

Scale-up for Safety Relief of Runaway Reactions

A best-estimate approach to sizing emergency relief systems for runaway reactions in large vessels must be based on homogeneous vessel behavior.

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Sizing of adequate emergency relief systems (ERSs) to protect against runaway chemical reactions is often made difficult by the general lack of thermal, as well as the necessary thermo-physical property, data [1]. The acquisition of such data in order to use computer models [2,3,4] can be time-consuming and very costly. A possible means for relieving this difficulty is to simulate, or determine, the vent-line systems during runaway reactions in test vessels [2,5,6,7].

However, in order for such an approach to become universally accepted, assurance must be provided that direct scale-up (i.e., on the basis of area-to-volume) will lead to a safe design while, at the same time, keeping the test-vessel volume relatively small* (i.e., on the order of 100 ml). At first glance these two requirements appear incompatible.

Keeping the test volume to a minimum is essential so as to 1) allow relatively unknown processes to be tested, and 2) quickly carry out experiments to determine relative hazards of various upset conditions. However, the use of potentially much smaller test volumes than previously used [6, 7] also increases the concerns related to non-prototypic effects leading to unsafe scale-up conditions. Principal concerns with a small vessel volume are:

- inadequate adiabaticity relative to large-scale;
- excessive vapor disengagement relative to large-scale; and

*A 260-liter vessel was used by Burchett [6] to simulate the effectiveness of the vent line involving two incidents with runaway reaction of chloroprene in large process vessels, while Harmon [7] used a 19-liter vessel to simulate runaway polymerizations.

- a small relief device and excessive non-equilibrium flashing-flow effects relative to large-scale.

These concerns are discussed below, and a new scaling approach is outlined allowing necessary scaling measurements to be made with a small test volume (approximately 300 ml).

TEST VESSEL SCALE-UP CONCERNS

Potential non-prototypical effects that will lead to unsafe scale-up results include adiabaticity, vapor disengagement, and non-equilibrium flashing-flow effects.

Adiabaticity

Ideally speaking, an adiabatic test vessel would be desirable. This would eliminate all concerns relative to altering the reaction path and, hence, the energy-release rate during runaway conditions. While perfect adiabaticity is difficult to achieve, the concerns can be alleviated by assuring that the heat losses per kg reactor contents are not greater in the test case than in the large-scale application [2].

This appears to be the case for the small-scale test experiments (approximately 260-liter) of Burchett [6] simulating known incidents of runaway reaction of chloroprene in large-scale (approximately 7570-liter) process vessels. It is estimated that the effective heat capacity of the vessel is about 15 to 20% of the fluid heat capacity in both cases [8]. It follows that the measured energy-release rates in the

260-liter test vessel can be safely extrapolated directly to the incident cases in question. However, because of the likely presence of non-prototypic effects of vapor disengagement and non-equilibrium vent flows as discussed below, scale-up from these experiments on the basis of area-to-volume, area-to-weight monomer, or area-to-energy release rate must be cautioned against.

The feasibility of eliminating the heat-capacity problem even with a very small test cell (of the order 100 ml) is further illustrated by Harmon and Stuper [7]. Since the test-cell wall thickness was designed to withstand moderate pressures (approximately 2 MPa), a tolerable adiabaticity was achieved converting the test cell itself into a heater. In this way the effects of the mass of heater and sample cell are minimized. It was shown that the kinetic data obtained from the small test cell were in good agreement with the 19-liter tests which were used for venting purposes. An acceptable adiabaticity can also be provided by the use of a thin-walled vessel, when the outside pressure is regulated to essentially coincide with the rise in inside pressure due to the runaway reaction. Therefore, adequate adiabatic conditions for runaway conditions, even for a small test apparatus are achievable.

Vapor Disengagement

Simple scale-up based upon area-to-volume is valid only as long as the scale does not affect the carry-over process (i.e., does not affect the vapor quality entering the vent line) [2]. From a practical point of view, this condition is difficult to achieve, since the superficial vapor velocity for a given energy-release rate per unit volume is directly proportional to vessel height [9].

