

Two Phase Flashing Releases following Rapid  
Depressurisation Due to Vessel Failure

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A programme of experimental work has been carried out at South Bank Polytechnic to provide detailed data on the behaviour of pressurised liquids in the event of vessel failure. A small-scale vessel using heated Freon-11 was used, and failed pneumatically. The resulting two-phase release was studied to discover how expansion rates and droplet sizes varied with the initial release conditions. Liquid remaining close to the vessel was also measured. The decay of pressure inside the vessel during the release was studied, and a model based on the thermodynamics and geometry of the situation has been developed.

Keywords:- Liquefied gases, pressure release, two-phase, flashing.

1 INTRODUCTION

The storage of normally gaseous materials, as liquids under pressure is a common and useful industrial practice. For example, Liquefied Petroleum Gas is stored in this way. However, accidents have occurred where such vessels have ruptured, releasing their contents as a Two-Phase mixture of liquid droplets and vapour, which have led to fires and explosions causing loss of life and property.

One of the major disasters in industrial history occurred on Monday, November 19th, 1984. In San Juan Ixhuatepec, a district of Mexico City, at approximately 5.45 a.m. a sequence of events was started at the Pemex State Oil Company facilities(1). These consisted of a bulk storage and distribution depot for Liquefied Petroleum Gas (LPG), a common industrial fuel. The site contained about 11,000 m<sup>3</sup> of LPG, in six large storage spheres and 48 other smaller tanks.

An intense fire and a series of explosions which took place between 5.45 a.m. and 8.00 p.m. on that Monday left the storage facility almost completely destroyed. The plant was surrounded by an area of high population in low quality housing. Much of this area was devastated by fire, and approximately 500 people were killed and 7,000 injured.

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Much of the damage was due to the sudden release of the entire contents of some of the storage vessels. This caused major explosions, creating large balls of flame and scattering fragments from the storage tanks over an area extending over 1 km from the site.

Of the six storage spheres, four were completely fragmented, and the remaining two suffered major ruptures. Of the 48 cylindrical tanks, 4 were totally destroyed and 12 were propelled off the site. The majority of the remaining tanks were seriously damaged; in many cases by being knocked from their supports by blast waves from the explosions.

As well as Liquefied Petroleum Gas (LPG), there are a number of other industrially important materials which can be liquefied and then stored as a liquid inside a closed vessel, using their own vapour pressure to maintain the liquid state.

These include flammable materials such as Propylene, and toxic ones such as Ammonia and Chlorine.

LPG, for example, is stored on many industrial and domestic sites, in vessels holding amounts from a few hundred grams up to several tonnes.

Normal, 'safe' working of pressurised storage should reduce the risks from such installations. However, as tragic incidents have occurred, the reasons for the failure of pressurised storage vessels are of concern.

The shell of a pressurised storage vessel is designed to withstand the normal storage pressure of its proposed contents, and the design codes allow for a significant safety margin on top of this pressure.

The vessel will fail if the stress at any point in the shell exceeds the ultimate strength of the material of which it is constructed. This can occur in three possible ways:

- i) An increase in internal pressure
- ii) A reduction in the yield strength of the material
- iii) A local increase in loading (e.g. due to impact).

There are also some effects which 'attack' the vessel in more than one way. A fire surrounding, or adjacent to the vessel can simultaneously lead to an increase in vessel pressure and a decrease in its strength.

If, for whatever reason, the integrity of the vessel is lost, then the pressure inside the vessel will fall. In the theoretical case of 'instantaneous' failure, the entire surface of the stored liquid is reduced to the atmospheric pressure at the moment of failure. The reduction in pressure is then transmitted through the liquid at the speed of sound.

In a real case there will be some interaction with the vessel. This may be merely a small resistance to expansion caused by the presence of relatively small vessel fragments, or there may be a substantial part of the vessel which remains intact. Examples of both these cases could be seen in the failure of the storage spheres at San Juan Ixhuatepec.

