ra_T and concentration Ra_C Rayleigh numbers were defined using the thermal and concentration diffusivities, respectively. It can be shown that the stability parameter of Zimmerman et al.¹⁹ as defined in Eq. 10 is proportional to Eq. 5, with ΔS corresponding to ΔC Pr and the proportionality constant being $\rho_0 g R^3 / \mu h$. Here, in the notation used by Zimmerman et al., ΔC is a characteristic concentration difference used for scaling, ρ_0 is the average liquid density, μ is the liquid viscosity, and R is the radius of the tank. We note that in their simulations, Zimmerman et al. set $Le = 50$, which implies that mass transfer is 50 times larger than heat transfer. While such a ratio of mass to heat transfer would be characteristic of the

rollover process once penetrative convection has been established, as occurs during the Phase 2 identified by Bates and Morrison,¹⁵ it is not representative of the longer Phase 1 period in which double diffusive mass transfer is occurring and most of the evolution is governed by heat transfer.

Quantitative Estimates of the Stability Ratios for Documented LNG Rollover Incidents

With the framework defined for the calculation of R_s for multicomponent mixtures, it is possible to use the available information about the few LNG rollover incidents documented in the literature to estimate quantitatively the R_s for these systems at various times. In Table 2, the initial values of $\beta_i \Delta S_i$ for the La Spezia LNGs are estimated from the specified initial compositions, temperatures and the GERG-2004 EOS.²¹ Such an analysis shows that the contributions of changes in concentration to changes in mixture density are not equal for all components (as would be assumed in a pseudobinary mixture model). The values of the β_i vary from 2×10^{-3} kg/mol for C_2H_6 to 8×10^{-3} kg/mol for C_5H_{12} . There is also some dependence on mixture composition and temperature apparent as the values of the β_i are slightly different for the top and bottom layers. The differences range from 3×10^{-4} kg/mol for C_2H_6 to 6×10^{-4} kg/mol for C_5H_{12} . For the purpose of calculating R_s , the average value of β_i for the two layers can be used for each solute

$$R_s = \frac{\sum \beta_i \Delta S_i}{-\alpha \Delta T} = \frac{0.0009 + 0.0034 - 0.0169 - 0.0063 + 0.0007}{0.0023 \times (-4.642)} = 1.7 \quad (10)$$

An initial R_s of 1.7 for the La Spezia LNGs places the system in Region 3 of the state map shown in Figure 3 as an initially stable system with the potential for rollover that would generate significant boil-off vapor. Whilst heat transfer between the layers would act to reduce the temperature

Table 3. Assumed LNG Compositions Chosen to Represent the Nantes LNGs by Matching the Reported Densities¹⁵

	<i>t</i> = 0 h		<i>t</i> = 36 h		<i>t</i> = 56 h	
	Lower layer	Upper layer	Lower layer	Upper layer	Lower layer	Upper layer
	Mole Frac.	Mole Frac.	Mole Frac.	Mole Frac.	Mole Frac.	Mole Frac.
Methane	0.8630	0.8970	0.86334	0.89666	0.87269	0.88731
Nitrogen	0.0050	0.0050	0.0050	0.0050	0.0050	0.0050
Ethane	0.1090	0.0690	0.1086	0.0694	0.0976	0.0804
Propane	0.0200	0.0210	0.02000	0.02099	0.020285	0.020715
Butane	0.0030	0.0080	0.00305	0.00795	0.004425	0.006575
<i>T</i> (K)	114.15	113.65	115.15	113.9	115.15	114.15
EOS α (K ⁻¹)	-0.00300	-0.00307	-0.00302	-0.00308	-0.00304	-0.00306
EOS ρ (kg/m ³)	462.97	456.82	461.51	456.54	459.64	458.01
Measured ρ (kg/m ³)	463	456.75	462	457	460.5	459
$\rho_u - \rho_L$ (kg/m ³)		-6.25		-5.0		-1.5
$(\rho_u - \rho_L)/\rho$		-0.0135		-0.0108		-0.0033
<i>T_U</i> - <i>T_L</i> (K)		-0.50		-1.25		-1.00
$\alpha(T_U - T_L)$		0.00152		0.00381		0.00305
Estimated $\Sigma \beta_i \Delta S_i$		-0.0150		-0.0146		-0.0063
Estimated <i>R_s</i>		9.9		3.8		2.1

The time to the end of Phase 1 was 36 h and the time to rollover was about 60 h.

difference, the reduction in temperature difference between layers was delayed because of the larger heat leak into the bottom layer which had a much larger surface area in contact with the external environment than the upper layer. Mass transfer between the layers was then able to drive the system toward the instability line at $R_s = 1$.

