STRATIFICATION AND ROLLOVER IN LIQUEFIED NATURAL GAS STORAGE TANKS

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During October 1993 a rollover occurred in a British Gas Liquefied Natural Gas Storage tank. The pressure in the tank rose rapidly and the two Process Relief valves on the Tank lifted. The Emergency Relief Valves subsequently lifted and Natural Gas vented from the tank for 2 hours. Approximately 150 tonnes of gas were vented to the atmosphere. The tank had been filled during July as part of the commissioning run of a modified liquefaction plant. The modified plant produced a product which was up to 13 kg/cm (3%) lighter than the heel of the tank. This was sufficient to cause a stratification in the tank. The tank stood for 68 days after which the rollover occurred.

BACKGROUND

The commissioning of British Gas' LNG reception terminal at Canvey Island, Essex in 1964, marked the beginning of a world-wide development of LNG production, transportation and storage facilities.

Over the last 30 years the trade in LNG has risen dramatically and traded volumes are now 83 Bcm per annum which represents 24% of the world wide trade in gas. This compares with the total UK gas market of 65 Bcm per annum.

The majority of LNG storage is utilised as Base Load supply in countries with little or no natural gas of their own. The rest is utilised as peak shave capacity covering inability to supply occasional very high demands or where system constraints dictate a need.

Under the requirements of the UK Gas Act, British Gas are legally required to provide security of supply, and the British Gas transmission and storage system is designed to provide sufficient supply capacity for both the worst winter day in 20 years and the worst winter period in 50 years, as agreed with the DTI.

Consequently the British Gas Storage portfolio incorporates one of the largest LNG peak shave undertakings in the world with a current capacity of 280,000 tonnes.

Possibly the least well understood aspect associated with the storage of LNG is a phenomenon known as rollover. During the past three decades a number of reports of rollover have occurred world-wide, the vast majority of which are associated with fast fill base load installations.

This paper will concentrate on the understanding of this phenomenon in relation to peak shave plants where fill rates are relatively slow and turnover has traditionally been low.

DEFINITION OF ROLLOVER

Rollover occurs as a result of density stratification in LNG tanks. Stratification can arise either by filling a tank with different density liquids or by 'autostratification' due to preferential loss of Nitrogen. In both cases, given sufficient density difference, separate layers can form which remain unmixed for a time.

Rollover is the name given to the subsequent mixing process which occurs when these separate layers approach each other in density by heat and mass transfer and merge together. This phenomenon is usually accompanied by a sudden increase in the generation of vapour.

At one time it was believed that the two layers actually inverted – hence the name rollover, however it has since been established that a rollover is a rapid mixing event.

NORMAL TANK BEHAVIOUR DURING LNG STORAGE

Before describing the mechanism of rollover it is first necessary to understand the normal behaviour of stored LNG.

LNG is a multi component mixture of hydrocarbons (mainly Methane with lower concentrations of higher hydrocarbons), and small quantities of inerts (N_2, He etc.). The LNG at British Gas sites is stored in 21,000 tonne tanks at pressures slightly above atmospheric (1.08 barg) and approximately -160°C.

The storage tanks are not provided with any external refrigeration to keep them cold but are highly insulated. A small amount of heat leaks into the tank (typically 50 kW per tank) from the surroundings and is released as latent heat of evaporation of the LNG. This results in the preferential loss of the more volatile components (N_2 & CH_4) of the LNG. This continuous vapour evolution is known as 'boil off'.

The liquid does not in fact boil but rather the heat input to the liquid from the walls and floor of the tank is absorbed and convected to the surface where evaporation takes place. A free convective circulation is set up with slightly warm and less dense liquid moving upwards close to the tank walls. The hydrostatic head suppresses boiling until the rising liquid approaches the surface and flashes – this is the phenomenon of boil off. (See Figure 1)

LNG Ageing

One aspect of peak shave LNG storage is the extended residence time of the liquid within the tank. Over time the preferential evaporation of the lightest component (methane) results in an increase in the density of the remaining stored liquid. This process is known as 'weathering' or 'LNG Ageing' and the rate at which it occurs is proportional to the quantity of heavier components in the LNG.

MECHANISMS OF ROLLOVER

The previous section has described the normal convective pattern and evaporative losses seen in a tank containing LNG of uniform composition and density.

The potential for rollover arises when two distinct layers of different density exist in a tank. How the layering can come about will be discussed later, but when it does occur, two independent cells are set up in the liquid. The upper layer is initially the lighter layer. (See Figure 2)

Density Equalisation

If stratification occurs, each layer is initially uniform in temperature and density by virtue of its own pattern of convective flow mixing.

