Emergency Relief System Design for Reactive and Non-Reactive Systems: Extension of the DIERS Methodology

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Simple mechanistic models for reactive and non-reactive chemicals are summarized. The DIERS methodology has been extended as well as simplified to account for vapor disengagement and frictional effects including laminar flow conditions—both principal objectives of the DIERS program

INTRODUCTION

The needs to account for two-phase flow phenomena in connection with relief system design for runaway chemical reactions were recognized by Boyle [*1*] and Huff [*2*] about two decades ago. The pioneering work by Huff led to detailed computer models to describe the two-phase, boiling-flow pressure relief process [*3*] through [*9*]. The computer simulation approach to vent sizing requires extensive thermokinetic and thermophysical characterization of the reacting system. Unfortunately, this data base is seldom available, and less complicated analytical methods [*10*], [*11*] allowing vent sizing from direct test data such as the DIERS[a] bench scale apparatus [*12*] are preferred [*13*].

For the first time runaway reactions in the DIERS bench scale apparatus can approximate the severity of those in industrial vessels [*12*]. The simplified models [*10*], [*11*] together with the bench scale equipment [*12*] is now commercially available under the trademark VSP (Vent Sizing Package).

Extension as well as simplification of the VSP methodology is summarized below including the effect of vapor disengagement and laminar flashing flow conditions. Gassy systems involving non-flashing two-phase flow are also discussed including a simple procedure for assessing the vent size without requiring specific knowledge about tempering conditions.

Finally, non-reactive systems involving fire exposure are discussed including atmospheric as well as high pressure systems. A possible preventive measure for boiling liquid expanding vapor explosions (BLEVE) is suggested.

REACTIVE SYSTEMS

The VSP equipment as currently configured can provide both reliable adiabatic thermal data [*14*] and vent sizing data [*13*]. In order to encourage widespread use of the DIERS vent sizing methodology a simplified VSP procedure is discussed below which is dedicated solely to provide vent sizing information. The procedure consists of analytical and experimental tools.

Analytical Tools

The venting characteristics in connection with runaway chemical reactions can be conveniently discussed in terms of vapor and gassy systems.

For pure vapor systems where the runaway reaction can be kept under control by latent heat of evaporation (tempered system), the following simple expression provides a quick estimate of the necessary vent size diameter (see Appendix A).

$$D_T \simeq \frac{3}{2}\left(\frac{m_o \dot{T}\,(\alpha_D - \alpha_o)}{FP_s\,(1-\alpha_o)}\right)^{1/2}\left(\frac{c}{T}\right)^{1/4} \qquad (1)$$

The quantity $\dot{T}$ in Equation (1) is very sensitive to the selected upset scenario [*15*] and together with α_D are generally not known *a priori* requiring experimental simulation. Furthermore, for some vapor systems viscosity consideration becomes important and is generally not known. For such cases the flow rate, G_o, can also be measured in a simulated vent line (same L/D ratio) of diameter, D_o. In terms of vent sizing, the following scale-up approach is recommended.

- If $G_o\,(D_T/D_o) \geq G_T \simeq F\,(dP/dT)\,(T/c)^{1/2}$ use D_T from Equation (1) as the vent size diameter.
- If $G_o\,(D_T/D_o) < G_T$ the required vent diameter for laminar flow, D_L, is given by

$$D_L = \left(D_T^2\, D_o \frac{G_T}{G_o}\right)^{1/3}$$

In case the vent diameter from Equation (1) becomes less than the value corresponding to all vapor venting, the latter value should be used. The above scale-up approach has only received limited verification by data obtained in the DIERS program [*16*]—additional data would be desirable.

a. *The AIChE Design Institute for Emergency Relief Systems (DIERS) recently completed a $1.6 million research program sponsored by 29 of the leading chemical companies in the United States and abroad.*