Using information about the initial compositions of the LNG layers and the GERG-2004 EOS, it is possible to calculate the system's stability ratio from the values of $(-\alpha \Delta T)$ and $\Sigma \beta_i S_i$ as shown in Table 2. However, information about the composition of the LNG layers over time is often unavailable. Nevertheless if information about the differences in the layer's densities and temperatures is available, either through measured data or LP models such as that of Deshpande et al.,¹⁸ then the value of R_s for the system may be evaluated

$$R_s = \frac{\Delta \rho}{(-\alpha \Delta T) \bar{\rho}} + 1 \quad (11)$$

Here $\Delta \rho \equiv \rho_U - \rho_L$ and $\bar{\rho}$ is the average mass density of the layers. Applying Eq. 11 to the information presented in Figures 6 and 7 from Heestand et al.,¹⁷ and assuming that the average value of α for the two LNGs does not change significantly, we estimate that for the La Spezia incident R_s decreased to 1.3 at $t = 20$ h and to 1.06 by $t = 30$ h. This is consistent with the conceptual evolution of the system toward the instability line in Figure 3.

It is of note that the initial value of $R_s = 1.7$ for the La Spezia LNGs was already quite close to the line of instability, and that this value is already below the critical value $R_C^{\text{saline}} = 2$ reported by Turner for saline solutions. If Turner's value of R_C^{saline} were assumed to apply to LNG, then in terms of Bates and Morrison¹⁵ model of LNG rollover, the initial La Spezia system was already in "Phase 2" with migrating interfaces rather than the double diffusive mass convection. This could explain why the use of the Reynolds analogy coefficients by Heestand et al.¹⁷ was successful in describing the La Spezia incident: because the system was already in a regime in which mass transfer rates were dominant. However, when Deshpande et al.¹⁸ applied the same approach to the description of the Partington incident, the model likely overestimated the mass-transfer coefficient which in turn led to a prediction of a very short time to rollover (18 h) in comparison with that reported by Baker and Creed of 68 days.

A similar analysis can be applied to the graphical density and temperature data provided by Bates and Morrison for the LNGs studied in Nantes.¹⁵ For example, Figure 2 from Ref. 2 shows that the lower LNG layer has an initial density of 463 kg/m³ and a temperature of -159°C while the upper LNG layer has an initial density of 456.75 kg/m³ and a temperature of -159.5°C. The fractional density difference between the upper and lower layers is -0.0135 and the fractional temperature difference is -0.004.

To estimate R_s from these data it is necessary to assume a value for the average volume expansivities of the LNGs. It is clear from the densities reported that the LNGs studied by Bates and Morrison were far leaner than those reported by Sarsten; modern LNGs in general tend to have much greater methane concentrations than was the case in the La Spezia incident. By using one of two extreme values for the average α of the LNGs studied by Bates and Morrison, corresponding to that for pure methane (-3.5×10^{-3} K⁻¹) or that for the La Spezia LNGs (-2.3×10^{-3} K⁻¹), the initial stability ratio in Ref. 2 lies in the range 7.6 to 12.6. These bounds represent a conservative estimate, which can be improved upon if reasonable assumptions about the LNG compositions are made, and a high-quality EOS is used to increase the confidence in properties predicted from the assumed compositions.

In Table 3, the assumed values of the compositions for the Nantes LNGs studied by Bates and Morrison¹⁵ are listed, together with the corresponding predictions of the GERG-2004 EOS for the LNG densities at the reported temperatures and at an assumed tank pressure of 0.15 MPa. The calculated densities are insensitive to the assumed pressure as long as it is above the saturation pressures of the two liquid mixtures (~0.13 MPa). The assumed compositions were guided by some simple principles: the components in the LNG were limited to methane, ethane, propane, butane, and nitrogen, and the mole fraction of methane was chosen to be 0.85 or higher. The initial densities obtained from the GERG-2004 EOS with the best guess compositions for top and bottom layers are 462.97 and 456.68 kg/m³, respectively, which are very close to the measured values of (463.0 ± 0.25) kg/m³ and (456.75 ± 0.25) kg/m³.

