ioMosaic®
Minimizing risk. Maximizing potential.®

RAGAGEP Considerations for Overtemperature Protection in Relief Systems

An ioMosaic Corporation White Paper

G. A. Melhem, Ph.D., FAIChE
melhem@iomosaic.com

IOMOSAIC CORPORATION

RAGAGEP Considerations for Overtemperature Protection in Relief Systems

Process Safety and Risk Management Practices

authored by

Georges A. MELHEM, Ph.D., FAIChE

July 19, 2021

Contents

1 Introduction

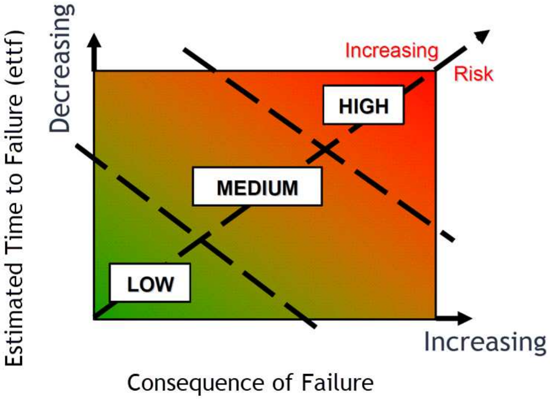
A properly sized reclosing pressure relief valve (PRV) can protect process equipment against a variety of overpressure scenarios. Fire exposure scenarios leading to overpressure are particularly challenging, especially where a reclosing pressure relief device provides the only means of protection.

It is widely known, that if the fire duration is long enough, the process equipment will ultimately yield or fail at the reseat pressure of the reclosing PRV. A reclosing PRV can only provide overtemperature protection up to a maximum allowable duration of fire exposure. We define the maximum allowable duration of fire exposure as the expected time to failure (**ettf**). Another useful maximum allowable duration of fire exposure criteria is based on equipment deformation or yield but not failure or expected time to yield (**etty**).

The maximum allowable fire duration depends on many variables including but not limited to type of fire (pool fire or flame jet), type of fuel, size and geometry of process equipment, equipment wall thickness, equipment pressure and temperature rating, initial liquid fill level, etc. As a result, expected **ettf** or **etty** values can range from few minutes to a few hours.

Because the hazard of a long enough fire exposure scenario is already recognized, relief systems design basis documentation should provide calculated best estimates for **etty** or **ettf** or both. A hazard is ”recognized” under the OSHA General Duty Clause where (a) the employer has identified it, (b) it is known in the industry, or (c) it is blatantly obvious.

Reasonable estimates of **etty** or **ettf** are required for strict OSHA compliance. They are also necessary for effective risk management as well as effective emergency response and fire protection. This is particularly important for systems that contain reactive chemicals, chemicals with high boiling points, and process equipment that are gas filled or process equipment containing liquids where the vapor space can be engulfed/impinged by fire or exposed to flame thermal radiation.



A reclosing pressure relief device can only be considered adequate for overtemperature protection if the calculated **ettf** or **etty** exceeds the estimated fire duration or the estimated failure time for vessel structural supports, whichever is less. Vacuum protection may also be necessary if a reclosing relief device is the only mean of overpressure and overtemperature protection.

2 Overpressure vs. Overtemperature

Fire exposure scenarios are probably the most widely used as the dominant pressure relief design basis, especially in the hydrocarbons industries. Recognized and generally accepted good engineering practices (RAGAGEP) such as API-521/520[1, 2] are used to determine the relief requirements by first determining the heating rate or heat absorption rate from fire exposure into the liquid vessel contents. Only heating through the wetted surface area is considered. The heating rate is then divided by the latent heat of vaporization of the vessel liquid contents to generate a rate of vapor generation. The volumetric rate of vapor generation determines the relief requirement and relief device sizing assuming all vapor flow.