For gassy systems (including hybrid systems where vapor stripping may be sufficient to control the runaway by latent heat of vaporization) a pressure increase following relief actuation is generally dominated by noncondensables (i.e., $P_g >> P_v$ where P_g and P_v are the partial pressure of gas and vapor, respectively). In contrast to pure vapor systems, this overpressure is reached quickly causing the discharge to be controlled by non-flashing two-phase flow. For choked conditions the volumetric discharge rate for such flows is largely invariant with the vessel void fraction resulting in the following approximate expression for the vent diameter, D,

$$D \simeq \left(\frac{\dot{Q}_g}{F}\right)^{1/2} \left(\frac{\rho_l}{P}\right)^{1/4} \tag{2}$$

where $\dot{Q}_g$ is the maximum volumetric gas generation rate, ρ_l is the reactant density, P is the pressure which can be taken equal to the maximum allowable working pressure (MAWP), and F is a flow reduction factor ($L/D = 0$, $F \simeq 1.0$; $L/D = 50$, $F \simeq 0.7$; $L/D = 100$, $F \simeq 0.6$; $L/D = 200$, $F \simeq 0.45$, $L/D = 400$, $F \simeq 0.33$). The quantity $\dot{Q}_g$ is generally very sensitive to the selected upset condition and is not known *a priori* therefore requiring experimental simulation. Equation (2) applies for turbulent flow conditions which is generally the case for most gassy systems, and agrees quite well with the more detailed expressions provided in Leung and Fauske [*13*].

EXPERIMENTAL TOOL

The basic features of the simplified VSP procedure are illustrated in Figure 1. An open 120 ml low ϕ-factor test cell is placed in a four liter high pressure containment vessel which serves as the pressure simulator. The apparatus indicates sample temperature (T) and pressure (P).

The test cell can be enclosed by a single heater element which is in turn enclosed by thermal insulation material. The heater is controlled to assure a small heat input (< 1°C/min.) during the accident simulation. This heat input is small compared to the large uncertainty associated with the upset scenario.

System characterization data are obtained by first setting the back pressure or the containment pressure equal to MAWP of the process vessel and letting the reaction run to completion. If the system is gassy in nature, the rate of pressure change in the containment vessel will be significant, i.e. $\dot{P} >> 0$, and the maximum volumetric gas generation rate can be estimated as follows.

$$\dot{Q}_g = \frac{m_o}{m_t} \frac{T_t}{T_c} \frac{V_c}{P} \dot{P}_{max}$$

where m_t is the sample mass, T_t is the sample temperature, T_c is the containment temperature, V_c is the containment volume, and P is the MAWP.

In the case the system behaves like a vapor system, vapor condensation will occur in the containment vessel with no significant change in pressure, i.e. $\dot{P} \simeq 0$. For systems where the reaction is not completed, the test is repeated with a back pressure set equal to the relief set pressure (generally well below MAWP to minimize the energy release rate) in order to establish the boiling temperature. A good measure of the corresponding self-heat, $\dot{T}$, is then obtained from the temperature-time data from the first test where boiling is suppressed.

Following onset of boiling, the depressurization procedures discussed in Fauske and Leung [*12*] can be used to establish the void fraction, α_D, corresponding to complete vapor disengagement. If viscosity characterization is desired, the second test is repeated using a bottom