The primary purpose of assuming the composition is to improve the estimate of the average volume expansivity of the two LNG layers. Using the initial compositions that

result in EOS densities very close to those reported, the EOS may also be used to predict an average value of $\alpha = -0.00303 \text{ K}^{-1}$, which is approximately half-way between the two limiting cases described above. Accordingly, the estimate of the initial R_s for the LNGs at Nantes studied by Bates and Morrison¹⁵ can be refined to 9.9.

The evolution of the system's hydrostatic stability can then be calculated from the graphical data in Ref. 15 by assuming that the average value of α does not change significantly. Alternatively, the compositions of the two LNGs can be estimated in a manner similar to that done for the initial condition calculation. In Table 3, the initial condition calculation is repeated for $t = 36 \text{ h}$, which corresponded to the end of Phase 1, and for $t = 56 \text{ h}$, which is approximately three-quarters of the way through Phase 2. The results shown in Table 3 indicate that the two methods of estimating the evolution of α are essentially equivalent. Of more significance is the value of $R_s = 3.8 \pm 0.5$ at the transition from Phase 1 to Phase 2, where the uncertainty bound comes from the sensitivity to the value of α used. This is somewhat higher than the critical value of 2 observed by Turner for saline solutions. In fact, the calculation at $t = 56 \text{ h}$ gives $R_s = 2.1$, which is still larger than Turner's critical value, even though Phase 2 is only about 4 h from completion.

Assuming values of the initial LNG compositions that are constrained by the measured densities also allows the relative effects of heat and mass transfer on the LNG mass density to be assessed. At $t = 36 \text{ h}$, the temperatures for the two LNG layers were used with the original compositions and the GERG-2004 EOS²¹ to calculate a density. Then the compositions were modified to force the EOS density to match the reported density at $t = 36 \text{ h}$. The composition changes were constrained to be representative of double diffusive convection in that each layer's mole fraction for a given species changed by an amount with the same magnitude but opposite sign, toward the average value for that component for the two layers. The results of these calculations at $t = 36$ and 56 h are also shown in Table 3.

For the period of $t = 0$ to $t = 36 \text{ h}$ (Phase 1) the compositions remained fairly constant and the temperature change was enough to account for almost all of the density change. This suggests that virtually no mass transfer occurred in Phase 1; of the total possible mass transfer required to equalize the layers' compositions, the amount calculated in Table 3 corresponds to only 2%. For the period of 36 h to 56 h (three-quarters of Phase 2), the temperature change is small and in isolation would leave the density virtually unchanged. It is necessary to have significant mass transfer during this time to achieve the observed change in density. The calculated change in composition is over 50% of the total change required to equalize the layers' compositions. It should be noted though that the EOS densities predicted using the compositions estimated at $t = 36 \text{ h}$ and $t = 56 \text{ h}$ are in slightly poorer agreement with the measured densities than was achieved at $t = 0 \text{ h}$.

Unfortunately, without knowing further details (such as total mass or tank size) about the two LNGs reported by Bates and Morrison, this is as far as the reanalysis of their data can extend in terms of estimating the mass- and heat-transfer coefficients between the layers. However, the reanalysis that can be performed confirms that in Phase 1 mass transfer is negligible and heat transfer dominates the change in LNG density, while in Phase 2 the situation is reversed.

The initial stability ratio for the stratified LNGs reported by Baker and Creed for the Partington rollover incident can

Table 4. Hydrostatic Stability Ratios, R_s , (Calculated Using Eq. 11) and Time to Rollover for Documented LNG Rollover Incidents

LNG rollover incident	Initial R_s	Rollover time [h]	t_{int} [h]	$R_s (t = t_{\text{int}})$
La Spezia (1971) ^{13,17}	1.7	31	20	1.3
			28	1.06
Nantes (1987–89) ¹⁵	9.9	60	18	4.9
			36	3.8 ± 0.5
			52	2.1
Partington (1993) ¹⁴ USA (2007) ¹⁶	5.4 4.6	1632 69	—	—
			18	3.1
			30	2.9
			32	2.8

