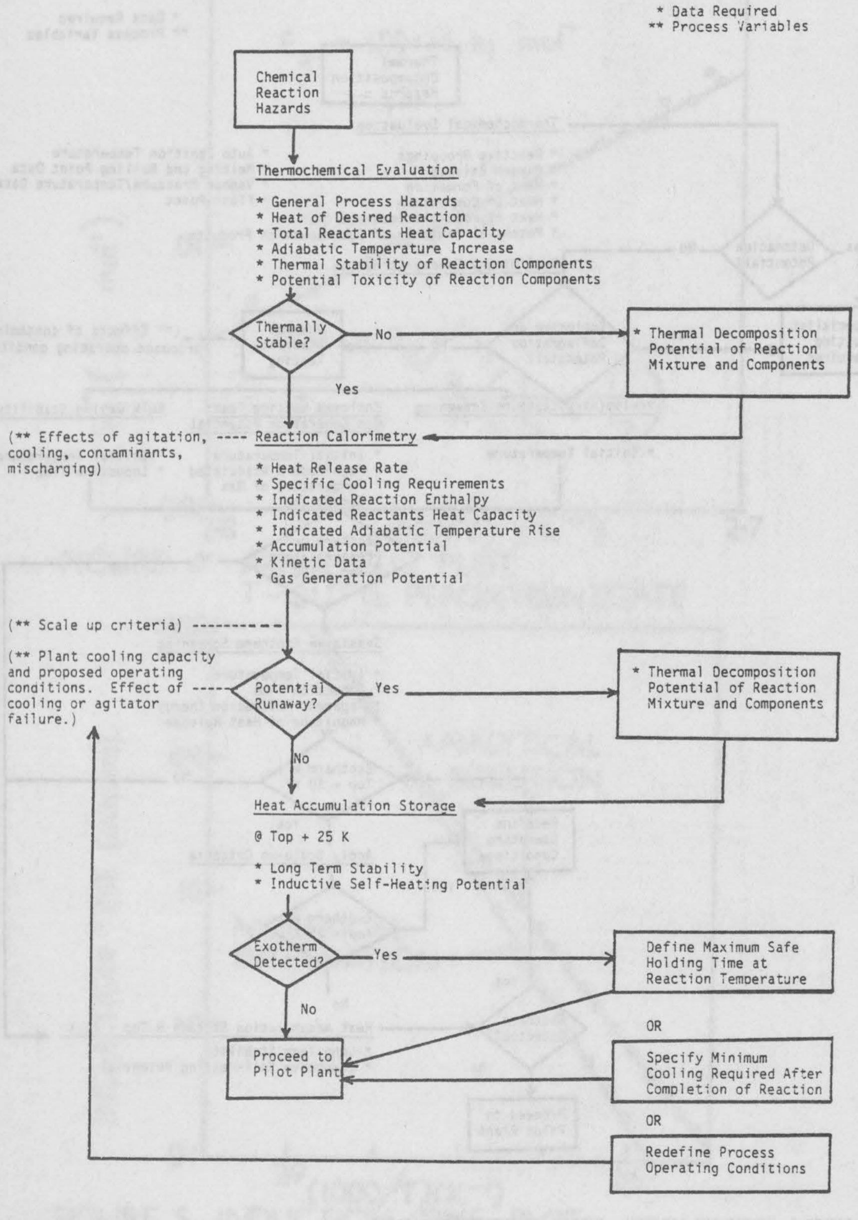

FIGURE 7: ASSESSMENT STRATEGY, CHEMICAL REACTION HAZARDS

PRESSURE RELIEF AND VENTING: SOME PRACTICAL CONSIDERATIONS RELATED TO HAZARD CONTROL

Hans K. Fauske*

Newly developed practical methods for assessing pressure relief requirements for reactive and non-reactive systems are summarized. Considerations include runaway of liquid-phase exothermic reactions and fire exposure to liquid-filled storage vessels. Special emphasis is given to emergency releases involving two-phase flows.

Keywords: Relief, Venting, Reactors, Two-phase flow.