Heat entering the upper cell (top layer) does so mainly through the sides of the tank. Liquid adjacent to the sides of the tank warms slightly becomes less dense and is transported to the top surface by free convection, where it loses heat by evaporation. This is similar to the behaviour of the single cell in an unstratified tank. As light gases are preferentially evaporated the liquid in the upper cell becomes more dense.

Meanwhile the lower cell gains heat from the floor and sides of the tank and warmed liquid flows to the interface by free convection. However, since it is under the hydrostatic head of the upper cell it does not evaporate, but superheats. Although there is some heat transfer across the interface this is relatively small and can be ignored. The lower cell thus becomes progressively warmer and less dense. Exactly what happens at the interface is not clear but some diffusion must occur and since the top cell is circulating at a higher rate than the lower cell it is thought that the interface will slowly migrate down the tank until only one cell exists. In this case nothing will be noticed by the operator.

However, as the densities of the two cells approach each other it is also possible that the interface will become less stable and the two cells will mix rapidly. As it does so the liquid from the lower cell, which is normally superheated, will give off large amounts of vapour as it rises to the surface. It is this phenomena that is known as rollover.

Other Mechanism

The mechanism described above presents a simple picture of rollover, adequate for the purposes of an initial understanding. However, it has been suggested that stratification may also be dispersed by the onset of boiling in the lower layer.

This is conceivable, at the tank wall near the interface, if the vapour pressure of the liquid in the lower layer becomes greater than or equal to the pressure in the vapour space of the tank plus the hydrostatic head of liquid at the interface.

THE CAUSE OF STRATIFICATION

Having discussed the mechanism of rollover which requires stratification it is necessary to understand the different causes of stratification.

Fill induced stratification

If a storage tank containing LNG is further filled with LNG of different density it is possible for the two layers to remain unmixed forming independent layers. The stratification is stable with the more dense layer at the bottom.

Fill induced stratification may occur if the added liquid (cargo) is less dense than the liquid already in the tank (heel) and filling is at the tank top. Conversely, a cargo denser than the heel but added at the bottom will cause the same effect.

In both cases, rollover can result as the interface becomes unstable and the two layers mix as described in the previous section.

Autostratification

It is believed that the presence of sufficient nitrogen in LNG can cause an initially unstratified (or homogeneous) liquid to stratify. This is called autostratification or nitrogen induced stratification.

In this mechanism, unstratified liquid gains heat at the walls and rises by convection as shown in Figure 1. On reaching the surface the liquid flashes. If there is sufficient nitrogen present, currently thought to be greater than 1.0%, its preferential loss can cause the flashed liquid to be less dense than the remaining liquid.

This creates a thin layer of less dense liquid at the surface which effectively seals in the lower layer and can cause it to superheat in the same way as the fill induced stratification.

There are some significant differences however. Because the thickness of the upper cell is relatively thin it takes only a few days for the stratification to break down, but because the mixed liquid may still contain appreciable amounts of nitrogen the process of autostratification may be repeated.

Autostratification tends to occur only in peak shaving facilities immediately after filling or topping up of tanks.

POTENTIAL HAZARDS OF ROLLOVER

The main cause for concern is that rollover causes an uncontrolled increase in the generation of vapour which can develop into a hazardous situation.

From previously recorded incidents it has been estimated that about 65% had a peak vapour evolution of less than ten times the normal boil off rate with only 15% exceeding twenty times the normal boil off rate. At the higher rates it is possible that the combined normal boil off handling system and the atmospheric relief valves may not be adequate to prevent a pressure build up in the tank in excess of the design pressure.

However it must be emphasised that we are not aware of any reported rollover incidents which have led to fires, explosions or structural damage to storage tanks.

LNG Storage Tanks in the UK have relief valve systems which are typically sized for 300 times the normal boil off rate.

FACTORS WHICH AFFECT ROLLOVER

Density Difference

A survey of technical papers suggests that stratification can occur with density differences as small as 1 kg/m^3 , (based on empirical laboratory scale experiments) but the critical density at which the two layers will not mix is not known with any certainty.

Examination of historical data available to British Gas has led to the conclusion that density differences of the order of 5-10 kg/m^3 have existed between heel and cargo without rollovers occurring.

Variations in the C_{2+} content of the feed will vary the product density so the Ethane content of the product should be closely controlled.

Nitrogen Content

As discussed earlier, autostratification may occur in an LNG containing more than about 1% nitrogen. The limiting quantity of Nitrogen that can be tolerated in the feed gas is dependent on the design of the liquefaction plant and its ability to produce product at different temperatures. The higher the product temperature the greater the flash as it is depressurised into the tank and the lower the nitrogen content of the liquid.