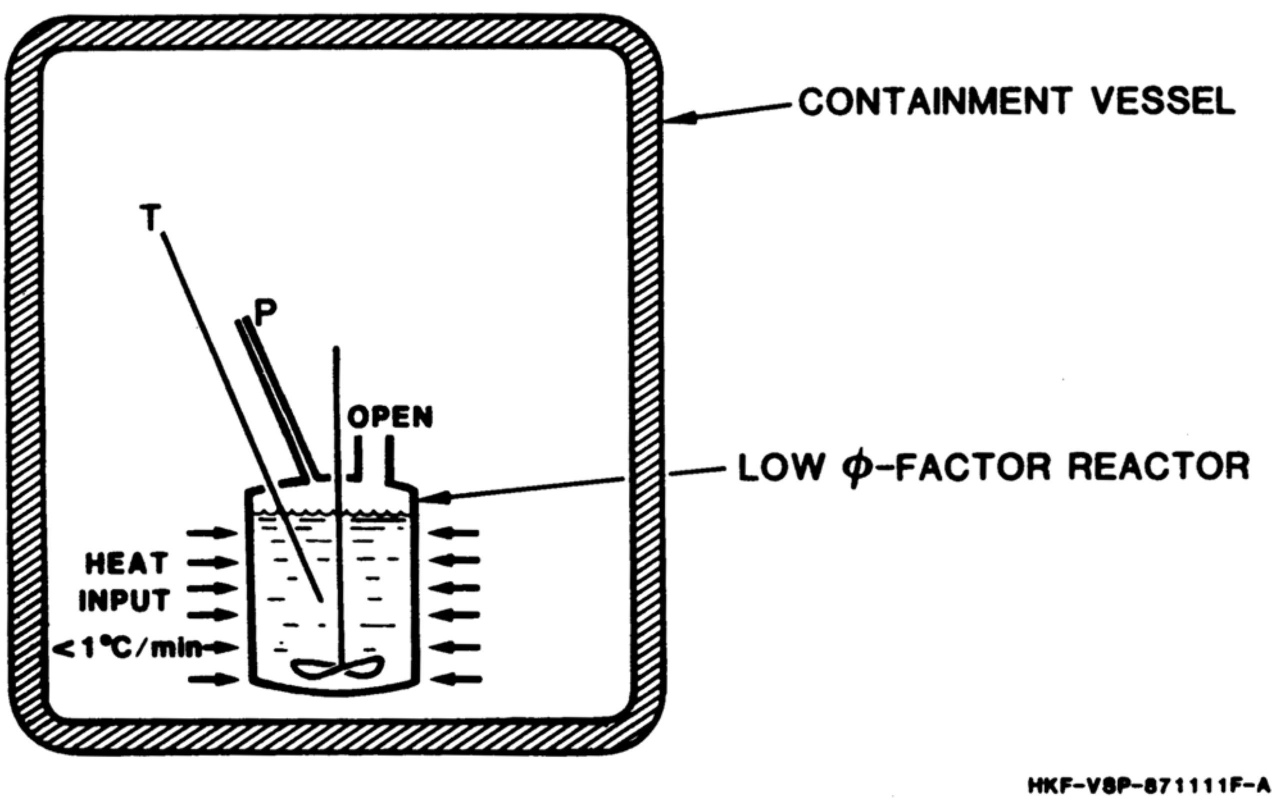

Figure 1. Pressure simulator.

vented test cell with the procedures described in Fauske and Leung [12]. Illustration of vent sizing based on the above approach is provided in Appendix B. If the upset scenario is defined, the vent size requirement for a largely unknown chemical system can readily be accomplished during a one day activity.

NON-REACTIVE SYSTEMS

Current methods and regulations for sizing pressure relief systems for atmospheric and high pressure storage vessels subjected to an external fire are based on all vapor flow [17]. However, in terms of overall hazard control it is of interest to discuss atmospheric and high pressure storage vessels separately. For the latter class of vessels the occurrence of over temperature is just as serious as over pressure as it can lead to so-called BLEVE [18]. Furthermore, for high pressure storage vessels controlled depressurization may lead to significant two-phase discharges through the relief system.

Atmospheric Storage Vessels

For large atmospheric storage vessels the potential occurrence of sufficient liquid swell resulting in two-phase flow is of special importance since little or no overpressure (< 0.1 psi) can be accommodated in many cases of interest. In addition, overfilling is one of the most frequent causes of fire at a storage vessel [18].