Even with systems showing "bubbly-like" behavior and using relatively large test vessels, the results can be misleading relative to large-scale behavior (for example, Burchett's experiments [6] in a 260-liter test vessel simulating two incidents involving actual runaway chloroprene reactions in large-scale process vessels*). At a set pressure of 0.61 MPa, the average superficial velocity (approximately 2.5 cm/s) in the test vessel is well below the maximum achievable superficial velocity (approximately 5 cm/s) in the bubbly regime at an average void fraction of 0.50. The actual liquid swell, estimated from the bubbly drift-flux function [$j_s/V_b \sim \alpha(1 - \alpha)$, where j_s is the superficial velocity, V_b (approximately 20 cm/s) is the bubble-rise velocity, and α is the average void fraction] is approximately 15%. This value is of the same order as the freeboard volume at the set pressure condition, suggesting that, on a volume basis, mostly vapor is entering the relief line. Assuming a volume fraction, α , of 90% entering the relief line, an equilibrium balance written at the set pressure

$$\frac{Wq}{h_{fg}\rho_g} = \frac{GA}{\rho_l(1-\alpha)} \quad (1)$$

where W (~ 191 kg) is the weight of monomer in the test vessel, q (~ 0.33 kJ/kg-s) is the energy release rate per unit mass at the set pressure (~ 0.61 MPa), h_{fg} (~ 253 kJ/kg) is the latent heat of vaporization, ρ_g (~ 16.4 kg/m³) is the vapor density, ρ_l (~ 800 kg/m³) is the liquid density, and G (~ 5700 kg/s-m²) is the calculated flow rate through the orifice assuming frozen flow (see further discussion below), results in a vent area, A , of approximately 2.1 cm², which corresponds to Burchett's measured value.*

*The first incident involved a 11,355-liter reaction vessel with ~ 0.3-MPa, 10.16-cm diameter safety disc and an equivalent-sized tail pipe. The vessel vented safely, and, following the incident, the vessel was found to be essentially empty. The second incident involved a 7570-liter vessel, again with a 10.16-cm diameter safety disc (and an equivalent-sized tail pipe) but set at ~ 0.61 MPa. In this case the runaway reaction resulted in vessel rupture.

* Direct scale-up of this value, even when obtained for zero overpressure conditions, leads to a large-scale vent size of 8.9-cm diameter as compared to the 10.16-cm diameter vent line attached to the 7570-liter incident vessel which experienced vessel rupture.

In contrast, the average superficial velocity (approximately 8 cm/s) in the incident 7570-liter vessel is well above the maximum achievable value in the bubbly regime, suggesting on a volume basis that mostly liquid would be entering the relief line. This is consistent with calculated behavior [10] which requires homogeneous venting (homogeneous vessel behavior and homogeneous equilibrium vent flow—the latter assumption is justified below) in order to explain the noted explosive runaway in pressure (i.e., vessel rupture) for the 7570-liter reaction vessel. (See Figure 1). Note that assuming bubbly-flow behavior in the vessel leads to essentially the same result. On the other hand, assuming churn turbulent vessel behavior [9] (i.e., significant vapor disengagement) clearly suggests that the 7570-liter vessel also should have vented safely.

References [10] and [11] provide further discussion relative to anticipated vapor-disengagement behavior in large-scale process vessels and conclude that a safe design practice must consider a homogeneous liquid-vapor mixture entering the vent line, unless flow-regime characterization data are available for a given system under realistic runaway relief conditions. As such, scaling on the basis of top venting in a small test vessel would be misleading unless the system is inherently "foamy" or sufficiently viscous. The latter would appear to be the case for the small-scale (approximately 19-liter) tests reported by Harmon and Stuper [7], which demonstrated little difference in the pressure characteristics by comparing top and bottom venting tests, hence validating their scaling approach [9]. These tests also used sufficiently long vent lines (L/D of approximately 100), which eliminates concern relative to non-prototypic, non-equilibrium flashing-flow effects as discussed further below.

Non-Equilibrium Flashing Flow

Scaling considerations also require consideration of non-equilibrium flashing-flow effects in the vent line. In this context, the use of short nozzles and orifices in small-scale tests to simulate large relief devices can also be misleading, since a smaller vent is needed to handle non-equilibrium flashing flows than equilibrium flows [12]. In a frictionless duct, deviation from equilibrium flashing is to a first order described by the parameter N in the