As the pressure falls, the thermodynamic equilibrium changes, and in order to regain an equilibrium state some of the liquid will rapidly 'flash' to vapour. The latent heat of vapourisation required to achieve this flash boiling is obtained by cooling the remaining liquid to its normal boiling point at atmospheric pressure.

At this point the Two-Phase release consists of three separate parts; the flashed vapour, the entrained droplets and any remaining liquid.

A study of published literature on the subject of hazards related to the pressurised storage of flammable and toxic materials reveals that this area has received little study in comparison with other topics in safety research. The study of the catastrophic failure of vessels being used for this purpose has received even less study.

In two 'survey' papers on the hazards presented by fireballs(2,3) Roberts notes the catastrophic failure of a pressurised storage tank as a possible source of the flammable cloud which could be ignited to form a fireball. He refers to only two groups of workers in connection with the study of the formation of this cloud. These are Hardee & Lee(4) and Hess et al.(5,6).

Jagger, too(7), notes these authors and also mentions the Canvey Report(8) and the Covo Study(9) as examples of the techniques used to predict the behaviour of such systems.

The lack of research in this area is pronounced, especially when the frequency of catastrophic failures is estimated by Hess et al.(6) at  $> 10^{-6}$  failures per vessel per year, and the consequences can be as devastating as those seen in Mexico City(1).

The study of Two-Phase releases in general has concentrated on the releases produced when superheated mixtures are discharged through a limited area. Under these circumstances the release is relatively slow and can be regarded as a 'steady state' process for many calculations. Several authors have published work on such topics, including Van Den Akker(10), Moody(11) and Fletcher(12).

As noted by several authors, including Lees(13), and Richardson(14), the sudden, total failure of a pressurised storage vessel is one of the most hazardous occurrences which could take place on a chemical plant.

Experimental work to investigate this type of release has been reported by Hess et al.(6), Sato(15) and Reed(16). This has been undertaken using small and medium scale vessels, and artificially causing the failure of the vessel, followed by observation of the resulting Two-Phase release.

The experimental work described in this paper represents an attempt to provide a model for such releases which can be relied on to give suitable source terms for existing and future 'consequence' models.

The experimental work, described in Sections 2 and 3, is based on the use of a small vessel and a model material, in this case Freon-11. The failure mechanism is a pneumatically controlled separation of the vessel into two halves. This produces a release which occurs simultaneously from both above and below the normal 'fill level' of the vessel.



The release is not considered to be 'instantaneous', but to take place over a brief but finite period of time. This is controlled by the opening of the vessel, and is a more realistic approach than modelling the release assuming the vessel plays no role at all.

## 2 EXPERIMENTAL EQUIPMENT

The type of Two-Phase release under study is produced when a vessel, containing a liquid under pressure above its normal boiling point, undergoes a rapid depressurisation caused by a major failure of the vessel wall. This failure may lead to the breakup of the vessel into several separate fragments, or may produce a large gap in the vessel wall.

In either case, the depressurisation will take place over a brief, but finite, time interval. The 'ideal' theoretical model reduces this time to that required to propagate the pressure drop throughout the liquid. This time is determined by the mass of liquid present and the sonic velocity within that liquid. In practice the time required for the equalisation of the pressure in the fluid with that of the atmosphere will be greater than this theoretical time, as the physical presence of the vessel will interfere with the expansion processes which reduce the pressure. This will be the case where the vessel fragments are moved out of the way of the expanding release, and will be even more significant where the whole vessel, or sizable portions of the vessel, remain substantially intact.

The experimental equipment constructed uses a small vessel relative to a full-size storage vessel, and also uses a model fluid which is heated above ambient temperatures to produce the internal conditions required for a Two-Phase release.

The vessel used for the majority of the experimental programme was a spherical container with an internal diameter of 0.115m thus giving a total volume of  $3.2 \times 10^{-3} \text{ m}^3$ . The vessel was formed in two identically shaped sections, thus allowing a circumferential fracture to be simulated by parting the two halves. The vessel is shown in Figure 1.