The vent area augmentation due to two-phase flow is to the first order proportional to $(\rho_l/\rho_g)^{1/2}$ where ρ_l and ρ_g are the liquid and vapor densities, respectively. For typical systems an increase in the vent area requirement of about 10 to 40 might, therefore, have been expected.

Fortunately, extension of the DIERS work [19] suggests a flow regime pattern for non-reactive systems with external fire in the absence of depressurization as illustrated in Figure 2. The two-phase liquid swell is largely limited to the boiling two-phase boundary layer with the bulk of liquid essentially bubble free [20]. Thus, the all-vapor venting design basis for non-foamy systems would appear safe unless the vessels are completely liquid-filled.

For initially liquid-filled atmospheric storage vessels where little or no overpressures can be tolerated (≤ 0.1 psi), a vent size bassed upon all vapor flow would only appear acceptable as long as the vapor velocity in the vent line is kept below the entrainment velocity given by [21]

$$u_{ent} \simeq 3.0 \left(\frac{\sigma g \rho_l}{\rho_g^{2}}\right)^{1/4} \tag{3}$$

where σ is the liquid surface tension and g is the gravitational constant. As long as the system can be characterized as non-foamy, the required vent area is then given by

$$A = \frac{Q_T}{h_{fg}\rho_g u_{ent}} \tag{4}$$

where Q_T is the total energy release rate due to the fire and h_{fg} is the latent heat of vaporization. Based on rather limited data, Fauske [22] suggests that an increase in the vent area calculated by Equation (4) by a factor of two would keep the overpressure to about 0.1 psi even for a foamy system.

High Pressure Storage Vessels

Liquified gases such as ammonia, propane, propylene, etc. (vapor pressure of the order of 1 MPa at 300K) are often stored in pressure vessels. These are generally of spherical or cylindrical construction.

In the absence of depressurization (see Figure 3), the two-phase liquid swell is again largely limited to the boiling two-phase boundary layer with the bulk of liquid essentially bubble free. For high pressure systems this liquid swell is quite small and all vapor flow through the relief system is assured if the maximum free board superficial vapor velocity is less than the entrainment velocity given by Equation (3). The necessary vent size can be estimated by the procedure outlined in Crozier [17].

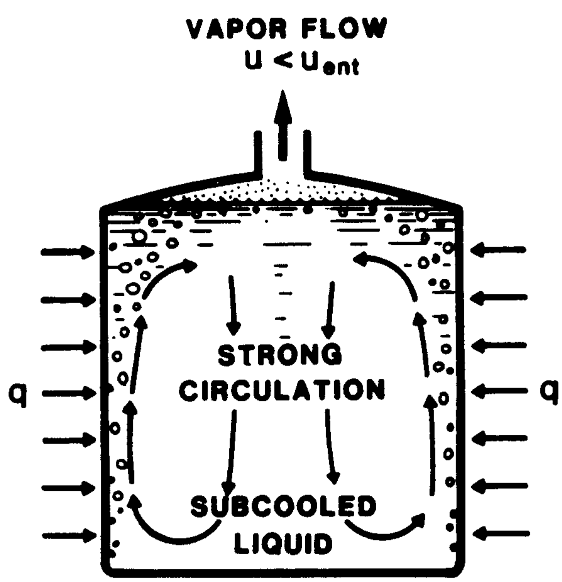

Figure 2. Atmospheric storage vessels.