The heating rate absorbed by the liquid is calculated empirically [1]:

$$Q_{fire} = qFA_w^a \tag{1}$$

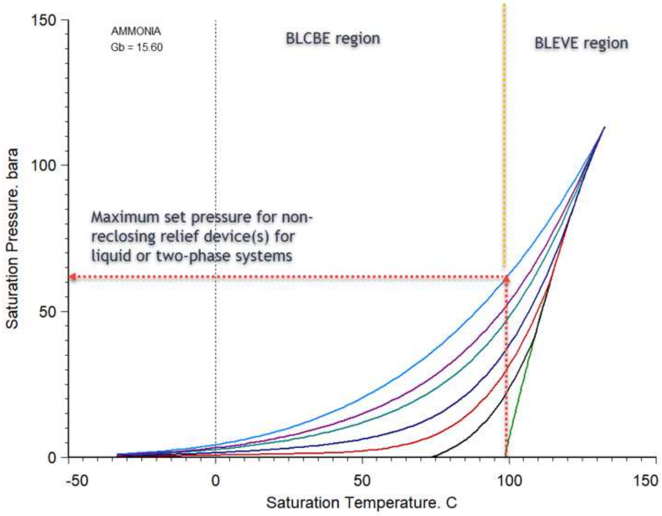
Where Q_{fire} is the total heating rate absorbed by the liquid in $\mathrm{J/s}$ or W, F is a mitigation factor that is used to allow reduction of the heating rate because of water sprays, firefighting, and/or insulation, and A_w is the wetted surface area in m^2, i.e. the inner wall surface area contacted by liquid. The constant q represents the heat flux absorbed by the liquid corrected for the presence of adequate drainage. Note that q includes a unit conversion factor associated with the fact that the wetted surface area is raised to a power less than 1. A similar form is used by NFPA-30 [3]. Note that NFPA and API correlations differ for wetted surface areas that are less than 2,800 ft^2 where NFPA yields a higher heating rate.

Equation 1 correlates the heat absorbed by the vessel liquid contents to the wetted surface area raised to the power $a = 0.82$ typically. Confined pool fires lead to higher heating rates. A value of $a = 1$ is substituted for $a = 0.82$ in API 521.

The heating rate calculated by Equation 1 is underpredicted for light hydrocarbons and overpredicted for heavy hydrocarbons [4]. The NFPA and API correlations are primarily used to establish the relief requirements and should not be used to establish vessel wall temperatures or to assess potential vessel failure due to excessive wall temperatures.

Equation 1 completely ignores the impact of fire exposure on vessel integrity if the fire duration is long enough to heat the metal vessel walls to excessive temperatures. We note that heat transfer in the vapor space is typically driven by natural convection and as a result the vapor to metal heat transfer coefficient is low, typically between 30 and 75 $\mathrm{W/m^2/K}$. The corresponding heat transfer coefficient during nucleate boiling for the liquid space ranges from 1,000 to 3,000 $\mathrm{W/m^2/K}$ [1].

During a fire exposure scenario and depending on liquid fill level, the vapor space walls will heat up faster than the liquid space walls. As a result, it is typical for vessel wall failure to occur at the interface between the liquid and vapor. In addition, during onset of two-phase flow, the energy stored in the vapor space vessel walls will be recovered during venting and can lead to additional venting requirements [4].



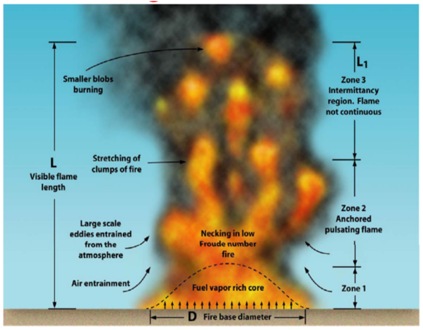
As wall temperatures increase due to fire exposure, internal fluid temperature and pressure also increase. As the walls temperatures increase to excessive levels, the walls will stretch and thin out. This is most important for localized heating such as flame jet impingement. Eventually, the walls thin out to a level that will cause the metal to tear under the increasing internal pressure. This type of failure can cause a boiling liquid expanding vapor explosion (BLEVE) or a boiling liquid compressed bubble explosion (BLCBE) with severe consequences [5, 6, 7, 8].