The vessel was fabricated from cast aluminium, and was designed to withstand internal pressure in excess of 2000 kPa. An external flange allowed the two halves of the vessel to be fastened together during filling. The two vessel halves were sealed against a neoprene gasket held between the two flanges.

The vessel was instrumented for pressure measurement using a pressure transducer and for temperature measurement using thermocouples at the top and bottom of the vessel.

The model fluid used was Freon-11 (Dichlorodifluoroethylene) which has a normal boiling point of  $c.23^\circ\text{C}$ , allowing easy handling as a liquid and heating to superheated conditions inside the closed vessel.

## 3 OPERATIONAL PROCEDURE

The vessel halves were held together using two horizontally opposed pneumatic rams, operating at 1000 kPa (10 bar). A known mass of Freon-11 was placed in the vessel, which was then sealed.

A small internal electrical heater was used to supply energy to the closed system until a steady state at the desired internal conditions was indicated by the pressure and temperature measurements. The vessel halves continued to move apart during the subsequent release.

Each of the vessel halves was attached to one of the pneumatic rams, and when the desired initial conditions had been achieved the air flow was reversed, pulling the vessel apart to create the "failure".

The vessel has been used to produce Two-Phase releases of Freon-11 at various elevated pressures ranging from c.200 kPa to c.500 kPa, although releases at higher pressures would be possible with the current equipment. Freon-11 at 500 kPa has a boiling point of  $c.65^\circ\text{C}$ , giving a  $40^\circ\text{C}$  superheat which is similar to that of Propane stored at  $15^\circ\text{C}$ .

Production of the Two-Phase release gives rise to three distinct components. These are:

- (i) The liquid which remains in or near the vessel, which is not affected by the release other than being cooled.
- (ii) The liquid which is broken up into small droplets during the rapid boiling, and is then carried away from the vessel.
- (iii) The vapour produced during the boiling of the liquid, the expansion of which causes the spreading of the release away from the vessel.

### (i) Liquid

The method chosen to measure the residual liquid consists of capturing the liquid in a simulated 'bund'. This is a tray mounted beneath the vessel into which any liquid remaining in the vessel after depressurisation will fall. The tray will also collect any aerosol-borne droplets which have very steep downward trajectories. In this respect it acts in an identical manner to a fixed bund.

The tray is mounted on a balanced system of three load cells, the signals from which are summed directly and then amplified. The output from this system is recorded on a chart recorder for later analysis.

### (ii) Droplets

The Two-Phase release produces a body of expanding vapour, in which much of the liquid is entrained as small droplets(13). The cloud of droplets is of interest on two levels. Firstly the shape and size of the cloud, together with its rate of expansion, can be interpreted to show significant processes which are affecting its evolution, such as the rate of air entrainment. Secondly, the droplets which form the cloud will possess properties, such as their size distribution and concentration which are characteristic of the mechanisms which produced them.

Such a wide range of droplet cloud parameters requires a variety of measurement techniques, and this part of the Two-Phase release is the one which has been studied in greatest detail in this experimental programme.

The general shape and expansion of the droplet cloud was studied using video photography. The experimental releases were recorded from a number of angles, and the recordings were later studied using 'freeze-frame' techniques.

The droplet sizes were initially studied using direct photography, but it was found that the required magnifications meant that only a small, statistically non-significant number of droplets were observed.

The main method of particle size analysis involved the use of a Malvern HSD2600 Laser Particle Analyser. This is a commercial instrument for the measurement of particle size distributions. It depends on the scattering of laser light by the particles, and because it uses only a low power laser beam within the spray, it has no discernable effect on the spray pattern(17). The results are collected and processed using a dedicated microcomputer.

The software of the Malvern is designed to take readings of dusts or continuous sprays of high statistical certainty. It achieves this by taking several tens of consecutive readings from the detector, and producing a single average. This means that a significant amount of intermediate processing is required to produce the single, final result. The software supplied with the machine is capable of taking several single readings, but it requires nearly 2 seconds to process each result before taking the next one.