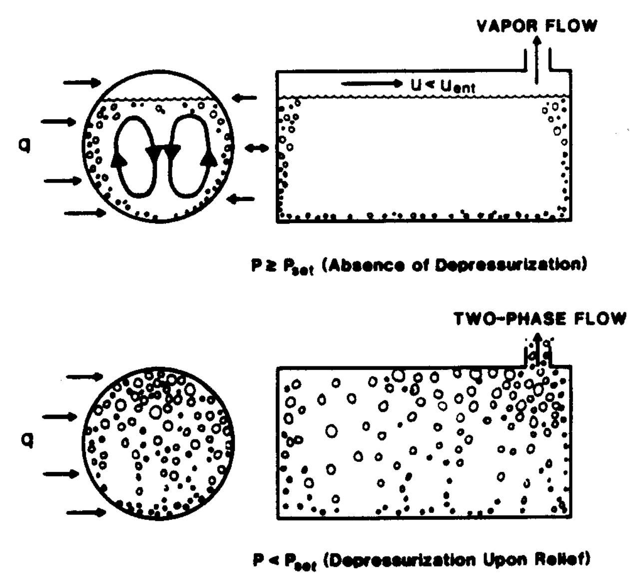

Figure 3. High pressure storage vessels.

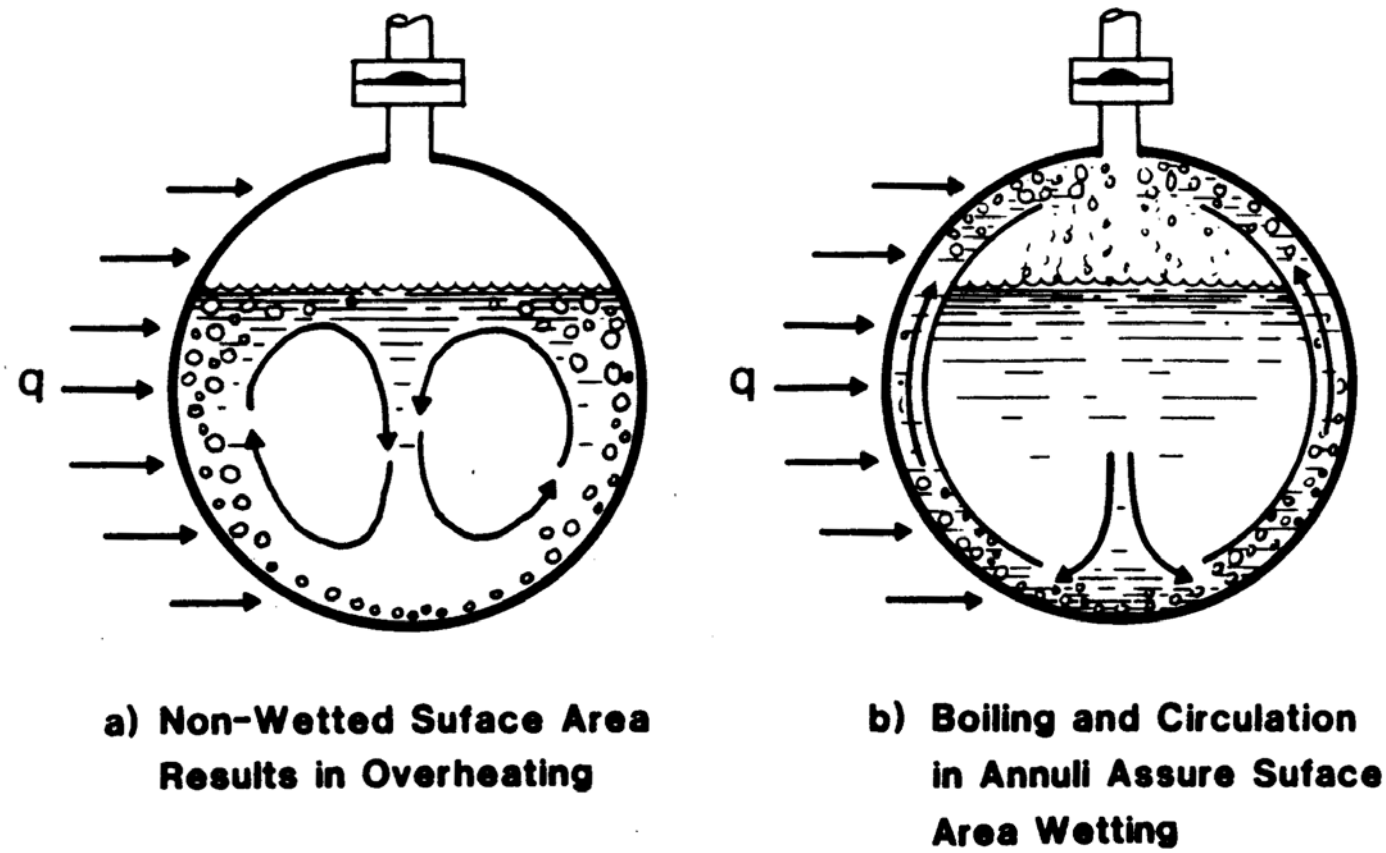

Figure 4. Prevention of Bleve.

In the case of depressurization following relief actuation, bulk flashing will occur (see Figure 3) resulting in significant two-phase flow through the relief system. This behavior was clearly evidenced during a series of kerosene pool fire engulfment trials on insulated propane tanks of up to five tonnes capacity [23]. Consistent with the above discussion, however, these tests illustrated the adequacy of a vent design based upon all vapor venting. Pressurization would arrest bulk flashing and the relief flow would return to all vapor conditions. From an effluent control point of view, the two-phase discharges remain of considerable importance.

Finally it is noted, even if homogeneous two-phase flow conditions are assumed to persist during pressurization, the pressure level reached even with a relief system design based upon all vapor venting will be well below the ultimate pressure capability [24]. Such a failure could come about from unwetted parts of the vessel becoming hot and lose strength. As a result the vessel may burst and produce a BLEVE, even though it is below its design pressure [18].

A remedy to the BLEVE problem is suggested in Figure 4, where an inner, incomplete, thin shell provides an annuli for boiling and circulation assuring surface wetting. The annuli space dimension could be made such that the superficial velocity exceeds the entrainment velocity [Equation (3)] resulting in liquid droplet impingement at the top of the vessel.

CONCLUSION