Where possible, R_s values at some intermediate times, t_{int} , during the system's evolution to rollover are also given. For the Nantes rollover, when $t_{\text{int}} = 36 \text{ h}$ the system transitioned from the diffusive Phase 1 to the convective Phase 2, and thus the corresponding value of R_s is the critical stability ratio for LNG, R_c .

also be estimated from Table 2 of Ref. 14. The LNG compositions reported were even leaner than those assumed for the LNGs in Table 2, with methane mole fractions of 0.926 and 0.975 for the lower and upper layers, respectively, and only N_2 , C_2H_6 and C_3H_8 being present in the mixtures. The initial temperatures were 114 and 112 K for the lower and upper layers. Baker and Creed report that the LNG densities were calculated to be 446 kg/m^3 and 433 kg/m^3 , although they did not specify the method used for this calculation. Using the GERG-2004 EOS with the reported compositions and temperatures leads to predicted densities of 441 and 429 kg/m^3 and an average volume expansivity for the two LNGs of -0.0033 K^{-1} . These values correspond to an initial $R_s = 5.4$ for the Partington LNGs. A similar calculation using Eq. 11 for the LNGs involved in the 2007 USA rollover incident described by Lukaszewski et al.¹⁶ gives an initial $R_s = 4.6$.

Table 4 contains a summary of the R_s values calculated from the initial layer densities and temperatures reported for four LNG rollover incidents: La Spezia (1971),¹³ Nantes (1987–89),¹⁵ Partington (1993),¹⁴ and USA (2007).¹⁶ Also shown is the time to rollover from the stated initial condition and, for three cases, the value of R_s at an intermediate time. For the La Spezia incident, the intermediate values of R_s were estimated from the layer densities and temperatures predicted from the model of Heestand et al.¹⁷ The system started in the convective Phase 2 of the rollover process and remains there, which is consistent with (and reflects) the successful use of the Reynolds analogy when modeling the La Spezia incident. For the 2007 USA incident reported by Lukaszewski et al.,¹⁶ the intermediate R_s correspond to the times at which the LTD profiles used for their normal-equations inverse model were measured. Interestingly, while the initial R_s indicates the system started in the diffusive Phase 1, at the three times used by Lukaszewski et al.¹⁶ to determine the k_i and h values used in their LP model, the system was in the convective Phase 2. This might partly explain why the rollover time predicted by their model was 10% too short: the values of k_i derived from the LTD data were representative of a convective mass transfer regime, whereas the system in fact started in a diffusive mass transfer regime.

Conclusions

LNG rollover and the approaches used to simulate and predict it described in the open literature have been

reviewed, to produce a holistic picture of current knowledge which is not otherwise available. Differences between lumped-parameter models and numerical, distributed models were explored, with the conclusion that lumped-parameter models are still the best placed to describe the slow evolution of large-scale systems toward rollover. Models utilizing CFD methods provide potential, complementary insight into the rapid dynamics that occur just prior to the rollover.

LP models provide a reasonable approximation for describing Phase 1 in which diffusion controls the interlayer transfer of heat and mass. The most prominent of the lumped-parameter models reported in the literature used the Reynolds analogy to estimate the mass transfer coefficient from the heat-transfer coefficient, which leads to rapid density equalization and significant sensitivity to the particular heat-transfer correlation. The choice of the Reynolds analogy by those who have developed lumped-parameter models was driven by the need to describe the La Spezia incident combined with a lack of knowledge regarding the observations of Bates and Morrison. However, as demonstrated by Deshpande et al.,¹⁸ models using the Reynolds analogy are not able to predict reliably the rollover times observed in other incidents. This suggests that at least two different heat-to-mass transfer analogies should be used in LP models of rollover corresponding to the two phases observed by Bates and Morrison.¹⁵ In Phase 1, the mass-transfer coefficient should be much smaller than would be predicted using the Reynolds analogy.

The graphical data of Bates and Morrison were analyzed in terms of a hydrostatic stability framework similar to that developed for saline solutions but extended to cover multicomponent LNG mixtures. This framework enables the evolution of R_s to be calculated, with the critical value of $R_s = 3.8 \pm 0.5$ corresponding to the transition from Phase 1 to Phase 2. This is much larger than the critical value of 2 observed by Turner for saline solutions. Analysis of the La Spezia incident indicates that initially that system had $R_s = 1.7$, which suggests it was already in Phase 2 and explains why the use of the fully turbulent Reynolds analogy in LP models was reasonably successful. In contrast, the initial value of R_s was 5.4 for the Partington incident, which indicates it was still in Phase 1 and explains why the use of the Reynolds analogy predicted times to rollover much shorter than that observed.