As the total release time is approximately 0.5 seconds this is not a satisfactory system. Consequently the data acquisition and processing software was modified.

The eventual system is made up of three parts, the original acquisition routine, a machine code 'driver' for this routine, and a BASIC control program. This system gave a sampling rate of 8 samples per second, and could store 20 separate samples in the available memory within the microcomputer.

(iii) Vapour

A preliminary investigation has been made into the use of hot-wire anemometry for studying the vapour concentration in the two phase release. This system is currently under development and results from these experiments will be available shortly.

(iv) Vessel Internal Pressure

The change in internal pressure, as the superheated liquid boils and the resulting Two-Phase mixture escapes, is characteristic of the release. The pressure difference across the opening provides the driving force for the acceleration of the release, and the reduction of pressure acting on the mixture provides the thermodynamic change leading to the boiling of the liquid.

The vessel is already instrumented for measuring the internal pressure prior to the initiation of the release. In order to extend this reading to give a record of the pressure change during the release it was decided to record the output from the pressure measurement system.

This was done using a transient recorder sampling at 4 kHz.

It was found that the time required for equalising the internal pressure with the atmosphere was of the order of 250 ms. Thus the recorder samples approximately 100 points on the pressure decay curve.

4 EXPERIMENTAL RESULTS

4.1 RESIDUAL LIQUID

The output from the load cell system shows four distinct sections (see figure 2):

(a) There is an initial, slight drop in the apparent tray weight. It is assumed that this is due to slight movements of the tray supports as the release is initiated, which was observed during the course of the experiments.

(b) Following the failure of the vessel, there is a very large and rapid increase in tray loading, which is due to a number of factors. The released vapour and flashing liquid produce a pressure wave, part of which is absorbed by the tray. The residual liquid falls onto the tray, contributing a load due to its mass, and also to impact loading as the tray absorbs the inertia of the falling liquid.

It is also assumed that the initial 'drop', (a), is restored during this period as the support framework regains its original position.

(c) The initial loading rapidly falls away as the vapour and liquid momentum is dissipated. This period is characterised by relatively large oscillations in the measured tray loadings. These are caused by vibrations in the tray induced during the initial impact.

(d) The oscillations die away as the tray ceases to flex, and a smooth curve showing a slow fall in loading follows. The load now is due to the Freon-11 present on the tray, and the load falls as the Freon-11 evaporates.

By extrapolating this curve back through the initial extra loading of the tray to the release time, the amount of residual liquid which actually fell onto the tray can be estimated. This is shown in Figure 2.

Mean values from experiments at various initial conditions are shown in Table 1.

4.2 DROPLET SIZES

The results from the Laser Particle Size Analyser were examined.

The general shape of the raw data suggested a log-normal distribution, following the equation:

$$f(d) = \frac{1}{\sqrt{2\pi} \log(n)} \exp \left[ \frac{-1}{2} \left( \frac{\log(d) - \log(\bar{d})}{\log(n)} \right)^2 \right]$$



where:  $f(d)$  is the frequency with which particles of diameter  $d$  occur.  
 $\bar{d}$  is the mean diameter, and  $n$  a distribution parameter.

The best log-normal curves were fitted to the experimental data e.g. Figure 3 and it was found that 'smoothing' the resulting curves introduced only slight changes. The resulting parameters are shown in Table 2.

4.3 DROPLET VELOCITIES

The video recordings show the failure of the vessel, and the subsequent two-phase release. These have been used to provide an estimation of the droplet velocity, and the final expansion of the cloud.

The cloud of droplets was circular, expanding radially from the opening in the vessel.

The video recordings could only follow the release over its initial stages, until the droplets evaporated. No detection of the vapour cloud was possible. In order to give an overall view of the release a distant viewpoint was chosen, and from this position the video camera could not resolve individual droplets.