These consequences include overpressure due to vessel burst, thermal radiation due to fireball if the contents are flammable, vapor cloud explosion if the contents are flammable, ground shock, and flying vessel fragments or projectiles.

3 Fire Exposure Scenarios

The vast majority of existing or legacy pressure relief requirement calculations are based on pool fire exposure and use of Equation 1 to establish the fire heating rate absorbed by the vessel liquid contents. Where flame jet exposure is a concern, depressuring systems are more appropriate since the exposure tend to be highly localized. It is difficult to eliminate fire exposure scenarios from design basis consideration for emergency relief systems although the frequency of such scenarios can be reduced. It is estimated based on historical data that the likelihood of a fire exposure scenario is 1 in 250 years [9].

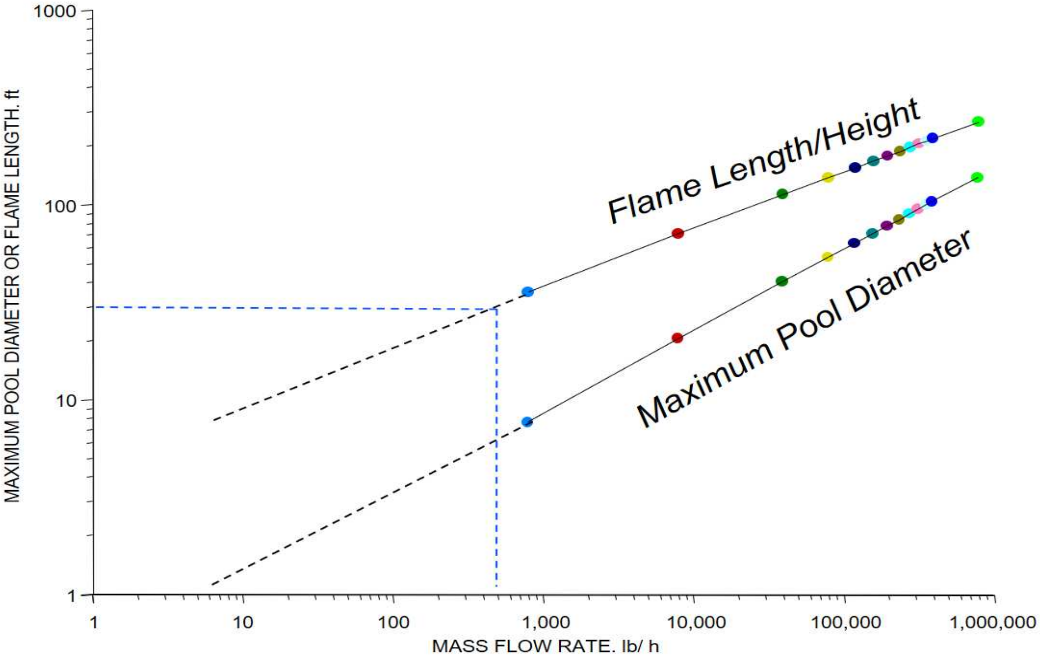
Equation 1 underestimates the pool fire heating rate for light hydrocarbon fuels ($< C6$) and overestimates the heating rate for heavy hydrocarbon fuels. LNG pool fires can generate peak flame emissive power values close to 300 $\mathrm{kW/m^2}$ [10].



The wetted surface area is often underestimated where two-phase flow is possible. Furthermore, existing guidance by API and NFPA restrict the flame height to 25 or 30 ft regardless of leak size and spill surface geometry. Restricting the flame height when using Equation 1 can lead to an underestimate of the fire heating rate due to reduction in wetted surface area exposed to flame. We note that the dominant fire heating mode is by thermal radiation and a vessel does not have to be engulfed to receive large heating rates.

Furthermore, as shown by Melhem [11], limiting the flame height to 25 or 30 ft assumes a small leak as shown in Figure 1. Figure 1 was developed for an unconfined liquid cyclohexane leak on a concrete surface. The flame height for a pool fire depends on the geometry of the spill, burning

Figure 1: Calculate cyclohexane pool fire flame height using SuperChems Expert as a function of leak rate [11]



Source: SuperChems Expert

rate of the liquid and prevailing wind speed. In general, the flame height for a circular pool fire is expected to be approximately two times the pool diameter. Several correlations for the estimation of pool fire flame height, burning rates, flame drag, flame tilt, and geometric view factors, have been published and validated with field test data for both circular and rectangular pool geometries [10].