ROLLOVER MAGNITUDE

The magnitude of the rollover i.e. quantities of vapour evolved is likely to be affected by:

a. Lower layer inventory.
b. Initial density difference.
c. Upper layer depth.
d. Recent boil off history.

The greater the density difference between the two layers, the more energy will have to be absorbed by the lower level before rollover occurs. A larger amount of superheat stored in the lower layer might be expected to create a higher level of vapour evolution.

An increase in the upper layer depth will increase the hydrostatic head acting on the lower layer. This again results in a greater degree of superheat being required before rollover occurs. The size of the top layer will affect the timescale involved before mixing occurs. (It is important to remember that events are both time and liquid quality dependent).

CASE STUDY

In late 1993 a roll over occurred at the British Gas storage site at Partington, near Manchester, England. During this incident, which lasted two hours, about 150 tonnes of natural gas were vented to atmosphere. No major physical damage was done to the tank which was quickly put back into service.

The cause of this incident was subsequently shown to be the result of a stratification within the tank which had occurred during the previous production run. Top filling of a tank with about 1900 tonnes of an LNG, containing less than 2% non methane hydrocarbons, on top of 18,650 tonnes of a much richer LNG.

Background

As a consequence of the commissioning of new gas fields in the Northern North Sea the heavy hydrocarbon content and the carbon dioxide content of the feed gas for the liquefaction plant had increased over a period of a few years.

New plant had been installed to overcome this problem and it consisted of an absorption column to remove most of the carbon dioxide and some of the heavier hydrocarbons, and a cryogenic distillation column to remove the remaining heavy hydrocarbons.

The autumn 1993 production run incorporated the commissioning of the cryogenic distillation plant and was also influenced by the downtime period of the Morecambe Bay gas field which feeds into the National Transmission System north of Manchester.

Partly due to the increase in heavy hydrocarbon content of the feed gas, but more significantly as a result of product ageing, the LNG stock composition was rich in Ethane and its' density has been calculated to have been about 446 kg/m^3 .

1993 Production Run

The tank in question initially contained 17,266 tonnes and a total of 3433 tonnes of new product were added over a period of 24 days. The first eleven days of production were operationally no different to previous production runs. However the cryogenic distillation plant was then commissioned and operated for the final 13 days. This period coincided with the shutdown of the Morecambe Gas Field significantly reducing the nitrogen content of the feed gas.

The feed gas for the liquefaction plants had contained progressively more heavy hydrocarbons over the preceding years resulting in a stock of LNG of density of about 446 kg/m^3. This problem had been identified and a new hydrocarbon stripping column had been just commissioned producing an LNG of density 433 kg/m^3.

Sixty eight days after filling ceased the tank pressure started to rise rapidly and the relief valves lifted. The tank continued to vent gas for 120 minutes until the relief valves closed.

Post Rollover Analysis

Following the rollover the operational information was analysed and indicated that the first phase of production had resulted in an LNG with a density of 449 kg/m^3. Being heavier than the heel LNG it was concluded that this liquid had mixed without difficulty. This information is given in Table 1.

TABLE 1 LNG COMPOSITION

	HEEL	PHASE 1	PHASE 2
Tonnes	17,266	1,533	1,900
Nitrogen %	0.38	1.60	0.50
Methane %	92.60	92.70	97.50
Ethane %	6.53	5.70	2.00
Propane %	0.46		
Butane %	0.03		
Density kg/m^3	446	449	433

The product from phase 2 of the production was calculated to have a density some $13kg/m^3$ lighter than the mixture of the heel and phase 1 production. This was sufficient in this case to form a stratification. The calculated situation at the end of the production is given in Table 2.

TABLE 2 STRATIFIED LNG COMPOSITION

	LOWER LAYER	UPPER LAYER	TOTAL
Quantity (Tonnes)	18,650	1,900	20,550
Level (m)	31.44	3.30	34.74
Composition:-			
N_2	0.47	0.50	
C_1	92.60	97.50	
C_2	6.47	2.00	
C_{3+}	0.46	-	
Molecular Weight	17.14	16.30	
Density (kg/m^3)	446	433	
Tank Diameter (m)			41.15
Tank heat leak (kW)	21.505	15.495	37.0

It is interesting to note that over the first 58 days after filling only about 160 tonnes had boiled off whereas about 350 tonnes would normally have been expected. Consideration of the heat leak into the two layers shows that the actual boil off roughly equates to the top layer behaving normally with the bottom layer warming up without vapour loss.

After 68 days, at the time of the rollover, there was a boil off deficit of about 200 tonnes. During the incident it is calculated that about 150 tonnes was vented from the tank over a period of about 2 hours , the rest being processed by the normal routes.