In order to obtain an estimate of average droplet velocity, the outer edge of the cloud was studied. This was the only part of the release whose position could be determined throughout the lifetime of the droplet cloud.

4.4 PRESSURE HISTORIES

These were taken across the full range of initial conditions studied, and are discussed in greater detail below.

5 THEORETICAL MODELLING

The theoretical models developed by previous workers have been discussed earlier. These models are all based on the assumption of 'instantaneous' vessel failure, in which the vessel itself plays no part in any stage of the development of the release. Because of this assumption such models are not directly applicable to the releases studied in the experimental work described above, nor, indeed, to actual incidents.

Thus a theoretical treatment which includes the effects of confinement by the vessel is indicated for both experimental and real-life situations, whether the vessel forms a constraint throughout the release or just at the beginning when energy is extracted to overcome the inertia of the fragments.

A typical pressure history is shown in Figure 3. This can be divided into two main sections. Point (A) corresponds to the moment of failure. This is followed by the first section (A-B) in which the pressure falls very rapidly. During the second section (B-C) the decay of pressure is much slower. By point (C) the pressure has fallen to atmospheric, and the pressure driven vessel evacuation has finished.

It is suggested that the initial, rapid pressure drop is due to the exit of vapour from the vessel, and occurs before flash boiling begins. The second section is then due to the two-phase part of the release, once the vessel contents are a boiling mixture.

Assuming that the flash boiling is isentropic, that the vapour behaves as an ideal gas, and that the droplet/vapour cloud is at a constant temperature, the vapour flow section can be modelled(18) using the equation:

$$t = \frac{\sqrt{\beta} V_v t_e^w (w+1)}{A_e} \ln \left[ \frac{2 \sqrt{P_i^2 - P_i P_a} + 2(P_i - P_a)}{2 \sqrt{P_t^2 - P_t P_a} + 2(P_t - P_a)} \right] \frac{1}{(w+1)}$$

where:

$t$  = time

$V_v$  = the initial vapour volume

$A$  = exit area

$P$  = pressure

$i, a, e$  denote initial, ambient and equilibrium conditions

$\beta, w$  are vessel dependent constants

Using similar assumptions a model for the two-phase flow can also be derived(19).

This is based on the additional assumption that the pressure drop can be modelled by assuming that it is due to vapour exit alone, but that the available area for vapour exit is constricted by the presence of liquid. In this way the flash fraction,  $X$ , is the measure of constriction.

$$t = \frac{\sqrt{\beta} V_v t_e^w (w+1)}{A_e} \int_{P_t}^{P_i} \left[ \frac{dP_t}{\sqrt{P_t^2 - P_t P_a} X(P_t)} \right] \frac{1}{(w+1)}$$

where  $X$  is the flash fraction, which can be described from third order polynomial expressions for the entropy pressure relationship as:

$$X(P_t) = \frac{X_i (i+jP_i+kP_i^2+lP_i^3) - (fP_t+gP_t^2+hP_t^3)}{(i+jP_t+kP_t^2+lP_t^3)}$$

where  $f, g, h, i, j, k, l$  are constants (dependent on the material).

The integral part of this equation has no simple analytical solution, and must be integrated numerically to provide the final Pressure-Time relationship.

6 DISCUSSION

The estimates of the amount of bulk liquid remaining close to the vessel, obtained as described, show that the amount of such liquid varies with both the initial pressure, prior to release and with the amount of material present in the release.

In percentage terms, this varied from a highest value of almost 70% of the initial contents (at an initial pressure of 310 kPa, and a fill of 45%), to a lowest value of below 13% (with initial pressure of 517 kPa and fill of 65%).

The current estimating techniques for this 'residual' liquid are based on the flash fraction, assuming that the proportion of liquid carried away from the vessel in the expanding cloud is simply related to the flash fraction. Estimates of this proportion vary from an amount equal to the flash fraction, to an amount twice the flash fraction(13).