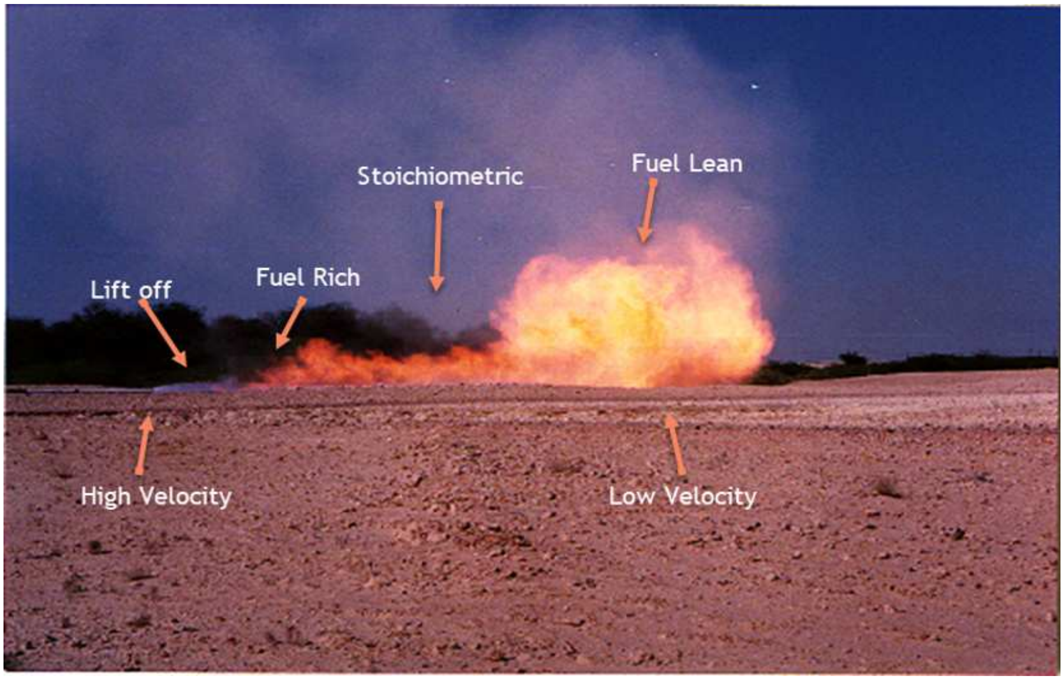
Flame jet exposure scenarios are very challenging due to the highly localized nature of heating where impingement is possible. Expected **ettf** durations can be less than 5 minutes. Single phase gas flame jets and also twophase jets can generate substantial heating rates as high as $350 \mathrm{~kW/m^2}$. SuperChems Expert can be used to establish flame jet length, velocity profile, orientation, vertical and horizontal thermal radiation profiles.

Flame jets can also subject the vessel insulation or metal walls to high mechanical loads in addition to thermal loads (see Figure 2). High jet velocities close to the jet source can cause erosive forces, or mechanical loads. The radiative fraction of a flame jet can be as high as 30 %. Note that a flame jet burns rich close to the source, stoichiometric in the middle, and lean near the flame jet tip.

Twophase jets can generate substantial heating rates. In addition, twophase jets can cause liquid droplet impingement, penetration, and subsequent flashing that can damage insulation. Jet confinement can lead to secondary combustion of soot leading to higher heating rates.

Escalation and domino effects of fire scenarios can be calculated using SuperChems Expert and can provide more insight into potential fire risks. The development of Exceedance curves can provide valuable insight into risks and cost effective risk reduction measures [12].

Figure 2: A ground level high pressure gas flame jet from a 4 inch diameter natural gas well pipe (courtesy of ioMosaic)



Source: ioMosaic Corporation

4 Fire Flux

In recent editions of API-521, a more fundamental and alternative fire heating equation is provided that enables a better assessment of both relief requirement and vessel integrity depending on fire type and duration.