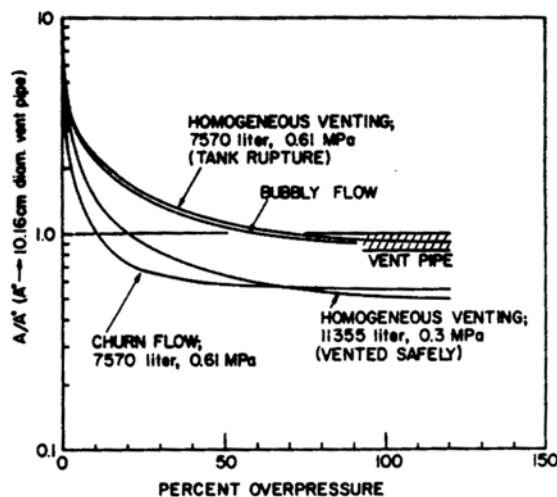


Figure 1. Predicted pressure behavior of two reported incidents involving runaway reactions of chloroprene in large-scale vessels. Shaded band reflects the estimated uncertainty in the actual discharge coefficient of the incident tail pipe. Calculations performed with a discharge coefficient equal to 1 (taken from Ref. [10]).

Henry-Fauske critical-flow model.* In Ref. [12] recommended values of N were based upon flashing-flow data through relatively small nozzles. This results in $N \ll 1$ in the low-quality range, which is indicative of large deviations from equilibrium.

Required relaxation lengths to approach equilibrium flow conditions have been demonstrated in a number of experiments reported in the open literature. In 1964 Fauske [13] illustrated the effect of geometry upon the critical flow rate for saturated water and a very wide range in the stagnation pressure (See Figure 2). The rapid decay in flows prior to reaching the asymptotic values [length-to-diameter (L/D) ratio of approximately 16] was attributed to increasing fluid residence times. For an $L/D = 0$ (sharpedged orifice), the residence time is zero, resulting in no flashing (i.e., $N = 0$ in the Henry-Fauske model), and the flow rate can be predicted by the standard incompressible single-phase flow equation [13]. On the other hand, at L/D approximately 16, sufficient time is available to allow the rate of flashing at the throat to approach equilibrium (i.e., $N \sim 1$ in the Henry-Fauske model). The relatively small decreases in the flow rates noted for larger L/D 's can be attributed mostly to frictional effects. For the given tube diameter ($D = 6.35$ mm), these experiments suggest an essentially constant relaxation length of the order of 100 mm over a wide range in the stagnation pressure.

A similar trend in the critical flow behavior starting from saturated or inlet quality conditions in terms of flow geometry dependency have been noted by Sozzi and Sutherland [14], Flinta [15], Uchida and Nariai [16] and Fletcher [17]. These experiments are summarized in Table 1 in terms of L/D ratios and relaxation lengths corresponding to a change to equilibrium critical-flow behavior. Table 1 clearly shows that the L/D ratio does not correlate the relaxation process, while a simple length criterion of the order of 100 mm appears to characterize the residence time requirement for both tubes and nozzles covering wide variations in diameter and stagnation pressure, including different fluid properties such as water and Freon-11.

Further support for the simple criterion is provided by the recent large-scale Marviken data with inlet quality conditions [18]. For a nozzle diameter of 500 mm, rela-

TABLE 1. ILLUSTRATION OF RELAXATION LENGTH, L OBSERVED IN DIFFERENT CRITICAL FLOW EXPERIMENTS

Source	D , mm	L/D	L , mm
Fauske (water)	6.35	~ 16	~ 100
Sozzi and Sutherland (water)	12.7	~ 10	~ 127
Flinta (water)	35	~ 3	~ 100
Uchida and Nariai (water)	4	~ 25	~ 100
Fletcher (Freon-11)	3.2	~ 33	~ 105
Marviken Data (water)	500	< 0.33	< 166

tively little change is observed in the critical flow rate when the L/D ratio is varied from 0.33 to 3.2 (see Table 2). It is particularly noteworthy that the predicted Henry-Fauske critical flow rate with $N = 1$ (hereafter referred to as the equilibrium-rate model [ERM]) is approximately the same as the observed flow rate at $L/D = 0.33$, suggesting that the relaxation length for the 500-mm nozzle also is of the order of 100 mm.

In fact, excellent agreement between the ERM predictions and the experimental data is noted at reduced critical pressures of the order of 0.1 and above, which is the range of interest for most chemical systems (see Figures 3 and 4). Also note that the well-known Moody [19] slip-equilibrium critical-flow model considerably overpredicts the data when based upon stagnation conditions (see Figure 3). The original Henry-Fauske model with N values less than 1 leads to similar overpredictions.*

Since the sizing of emergency relief systems for runaway chemical reactions generally involve inlet quality conditions (i.e., top venting) and relatively large flow devices, the above criterion suggests a best-estimate prediction of the critical flow rate can be based on the ERM.