INTRODUCTION

Hazard control in connection with both reactive and non-reactive systems requires considerations of pressure relief. Inadequate relief may lead to severe explosions, extensive property loss, injury and environmental insult (1). In case of reactive systems several steps need to be taken in order to assure adequate relief. Hazard identification and system characterization are especially important steps. Wrong recipes, uncontrolled addition, catalyst mischarge, solvent mischarge, etc., can have a profound impact on the chemical energy release rate (see Figure 1). Such mistakes can alter the temperature rise rate (commonly known as the self-heat rate in runaway reactions) at relief conditions by up to several orders of magnitude (2). For non-reactive systems energy release characteristics in connection with fire exposure are of special interest (3).

Recognizing that the relief vent area is directly proportional to the self-heat rate, clearly establishes the overall importance of hazard identification and system characterization in the relief system design process. If these steps are done poorly, the level of hazard control achieved will be equally poor. An example is the case where the relief system design is based on fire exposure alone ignoring the potentially large additional contribution from chemical energy release if heating can lead to chemical reaction.

The actual design of the emergency relief system to mitigate or control the hazards involves two major aspects. These include establishing the vent size to relieve the pressure and disposal of the emergency release safely. In this paper methods for assessing vent sizing requirements for both reactive and non-reactive systems will be reviewed. Some special considerations involving disposal of two-phase (liquid-vapor) emergency releases are provided in (2).

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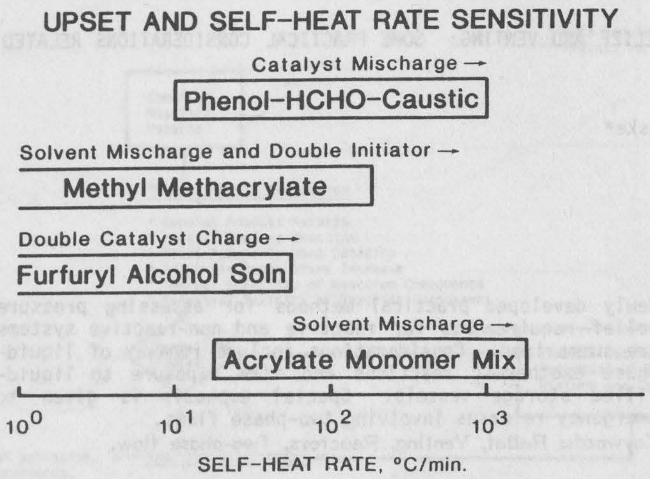

Figure 1 Examples of upset conditions and impact on the self-heat rate. Noted ranges represent measured values for a specified relief pressure (2).

REACTIVE SYSTEMS

The needs to account for two-phase flow phenomena in connection with relief system design for runaway chemical reactions were recognized by Boyle (4) and Huff (5) about two decades ago. The pioneering work by Huff led to detailed computer models to describe the two-phase, boiling-flow pressure relief process (6)-(12). 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 methods allowing vent sizing from direct test data such as obtained from the Accelerating Rate Calorimeter (ARC) emerged (13) (14). The inherent complications in the vent design approach via the ARC has been reviewed by Huff (1) and Fauske (2).

When deficiencies in being able to physically characterize systems under runaway conditions became apparent, the DIERS program* developed a bench scale apparatus to provide this information.† For the first time runaway reactions on a laboratory scale can approximate the severity of those in industrial vessels (15). At the same time simple analytical methods were developed (16) (17) to allow direct vent sizing from the data obtained in the DIERS bench scale apparatus. (This methodology including the bench scale equipment is now commercially available under the trademark VSP (Vent Sizing Package)). For tempered reactions, the nomogram method (18) which accounts for turbulent flashing flow and only requires information about the rate of temperature rise at the relief set pressure is particularly easy to use (see Figure 2). This approach has recently been extended to account for vapor disengagement and frictional effects including turbulent and laminar flow conditions - both principal objectives of the DIERS program (19).