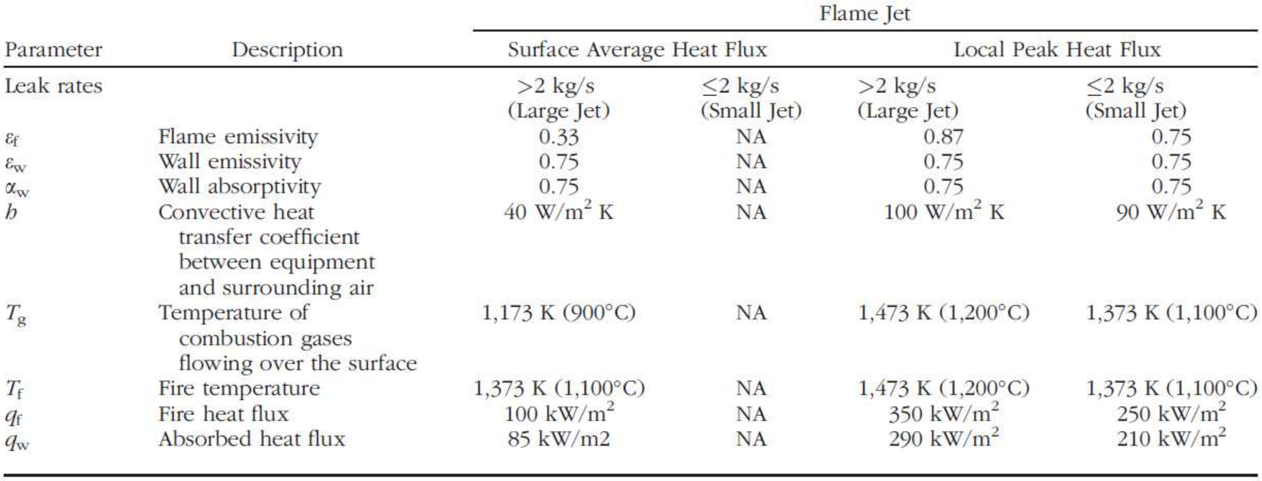
$$q_{fire,w} = \underbrace{\alpha_w \epsilon_f \sigma T_f^4}_{\text{Radiative Flux}} + \underbrace{h\left(T_{f,g} - T_{w,t}\right)}_{\text{Convective Flux}} - \underbrace{\epsilon_w \sigma T_{w,t}^4}_{\text{Re-radiated Flux}} \tag{2}$$

The first term in Equation 2 is the flame radiative heat flux into the external wall or insulation surface. The second term is the hot combustion gases convective heat flux into the external wall or insulation surface. The third term is the heat flux that is re-radiated by the external wall or insulation surface. Note that temperature in this equation must be absolute. The radiative heat flux is the dominant component of fire flux. An equipment does not have to be engulfed by fire in order to receive a large heating rate by thermal radiation.

When SI units are used, $q_{fire,w}$ is the net heat flux reaching the outer wall or insulation surface in $\mathrm{W/m^2/K}$, α_w is the external wall surface or insulation absorptivity, ϵ_f is the flame surface emissivity, σ is the Stefan-Boltzman constant = $5.67 \times 10^{-8}\ \mathrm{W/m^2/K^4}$, T_f is the flame surface temperature in K, h is the combustion gases convective heat transfer coefficient in $\mathrm{W/m^2/K}$, $T_{f,g}$ is the combustion gases temperature in K, $T_{w,t}$ is the time dependent wall surface temperature, and

ϵ_w is the outer wall or insulation surface emissivity.