The above observation suggests that the use in [6] of a simple ball valve with flow pattern similar to an orifice to simulate the 10.16-cm rupture disc and the relatively long tail pipe of the incident vessel is not scaleable. For the small-scale tests, the residence time through the ball valve is very short, suggesting non-equilibrium effects (in fact, very little flashing), while the flow in the incident tail pipe can be approximated by an equilibrium flashing process. Flow per unit area in the two cases can therefore differ widely, and the simple scale-up rule based upon area to volume is therefore not valid. On the other hand, the relatively long vent line (L/D approximately 100) used by Harmon and Stuper [7] eliminates concern relative to significant non-equilibrium flashing effects. In fact, interpretation of their reported bottom-venting data obtained with methyl methacrylate suggests an average flow rate of approximately 3000 kg/s-m^2 , which compares well to the ERM prediction of 2900 kg/s-m^2 . The following properties corresponding to a set pressure of ~ 0.17 MPa were used: h_{fg} approximately 317 kJ/kg , ρ_g approximately 8 kg/m^3 , c approximately 0.5 kJ/kg-K , and T approximately 400 K .

*In this model the flow is homogeneous with no mass transfer between the stagnation and the choking point, while the rate of flashing at the choking point is some specified fraction (N) of the equilibrium value, i.e.

$$\left. \frac{dx}{dP} \right|_{\text{choking}} = N \left. \frac{dx}{dP} \right|_{\text{equilibrium}}$$

where x and P are the vapor quality and pressure, respectively.

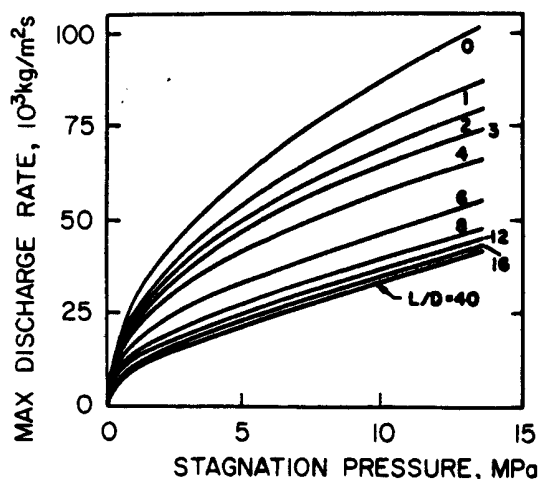


Figure 2. Maximum discharge rates of saturated water for 6.35-mm I.D. tube (taken from Ref. [13]).

*These methods are frequently used in nuclear reactor accident calculations, since in this application an overprediction of the critical flow rate from a safety point of view is considered conservative. The opposite is generally true for sizing emergency relief systems.

TABLE 2. MARVIKEN DATA—SATURATED FLOW $D = 500$ MM, $P_0 \sim 5$ MPa

Critical Flow Rate $\text{kg/m}^2\text{-s} \times 10^{-3}$	L/D
~ 24.5	~ 0.3
~ 23.3	~ 1.5
~ 22.0	~ 3
ERM \rightarrow 23	—

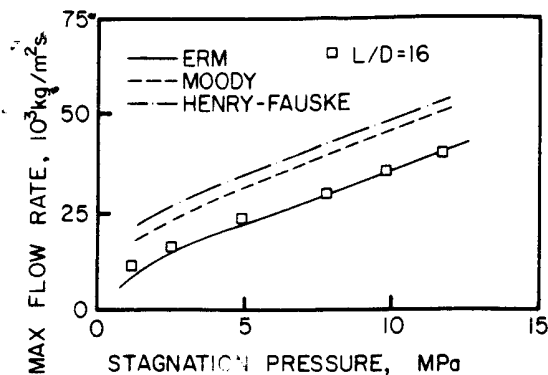


Figure 3. Comparison between measured critical flow rates [13] (L approximately 100 mm) and critical flow models evaluated for stagnation conditions.