Easy to use models are now available for assessing vent sizing requirements for reactive and non-reactive systems.

For reactive systems the necessity to consider two-phase flow is emphasized. In case system characterization data are lacking (such as self-heat rate, vapor disengagement and flashing flow characteristics), a bench scale apparatus (VSP) is commercially available that readily allows extrapolation of the data to full size process vessels.

For non-reactive systems, a relief system design based upon all vapor venting would appear adequate in most cases. For atmospheric storage vessels, the superficial vapor velocity in the vent line should not exceed the characteristic entrainment velocity.

For high pressure storage vessels, in addition to pressure relief considerations, potential overheating of non-wetted areas from the fire is of special interest as it may lead to BLEVEs. A possible passive preventive measure for this problem is suggested for future designs.

APPENDIX A

A Simple Disengagement Model for Vent Sizing of Reactive Vapor Systems

Based on lessons learned from the DIERS program it would appear virtually impossible to predict the liquid-to-vapor phase ratio entering the vent line from first principles. This situation can be attributed to the large uncertainties and lack of understanding nonequilibrium and flow regime phenomena in connection with runaway chemical reactions. In addition, the possible delay in vaporization impacts the tempering or turnaround temperature. Absence of equilibration within the reaction vessel may cause the temperature to continue to rise while no overpres-