There is much discussion in the literature about rollovers occurring when the densities of the two layers approach each other. Using thermodynamic computer models and the method described later, in the section entitled Prediction of Rollover, it is possible to show that the two layers in this case would not have equated in density for more than 120 days whereas this rollover occurred after 68 days.

However using the same models it is possible to show that at around 68 days the lower layer had reached its new bubble point under the hydrostatic head of the upper layer. It is believed that it is the creation of bubbles at the interface at the edge of the tank that caused the stratification to break down in this case.

Vapour release

The LNG tank at Partington is designed with a high relief valve capacity of:

2 Process RVs	20.2 Tonnes/h each
5 Emergency RVs	16.6 Tonnes/h each
Total Capacity	123.2 Tonnes/h.

During the incident all the RVs lifted. It is considered that the vapour evolution rate was in excess of 40.4 tonnes/h but somewhat less than the total system capacity. At no point did the tank pressure exceed the lifting pressure of the relief system.

This incident demonstrates the need for procedures to prevent stratification, identify where stratification has occurred, encourage product mixing, and to be capable of predicting the time at which a rollover is likely.

PREVENTION OF STRATIFICATION IN LNG STORAGE TANKS

Outlined below is the approach adopted by British Gas at its LNG peak shave storage facilities to prevent stratification occurring in LNG storage tanks.
The approach is based on preventing the two known methods of LNG stratification, namely density induced stratification during fill and nitrogen induced autostratification.

Filling of Tanks

The following guidelines have been adopted by British Gas for the filling of peak shave LNG tanks.

1. Prior to filling, an export trial is carried out to determine the composition and density of tank stock present. The density is derived by calculation from the gas export analysis.

2. With the information obtained in 1 above the liquefaction plant is commissioned to produce an LNG with a target density within $5kg/m^3$ of the tank stock.

3. The analysis of liquefaction product is routinely monitored to ensure it conforms to the required specification. This can be done by online analyser or by ad hoc sampling. The predicted analysis and density of actual liquid product entering the tank after flash is calculated using thermodynamic models.

4. Regular sampling and analysis of boil off/flash gas from the fill tank is carried out to compare this with the predicted LNG composition from 3 above. It is believed that stratification and autostratification can be detected in this way.

5. In order to minimise autostratification British Gas has set a target limit of 0.8% nitrogen content in the LNG remaining in the tank after fill.

   The nitrogen content of LNG entering the tank is adjusted by controlling the temperature at which the LNG is flashed from plant pressure of approximately 36 barg to storage tank pressure which is typically 80 mbarg. By analysing the results of the export carried out prior to the liquefaction period it is possible to aim at a nitrogen content in the product LNG.

6. Other factors. The density difference of $5 kg/m^3$ can be relaxed if recirculation of the tank stock is carried out during filling. This promotes mixing of the product LNG with the LNG present in the tank.

Identification of Stratification

Below is an outline of the methods adopted by British Gas to identify and deal with possible stratification in LNG storage tanks.

After Filling

1. After filling, the boil off gas quantity is monitored by a daily plot of tank level (or individual boil off flow) which is compared to the expected stock loss due to boil off for each tank.

2. After the filling of a tank, carry out regular sampling and analysis of boil off gas and plot the results against time. A tank recently filled will have high quantities of nitrogen in the boil off gas. Should autostratification occur the nitrogen content will fall very quickly. Should a density induced stratification be present the boil off gas will contain little or no other hydrocarbons apart from methane.

3. If a stratification is suspected, recirculation of tank contents from bottom to top is carried out. This has the effect of releasing any superheat which may have become stored in the lower layers and also promotes mixing of the tank contents.

TRAVERSING DENSITY/TEMPERATURE INSTRUMENT

One of the tanks at Avonmouth has installed a Scientific Instruments experimental liquid level, temperature and density tank gauging system (densitometer). These measurements are achieved using a multi sensor probe assembly which can be driven vertically up and down through the tank contents.

As a result of recent changes in feed gas quality a research programme has been established to determine the possible contribution that such an instrument can offer with regard to the general understanding of stratification.

PREDICTION OF ROLLOVER

If it is identified that stratification has occurred it is reasonably straightforward to predict when rollover is likely to occur. To calculate this the following data is required.