Applying such correlations to the experimental situation leads to estimates of between 50.5% and 67% in the case giving 70% experimentally, and between 22.9% and 48.7% in the case which actually gave 13%.

With no flashing, the residual liquid will be all of the initial contents. Hasegawa & Sato(16) state that the residual liquid falls to zero when the flash fraction reaches 35%. Roberts(2,3) suggests that, in the absence of other information, a linear interpolation between these points is made for intermediate flash fractions. This gives values of 53% and 28% for the two cases above.

There is no suggestion in the literature that the residual liquid fraction will vary with fill level. The distribution of the initial release mass between bulk liquid, vapour and aerosol can be calculated from the bulk liquid measurements assuming completely adiabatic flashing. The results of such calculations are given in Table 3.

The pressure history model was incorporated into a computer code, which was used to produce theoretical pressure-time curves for the experimental conditions. Appropriate vessel factors were included, using the experimental vessel dimensions etc.

A comparison of the model curve together with average experimental points is shown in figure 4.

The model also allows calculation of the exit velocity, values of which are given in Table 4. These compare fairly well with the velocities measured in the experiments.

#### 7 CONCLUSIONS

The experimental equipment described provides a method of producing repeatable two-phase releases from a major vessel failure at known initial conditions.

The distribution of material between liquid, vapour and aerosol in the release has been shown to depend (in this case) on fill level as well as superheat, which is the sole consideration in current models.

The size of droplets in the aerosol is also fill dependent, again this is not predicted by current theoretical models.

The model of pressure decay assumes both adiabatic flashing and significant vessel interaction, and closely follows the observed effects in the experimental work.

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Pressure	310 kPa	414 kPa	517 kPa
Percentage fill			
25	174	88	62
45	349	172	81
65	262	160	94
85	314	302	135

Average values in grams

TABLE 1 - Residual Liquid Estimates

Pressure	310 kPa		414 kPa		517 kPa	
	$\bar{d}$	n	$\bar{d}$	n	$\bar{d}$	n
% Fill						
25	100	1.45	90	1.50	70	1.58
45	*	*	90	1.45	70	1.45
65	60	1.45	50	1.50	30	1.50
85	85	1.47	70	1.43	60	1.40

\* - these showed large variations, but were early runs

TABLE 2 - Droplet Size Parameters  
(Log-Normal Distribution)

Pressure % Fill	310 kPa			414 kPa			517 kPa		
	Liq.	Vap.	Aer.	Liq.	Vap.	Aer.	Liq.	Vap.	Aer.
25	58.0	16.5	25.5	29.3	21.2	49.5	20.7	25.7	53.6
45	69.8	16.5	13.7	34.4	21.2	44.4	16.2	25.7	58.1
65	34.9	16.5	48.6	21.3	21.2	57.5	12.5	25.7	61.8
85	31.4	16.5	52.1	30.2	21.2	48.6	13.5	25.7	60.8

TABLE 3 - Mass Distribution in Release (%)

Pressure Fill Level	310 kPa	414 kPa	517 kPa
25%	5.801	5.097	4.737
45%	8.097	6.909	6.295
65%	10.076	8.402	7.528
85%	11.478	9.418	8.343

TABLE 4 - Calculated Exit Velocities

Note:

The values given are the average exit velocity, in metres per second, over the duration of the release.

These values compare well with those estimates from the video recordings of actual releases.