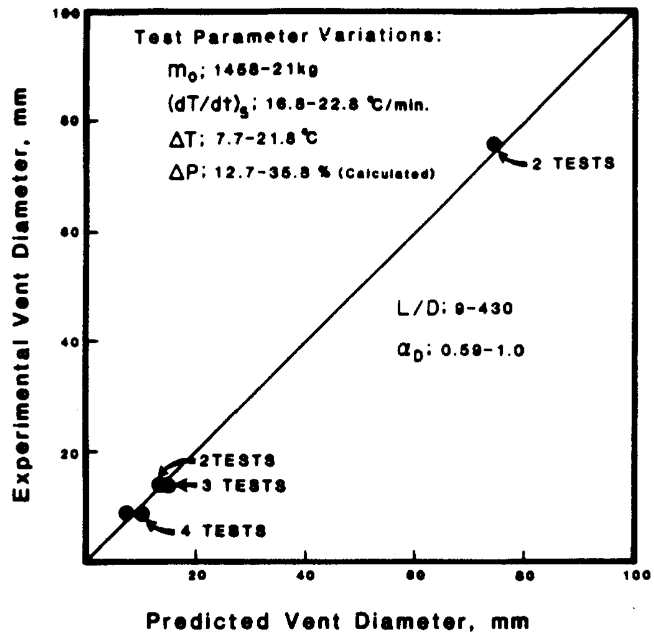

Fig. A-1.

sure may be experienced following relief actuation [25].

Fortunately, in most practical systems only modest superheating is likely suggesting that turnaround in temperature will be at least assured by the onset of complete vapor disengagement. Furthermore, the mass loss of reactants can be assumed to be largely independent of the liquid-to-vapor phase ratio entering the vent line prior to complete vapor disengagement. These assumptions allow a simple analytical expression to be developed for the required vent size.

The loss of reactants at the time of turnaround in temperature is approximated by

$$m_o\left(\frac{\alpha_D - \alpha_o}{1 - \alpha_o}\right) \simeq GA\,\Delta t_v \tag{A-1}$$

where m_o is the mass of reactants, α_D is the vessel void fraction corresponding to complete vapor disengagement, α_o is the initial free board volume, A is the vent area, G is the two-phase flashing flow rate and for turbulent flow is given by [26]

$$G_T \simeq F\left(\frac{\Delta P}{\Delta T}\right)\left(\frac{T}{c}\right)^{1/2} \tag{A-2}$$

where F is a flow reduction factor related to the length-to-diameter ratio ($L/D = 0$, $F \simeq 1.0$; $L/D = 50$, $F \simeq 0.85$; $L/D = 100$, $F \simeq 0.75$; $L/D = 200$, $F \simeq 0.65$; $L/D = 400$, $F \simeq 0.55$) [27], $(\Delta P/\Delta T)$ is the equilibrium change in pressure with respect to temperature, T is the temperature corresponding to relief actuation, c is the liquid specific heat, and Δt_v is the time to turnaround in temperature, $(T + \Delta T)$, following relief actuation and is approximated by

$$\Delta t_v \simeq \frac{2\,\Delta T}{\dot{T}} \tag{A-3}$$

where $\dot{T}$ is the rate of temperature rise corresponding to the relief set pressure, P_s. Equating Equations (A-1) through (A-3) and solving for the vent area results in

$$A \simeq \frac{1}{2}\,\frac{m_o\dot{T}}{F(T/c)^{1/2}\,\Delta P}\,\frac{(\alpha_D - \alpha_o)}{(1 - \alpha)} \text{ for } 0.1\,P_s \le \Delta P \le 0.3\,P_s \tag{A-4}$$

where ΔP is the equilibrium value corresponding to the actual temperature rise, ΔT, following relief actuation.

Comparisons between Equation (A-4) and the DIERS runaway reaction tests [28, 29], are summarized in Figure A-1—the agreement is very good (within 15%) accounting for self-heat rate, temperature rise, vapor disengagement and length-to-diameter effects. The stated range of applicability for Equation (A-4) in terms of equilibrium overpressures, ΔP, is consistent with the range covered by the experimental data. Equation (1) in the main text is obtained by setting ΔP equal to 0.3 P_s in Equation (A-4) and solving for the vent diameter, D_T.

For laminar flow conditions the pressure drop is largely due to frictional losses and the flow rate, G_L, is approximately given by [26]

$$G_L \simeq \left(\frac{\Delta P}{\Delta T}\right)^2\left(\frac{T}{c}\right)\left(\frac{1}{32\,\mu}\right)(D)\left(\frac{D}{L}\right) \tag{A-5}$$

where μ is the liquid viscosity. The scale-up approach discussed in the main text is based upon Equation (A-5).