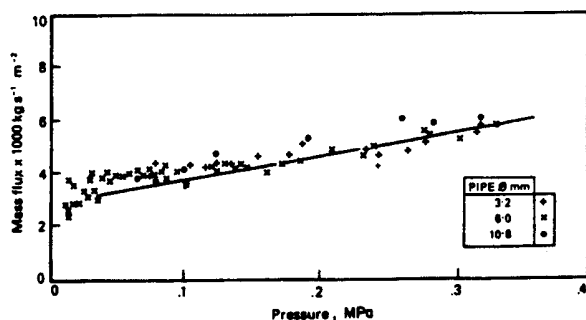


Figure 4. Effect of pipe diameter on mass flux through a pipe of length 120 mm [17] and comparison with the ERM predictions (solid line).

PROPOSED SCALING METHOD

If the necessary thermal- as well as physical-property data are not available to describe runaway conditions, the scale-up method summarized in Figure 5 is suggested for use in sizing emergency relief systems.* The approach al-

*If a small test-cell volume is not essential, the scaling approach outlined in [9], based upon bottom venting and using a sufficiently long vent line (> 100 mm), can be utilized. This approach provides a direct simulation of maximum overpressure and has recently been demonstrated by Harmon for the methyl methacrylate system [7, 20].

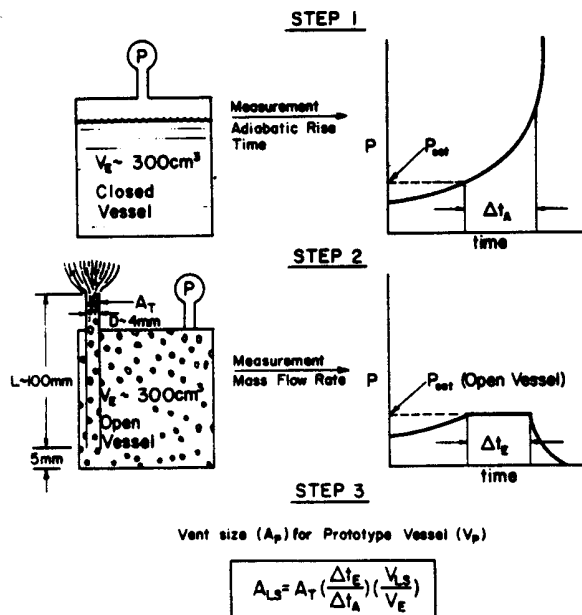


Figure 5. A practical approach to emergency relief-system sizing in the absence of necessary kinetic and thermo-physical property data for runaway conditions.

lows the use of a small test vessel of similar size to that often quoted for obtaining thermal data [1] (i.e., of the order of 300 ml) and eliminates problems relative to non-prototypic vapor-disengagement and non-equilibrium flow effects. The proposed method basically involves an evaluation of the relief area required to vent the test reactor completely of its content (bottom venting) within a time interval specified by the adiabatic rise time (closed vessel) to reach truly runaway conditions starting from the specified set pressure or reference temperature.* The determined vent area can then be scaled directly to the large-scale application on the basis of area-to-volume scaling. The method involves three steps as detailed below.

Step 1—Acquisition of Thermal Data

The adiabatic rise time (Δt_A) can easily be measured in a properly designed system. The heat capacity of the small test vessel can be made tolerable ($< 10\%$ of the vessel content) by employing either direct electrical resistance heating [7], or by using a thin-walled vessel, where the outside pressure is regulated to essentially coincide with the rise in inside pressure due to the runaway reaction.

Step 2—Acquisition of Mass Flow Rate Data

Problems related to non-prototypic vapor-disengagement and non-equilibrium flow effects are eliminated by placing the inlet discharge line close to the bottom of the test vessel (~ 0.5 cm) and using a sufficiently long vent line ($L > 100$ mm). Since the proposed method is based upon a measurement of the two-phase critical flow rate rather than overpressurization data, a vent-line diameter of approximately 4 mm is suggested. This results in an emptying time of a 300 ml test cell on the order of 10 secs. (The volume of the vent line is approximately two orders of magnitude smaller than the vessel volume). The flow rate is obtained by simply measuring the emptying time (Δt_E) as illustrated in Figure 5. The sharp knee in the curve indicates that the vessel is empty of liquid content.

Step 3—Vent Size for Large-Scale

A safe, but not overly conservative, vent size for large-scale is given by the following simple relationship

$$A_{LS} = A_T \left(\frac{\Delta t_E}{\Delta t_A} \right) \left(\frac{V_{LS}}{V_T} \right) \quad (2)$$

where A_T is the area of the test-vessel vent line, Δt_A is the measured adiabatic rise time, Δt_E is the measured emptying time, V_T is the volume of the test vessel, and V_{LS} is the volume of the large-scale vessel.