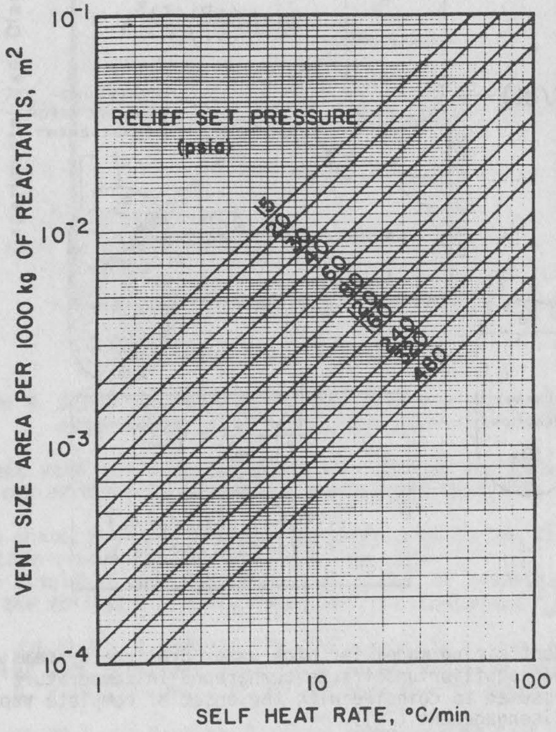

Figure 2 A vent sizing nomogram for tempered (high vapor pressure) runaway chemical reactions.

In case of turbulent flow the vent size area, A_T (m^2) is given by (see Figure 3)

$$A_T = \frac{1}{2} \frac{m_o (dT/dt)_s \; (\alpha_D - \alpha_o)}{F(T/c)^{1/2} \; \Delta P(1 - \alpha_o)} \quad \text{for } 0.1\, P_s \le \Delta P \le 0.3\, P_s \qquad (1)$$

where m_o (kg) is the initial mass of reactants, $(dT/dt)_s$ (K/s) is the self-heat rate corresponding to the relief set pressure, P_s (Pa), α_D is vessel void fraction corresponding to complete vapor disengagement, α_o is the initial free board volume, T (K) is the temperature corresponding to relief actuation, c (J/K-kg) is the liquid specific heat, ΔP (Pa) is the equilibrium value

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*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 U.S.A. and abroad.

†In addition to information about the self-heat rate and tempering (reaction heat removed by latent heat of vaporization) condition, the equipment can also provide information about vapor disengagement and flashing flows (15).

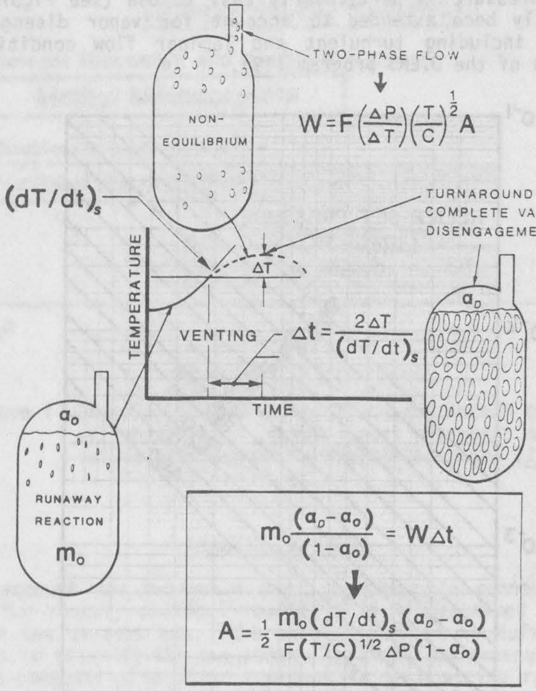

Figure 3 Vent sizing model for high vapor pressure systems; due to non-equilibrium effects turnaround in temperature is assumed to coincide with the onset of complete vapor disengagement (19).

corresponding to the actual temperature rise ΔT following relief actuation, and F is a flow reduction factor for turbulent flow ($L/D = 0$, $F \sim 1.0$; $L/D = 50$, $F \sim 0.85$; $L/D = 100$, $F \sim 0.75$; $L/D = 200$, $F \sim 0.65$; $L/D = 400$, $F \sim 0.55$) where L/D is the length-to-diameter ratio of the vent line.