While this hydrostatic stability analysis can be used to provide criterion for transitions between the Phases of rollover, it does not define the rates at which the evolution of the system proceeds toward instability. For example, the value of R_s at $t = 0$ for the Nantes LNGs¹⁵ was about 9.9, which decreased to 3.8 in about 36 h through Phase 1, with rollover occurring after about 60 h. Furthermore only 4 h prior to rollover, R_s was about 2. In contrast, the initial R_s in the La Spezia incident was 1.7 with a further 31 h required before the rollover occurred. In the case of the Partington incident, about 68 days was required for rollover from an initial R_s of 5.4.

Clearly the dynamics of LNG rollover depend sensitively on the details of heat transfer into the storage tank. However, the stability ratio will play a role in those dynamics by governing the transition between different regimes of heat and mass transfer. Thus it is the value of the critical stability ratio at which the evolution changes from Phase 1 to Phase 2 that is particularly important in predicting the time to rollover. Bates and Morrison¹⁵ stated that predicted rollover times were insensitive to the precise values of the heat- and mass-transfer coefficients used in the LP models, which is in

contrast to the findings of both Heestand et al.¹⁷ and Deshpande et al.¹⁸ because the latter authors used the Reynolds analogy for the entire simulation. The use of a smaller mass-transfer coefficient during Phase 1, such as might be predicted using the Chilton-Colburn analogy, would eliminate that sensitivity and produce more robust predictions of the time to rollover when combined with the critical value of the stability ratio for LNG layers deduced in this work.

Future research into the description of LNG rollover using LP models is likely to focus on the description of Phase 1 and its evolution in terms of R_s and its approach to R_c . For example, it may be possible to simulate the graphical data of Bates and Morrison by using mass-transfer coefficients derived from the Chilton-Colburn analogy and testing whether this allows the system R_s to reach a value of 3.8 after 56 h. The quantitative prediction of auto-stratification in LNG could be another aspect of the rollover phenomenon amenable to analysis with improved LP models.

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Notation

A	= tank cross section
a_z	= acceleration of the liquid parcel (Z-axis)
BOG	= boil-off gas
C_p	= molar heat capacity
c_p	= specific heat capacity
D	= tank diameter
D_{AB}	= molecular diffusion coefficient
E	= stability parameter (Hydrostatic)
F	= Rayleigh flow
f	= boil-off flow rate
F_B	= buoyancy force
F_S	= molar flux through layers' interface
F_W	= weight force
g	= acceleration of gravity
Gr	= Grashof Number
H	= heat flux
h	= heat-transfer coefficient
H_j	= molar enthalpy of layer
i	= refers to the component
j	= refers to the layer
k	= mass-transfer coefficient
L	= bottom liquid layer (Lower layer)
Le	= Lewis Number
$Mole_j$	= number of moles in layer "j"
n_{Total}	= total number of moles
Nu	= Nusselt Number
Pr	= Prandtl Number
q_L	= heat flux to the bottom liquid from outside
Q	= 0, adiabatic pathway
q_U	= heat flux to the top liquid from outside
q_{UV}	= heat flux to the top liquid from vapor
q_v	= heat flux to the vapor from outside
Ra	= Rayleigh Number
R_s	= stability ratio
R_c	= critical stability ratio
$S, (S_i)$	= molal concentration (of component i)
Sc	= Schmidt Number
T_j	= layer "j" temperature
t	= time
U	= top liquid layer (Upper layer)
V	= vapor
X_i	= liquid phase mole fraction of component "i" in Bottom Layer
Y_i	= liquid phase mole fraction of component "i" in Top Layer
Z	= vertical axis

Greek letters

- α = coefficient of volume expansion, due to temperature change
 $\beta, (\beta_i)$ = coefficient of volume expansion due to concentration change, (for component i)
 δ = variation in a quantity
 Δ = difference of a quantity (between layers)
 κ = thermal diffusivity
 κ_Q = Adiabatic compressibility
 κ_T = isothermal compressibility
 λ = Liquid thermal conductivity
 μ = absolute viscosity
 ν = Kinematic viscosity
 ρ = density
 $\bar{\rho}$ = average density

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