1. The initial quantity and quality of both layers.

2. The insulation characteristics of the tank.

3. The pressure at the top of the tank.

A general description of the method follows:

a. From the relative quantities of the layers the height of the interface can be established.

b. From the composition information the density of the upper layer can be calculated and hence the pressure at the interface can be estimated.

c. Having established the interface level the heat input rate to each layer can be calculated by applying the knowledge of the design of the insulation. A small adjustment should be made to account for heat transfer between the layers but this can be ignored for the first approximation.

d. Using a simple thermodynamic computer programme that predicts vapour liquid equilibrium for multicomponent hydrocarbons, the heat content (enthalpy) of the lower layer can be increased incrementally to simulate the heat input and the density plotted.

e Using the same model the loss of methane from the top layer, due to boil off, can be simulated and the density plotted.

f. The point at which the two densities converge is the point of time when rollover can be predicted as likely to occur.

g. The quantity of heat released as gas evolved is simply the heat input to the lower layer over that time, converted to latent heat of vaporisation.

As mentioned earlier, there is evidence that some rollovers occur when the lower layer boils at the interface. Therefore, a check needs to be made at each stage of the iteration that the lower layer has not reached its' bubble point given the interface pressure.

This prediction method can only be taken as a first approximation. Correction should be made for heat and mass transfer across the interface. Determination of the rate of mass transfer and subsequent migration of the interface is one of the current unknowns.

PREVENTION OF ROLLOVER

In the event that a stratification is identified and the potential for a rollover has been predicted, what tools are available to prevent the rollover from occurring ?

For density induced stratification the objective would be to promote mixing and release any trapped energy.

This can be achieved by circulating warm liquid from the lower layer back to the top of the tank where its' superheat can be released. In addition, this heavier liquid is then believed to make its way back to the lower layer. To do this it must penetrate the 'boundary layer' and is therefore believed to promote mixing.

A variation on the above is the transfer of some of the tank contents to other storage tanks (should they be available) or export to the pipeline network.

For nitrogen induced stratification the objective is to reduce the nitrogen content of the bulk liquid. This can be achieved again by circulating liquid from the bottom of the tank to the top. This warmer liquid flashes and the flash gas will be high in nitrogen. The resulting liquid may well be less dense and perpetrate the thin nitrogen top layer. This means that circulation may be required for extended periods in order to control energy release.

CONCLUSION

As stated at the outset, there are various aspects of the phenomenon of rollover which are still not fully understood. However, it is believed that the principles and strategy outlined above enable the storage of LNG to be managed in a way which minimises the potential for stratification occurring, and by detecting any stratification at an early stage, reduces the potential for such a situation developing into a rollover.

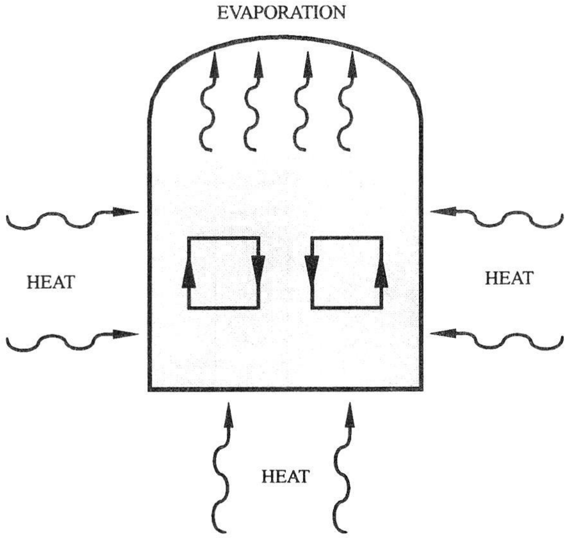

FIGURE 1 NORMAL TANK BEHAVIOUR

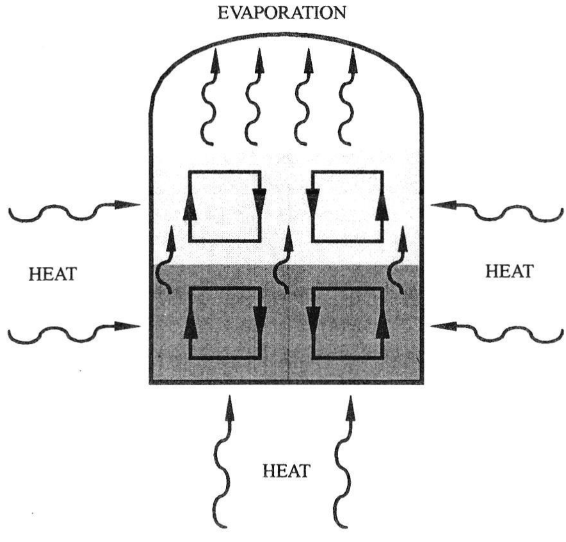

FIGURE 2 STRATIFIED TANK BEHAVIOUR