Comparisons between Equation (1) and the DIERS runaway reaction tests (20),(21) are summarized in Figure 4 - the agreement is very good (within 15%) accounting for self-heat rate, temperature rise, vapor disengagement and length-to-diameter ratio effects. The stated range of applicability for Equation (1) in terms of equilibrium overpressures, ΔP, is consistent with the range covered by the experimental data. Considering the large uncertainties involved in establishing credible "worst case" design conditions (see Figure 1), the noted accuracy is considered more than adequate. In fact, in many cases the easy to use nomogram method (18) may be adequate. The nomogram illustrated in Figure 2 is equivalent to setting $\alpha_D = 1.0$ (no vapor disengagement), $F = 0.5$ ($L/D \sim 400$), $\Delta P = 0.2\ P_s$, $c = 2500$ J/kg-K and $T = 400$K in Equation (1). In case information

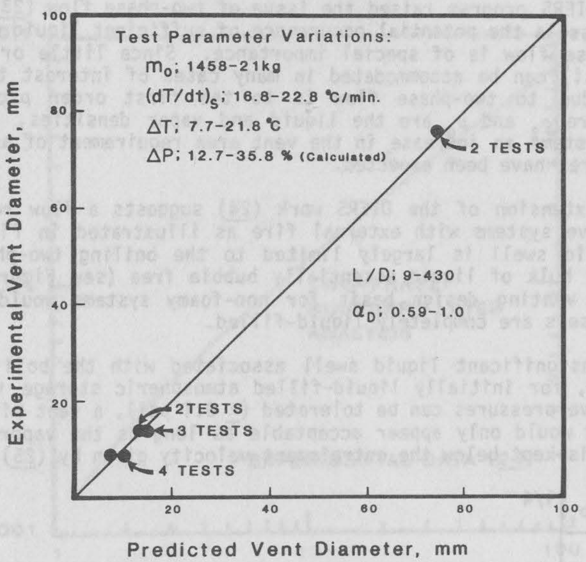

Figure 4 DIERS styrene-ethylbenzene reacting tests (20),(21); experimental versus predicted vent line diameters.

about self-heat rate and vapor disengagement is not available, which is often the case, it can be obtained in the VSP bench scale apparatus (15).

Flashing flow characteristics can also be determined in the VSP equipment using a special bottom vented test cell (15). The flow rate, G_o (kg/m^2-s) can 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 (19)

- If $G_o\ (D_T/D_o) \geq F\ (\Delta P/\Delta T)\ (T/c)^{1/2}$ where D_T is the vent diameter required for turbulent flow, use D_T as the vent size diameter, (i.e. $D_T = \sqrt{4\ A_T/\pi}$ where A_T is obtained from Equation (1).
- If $G_o\ (D_T/D_o) < F\ (\Delta P/\Delta T)\ (T/c)^{1/2}$ the required vent diameter for laminar flow, D_L is given by

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

The above approach has only received limited verification by data obtained in the DIERS program (22) - additional data would be desirable.

NON-REACTIVE SYSTEMS

Current methods and regulations for sizing emergency relief vents for storage vessels subjected to an external fire are based on all vapor flow (3).

However, the DIERS program raised the issue of two-phase flow (23). For large atmospheric 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 the vent area augmentation due to two-phase flow is to the first order proportional to $(\rho_\ell/\rho_g)^{1/2}$ 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 (24) suggests a flow regime pattern for non-reactive systems with external fire as illustrated in Figure 5. The two-phase liquid swell is largely limited to the boiling two-phase boundary layer with the bulk of liquid essentially bubble free (see Figure 6). Thus, the all-vapor venting design basis for non-foamy systems would appear safe unless the vessels are completely liquid-filled.

Despite the insignificant liquid swell associated with the boiling two-phase boundary layer, for initially liquid-filled atmospheric storage vessels where little or no overpressures can be tolerated ($\leq$ 0.1 psi), a vent size based 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 (25)

$$u_E \sim 3.0 \left(\frac{\sigma\ g\ \rho_\ell}{\rho_g^2}\right)^{1/4} \qquad (2)$$