The method can be illustrated by referring to Burchett's chloroprene example [6]. Using Burchett's measured energy-release rates obtained in the 260-liter test vessel, the adiabatic pressure rise-time curve can be constructed as illustrated in Figure 6. For the case in hand (P_{set} approximately 0.61 MPa), the adiabatic rise time, Δt_A , to reach rapid runaway conditions can be taken as approximately 100 secs.

Since in this case the necessary physical properties for the chloroprene system are known, the mass flow rate can be calculated on the basis of the equilibrium-rate model (ERM) conditions. Using the following properties evaluated at the set pressure (~ 0.61 MPa), h_p (~ 253 kJ/kg), ρ_g (~ 16.4 kg/m³), c (0.48 kJ/kg-K), and T (400 K), results in G of approximately 4800 kg/m²-s.

*This method is strictly applicable to systems under only their own vapor pressure; exothermically reacting liquid systems which have gaseous reaction products have not been considered in this paper.

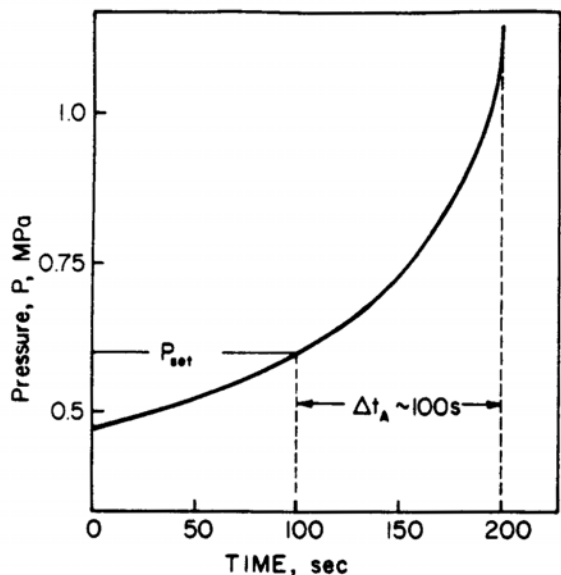


Figure 6. Illustration of adiabatic pressure-rise times based upon Burchett's measured energy-release rates.

The suggested vent area for the incident chloroprene vessel (7570-liter) reported by Burchett is then simply obtained from

$$A_{LS} = \frac{W}{G \Delta t_A} \quad (3)$$

where W (5265 kg) is the weight of monomer in the incident vessel, and results in a dimensionless vent area, A_{LS}/A^* , of approximately 1.5 where A^* (81 cm²) is the area corresponding to the 10.16-cm vent pipe attached to the incident vessel.* As illustrated in Figure 1, this vent area is equivalent to approximately 25% overpressure, basing the venting process upon Burchett's measured energy-release rates and assuming homogeneous behavior (i.e., homogeneous vessel behavior and vent-line dynamics based upon homogeneous equilibrium critical flow). This limited comparison suggests that the proposed scale-up approach, therefore, is safe, as well as not overly conservative. Additional evaluations with emphasis on decomposition reactions are required before this claim can be stated as a general conclusion.

Concluding Remarks

Available data (including actual loss data) strongly suggest that a best-estimate approach to sizing emergency relief systems involving runaway chemical reactions in large process vessels must be based upon homogeneous vessel behavior (i.e., the vapor quality entering the vent line is the same as the average vessel vapor quality) and homogeneous equilibrium flashing-flow behavior in the relief device. As such, direct scale-up from the test-vessel data employing top venting (i.e., leading to excessive vapor disengagement unless the system is inherently "foamy" or highly viscous) and short nozzles or orifices (i.e., resulting in non-equilibrium flashing flows) will lead to unsafe design practices.

In the absence of necessary thermo-physical properties to calculate anticipated behavior (i.e., nearly homogeneous venting), a new scale-up approach is outlined which eliminates concerns relative to non-prototypic disengagement and flashing-flow effects. In addition, the approach allows the use of a relatively small test cell (approximately 300 ml), assuring safe and easy handling of relatively unknown materials.

Recall that Burchett's measured vent area in the 260-liter test vessel, using top venting and zero overpressure, scales directly (area to volume) to a value of A_{LS}/A^ of approximately 0.67.

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