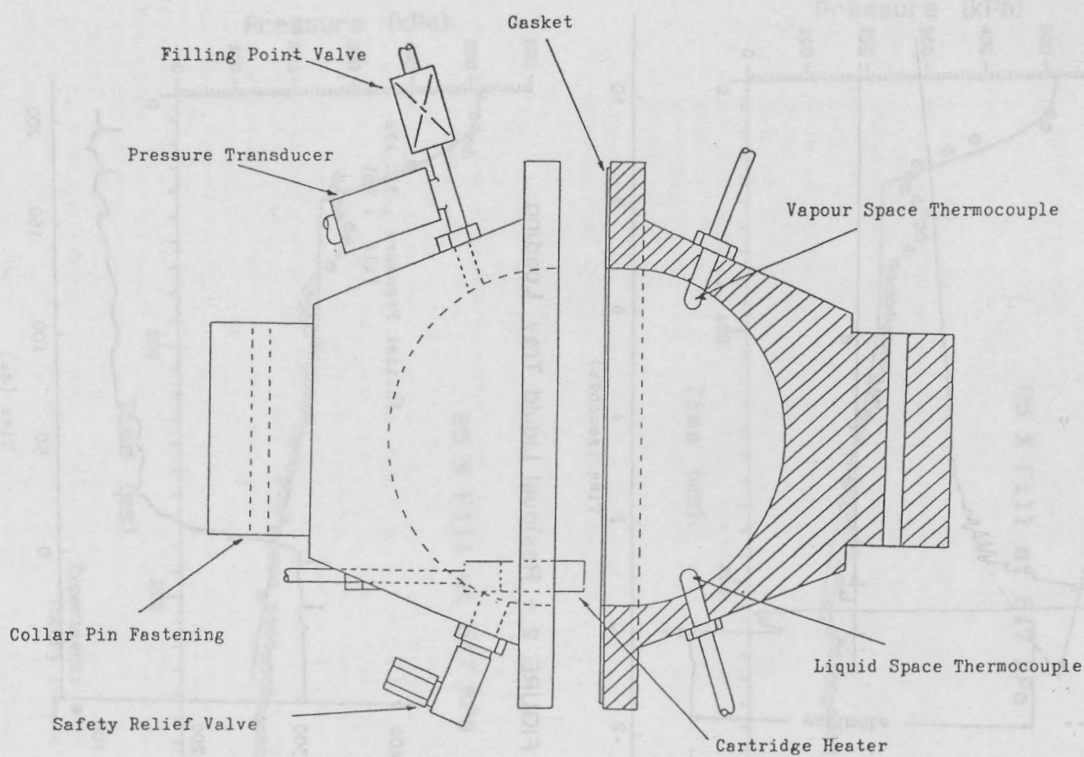


FIGURE 1 - Diagram of the Vessel



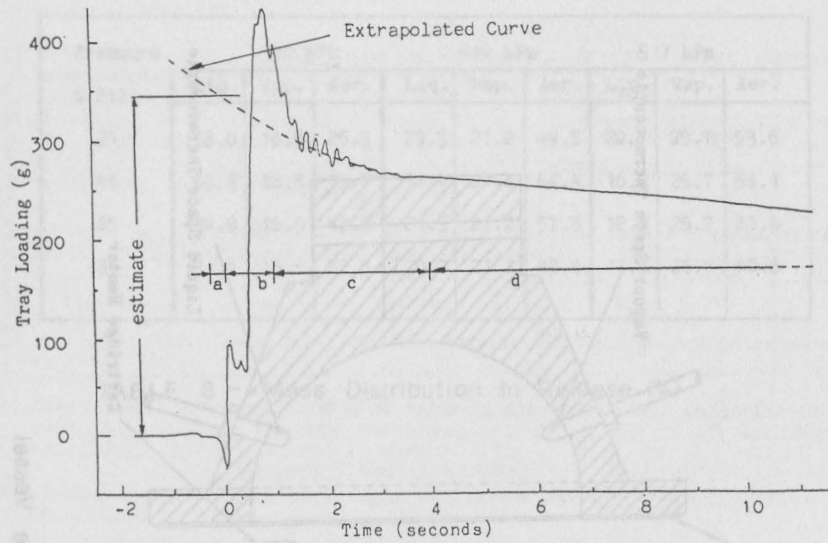


FIGURE 2 - Residual Liquid Tray Loading

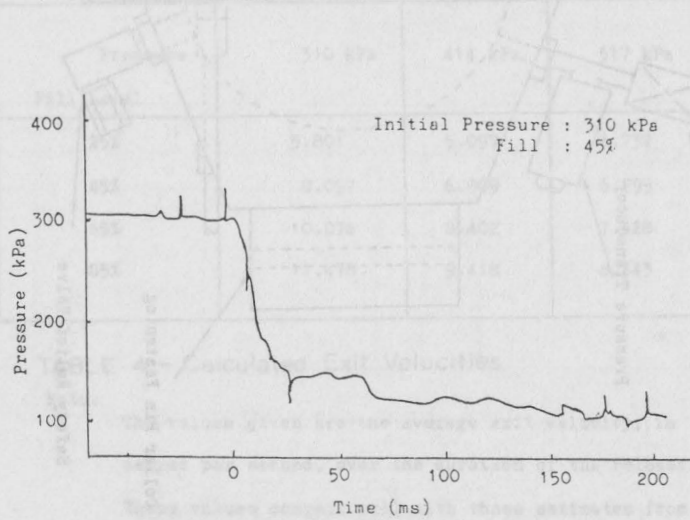