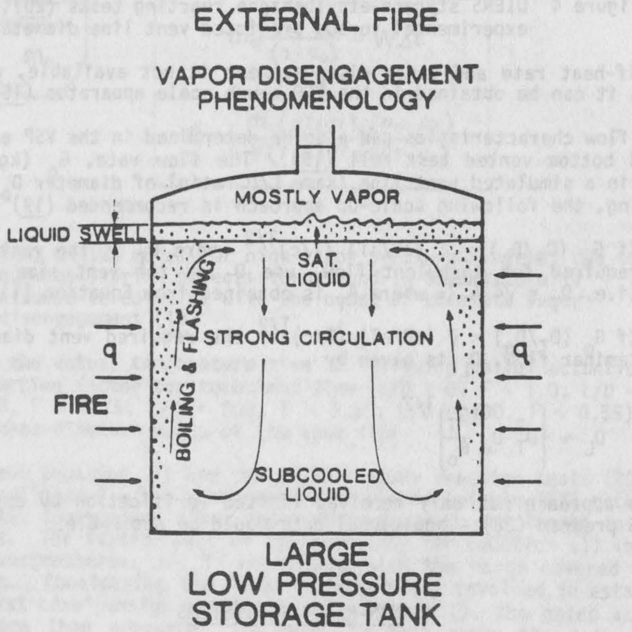

Figure 5 Illustration of expected flow regime pattern for non-reactive systems with external fire.

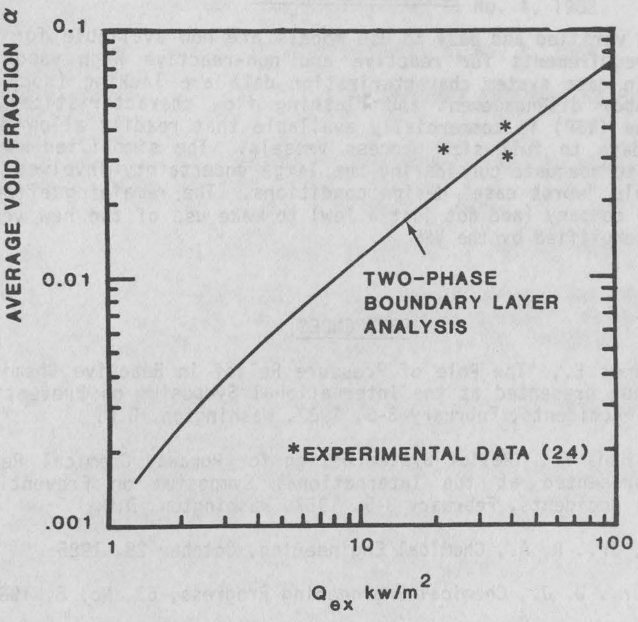

Figure 6 Comparison of calculated average void fraction values where vapor generation is confined to a wall boundary layer region (23) and measured values (24).

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

$$A = \frac{Q_T}{\lambda\ \rho_g\ u_E} \qquad (3)$$

where Q_T is the total energy release rate due to the fire and λ is the latent heat of vaporization. Based on rather limited data, Reference (26) suggests that an increase in the vent area calculated by Equation (3) by a factor of two would keep the overpressure to about 0.1 psi even for a foamy system.

In cases where substantially higher pressures can be tolerated, the velocity in Equation (3) can be replaced by

$$u \sim \frac{2\ \Delta P}{\rho_g} \qquad (4)$$

for non-foamy systems. Again, doubling the area calculated by Equation (3) should provide adequate venting in case of a foamy system, by allowing for modest overpressures of 10% to 30% above the relief pressure to compensate for two-phase flow effects (26). The limited data suggests that the two-phase flow rate for a foamy system can be estimated by assuming a vapor quality of about 5% - additional data support would be desirable.

CONCLUDING REMARKS

Experimentally verified and easy to use models are now available for assessing vent sizing requirements for reactive and non-reactive high vapor pressure chemicals.* 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 allow extrapolation of the data to full size process vessels. The simplified approach is considered quite adequate considering the large uncertainty involved in establishing credible "worst case" design conditions. The remaining effort is for every chemical company (and not just a few) to make use of the new vent sizing methodology exemplified by the VSP.

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*For low vapor pressure systems where little or no tempering is provided, pressure relief through venting may or may not be practical (27). Additional research efforts of the DIERS type would be desirable to clarify the role of propagating liquid-phase decomposition (LPD) reactions.

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