APPENDIX B

Venting sizing examples using the VSP methodology are illustrated below including both vapor and gassy systems.

Design Example (Existing Plant)

Bench Scale Data (Worst Case Upset)	Process Data
1st and 2nd Tests	$m_o \simeq 2500$ kg
$\dot{P} \simeq 0 \rightarrow$ Vapor System	$\alpha_o \simeq 0.2$
$\dot{T} \simeq 20$°C/min (1st Test)	$P_s \simeq 3.4 \cdot 10^5$ Pa (50 psia)
$T \simeq 475$ K (2nd Test)	$c \simeq 2400$ J/kg K
$\alpha_D \simeq 0.6$ (2nd Test)	$D \simeq 10.2$ cm (4-in.)
	$L/D \sim 100$; $F \simeq 0.75$

Turbulent Flow and No Vapor Disengagement ($\alpha_D \simeq 1$)

$$D_T \simeq \frac{3}{2}\left(\frac{(2500)(20)}{(0.75)(60)(3.4 \cdot 10^5)}\right)^{1/2}\left(\frac{2400}{475}\right)^{1/4} \simeq 0.129 \text{ m} \rightarrow 5.1 \text{ in.}$$

Vapor Disengagement Characterization ($\alpha_D \simeq 0.6$)

$$D_T \simeq 0.129\left(\frac{0.6\text{-}0.2}{1\text{-}0.2}\right)^{1/2} \simeq 0.09 \text{ m} \rightarrow 3.6 \text{ in.}$$

Conclusion: Existing vent size is adequate by accouunting for vapor disengagement.

Design Example (Existing Plant)

3rd Test—Viscosity Characterization

$m_t \simeq 0.070$ kg
$L/D \simeq 100$

$D_o \simeq 0.5$ cm

$$G_o \simeq \frac{0.070}{(1.96 \cdot 10^{-5})(35.7)} \simeq 100 \text{ kg/m}^2\text{-s}$$

$(\Delta P/\Delta T) \simeq 8000$ Pa/K
$\Delta t_E \simeq 35.7$ s
$G_T \simeq (0.75)(8000)(475/2400)^{1/2} \simeq 2670$ kg/m^2-s
Since $(100)(9/0.5) < 2670$

The required vent diameter is given by

$$D_L \simeq \left(9^2 \cdot 0.5 \cdot \frac{2670}{100}\right)^{1/3}$$

$$\simeq 10.2 \text{ cm} \rightarrow 4 \text{ in.}$$

Conclusion: Existing vent size is adequate accounting for viscous effects.

Design Example (New Plant)

Bent Scale Data (Worst Case Upset)	Process Data
1st Test	
$m_t \simeq 0.070$ kg	$V \simeq 2.5$ m^3
$V_c \simeq 4 \cdot 10^{-3}$ m^3	$m_o \simeq 2000$ kg
$T_t \simeq 500$ K	$\rho_l = 850$ kg/m^3
$T_c \simeq 300$ K	$P_{MAWP} \simeq 100$ psia ($\sim 6.9 \cdot 10^5$ Pa)

$\dot{P} \simeq 14.5$ psi/s (10^5 Pa/s)
(Gassy System)

$$\dot{Q}_g \simeq \frac{(2000)}{(0.070)} \frac{500}{300} \frac{4 \cdot 10^{-3}}{6.9 \cdot 10^5} 10^5$$

$$\simeq 27.6 \text{ m}^3/\text{s}$$

$$D = (27.6)^{1/2} \left(\frac{850}{5.9 \cdot 10^5} \right)^{1/4} \simeq 1.02 \text{ m} \rightarrow 40 \text{ in.}$$

Conclusion: Not practical, the vent size is of the same order as the vessel diameter. Review process design and worst case upset.

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