FIGURE 3 - Internal Pressure History

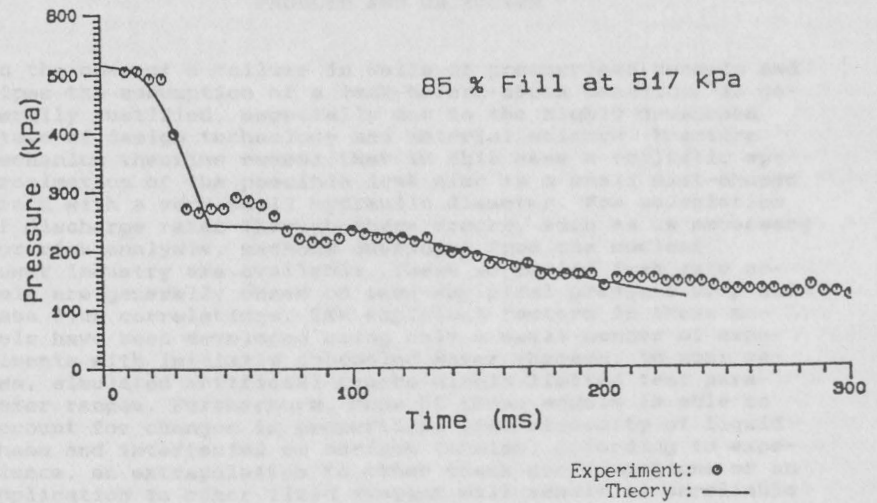
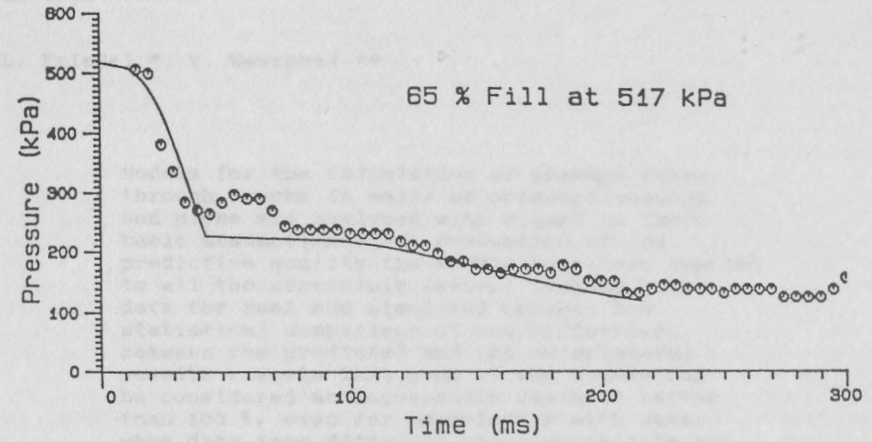


FIGURE 4 - Comparison of Model with Experiment