Table 1: Recommended parameter values for Equation 2 for flame jets by API-521 [1] where other data or information are not available



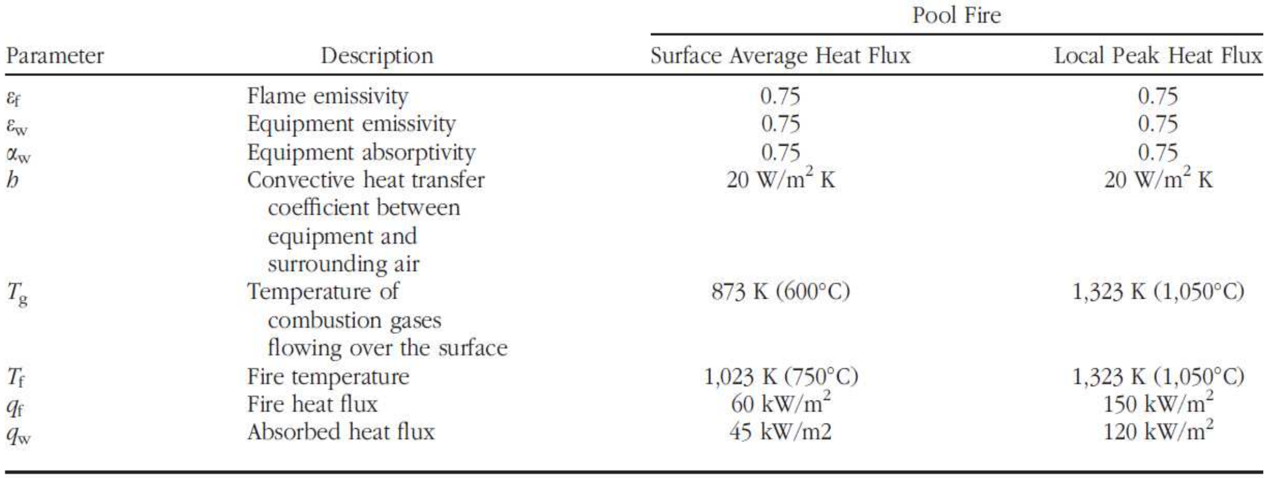
		Flame Jet			
Parameter	Description	Surface Average Heat Flux		Local Peak Heat Flux	
Leak rates		>2 kg/s (Large Jet)	≤2 kg/s (Small Jet)	>2 kg/s (Large Jet)	≤2 kg/s (Small Jet)
ε_f	Flame emissivity	0.33	NA	0.87	0.75
ε_w	Wall emissivity	0.75	NA	0.75	0.75
α_w	Wall absorptivity	0.75	NA	0.75	0.75
h	Convective heat transfer coefficient between equipment and surrounding air	40 W/m^2 K	NA	100 W/m^2 K	90 W/m^2 K
T_g	Temperature of combustion gases flowing over the surface	1,173 K (900°C)	NA	1,473 K (1,200°C)	1,373 K (1,100°C)
T_f	Fire temperature	1,373 K (1,100°C)	NA	1,473 K (1,200°C)	1,373 K (1,100°C)
q_f	Fire heat flux	100 kW/m^2	NA	350 kW/m^2	250 kW/m^2
q_w	Absorbed heat flux	85 kW/m2	NA	290 kW/m^2	210 kW/m^2

Recommended values are provided by API-521 [1] for a typical unconfined heptane pool fire engulfing an uninsulated carbon steel vessel for a surface average heat flux ($\alpha_w = 0.75$, $\epsilon_f = 0.75$, $T_f = 750$ °C (1023 K), $h = 20\ \mathrm{W/m^2/K}$, $T_{f,g} = 600$ °C (873 K), and $\epsilon_w = 0.75$) and local peak heat flux parameters ($\alpha_w = 0.75$, $\epsilon_f = 0.75$, $T_f = 1050$ °C (1323 K), $h = 20\ \mathrm{W/m^2/K}$, $T_{f,g} = 1050$ °C (1323 K), and $\epsilon_w = 0.75$). These recommended values are consistent with a fire flux of 60 $\mathrm{kW/m^2}$ and 150 $\mathrm{kW/m^2}$ for surface-averaged and local peak values and wall absorbed values of 45 $\mathrm{kW/m^2}$ and 120 $\mathrm{kW/m^2}$, respectively. Recommended values for jet fires are also provided by API-521 [1](as shown in Table 1) where actual test data are not readily available for establishing the flame characteristics.

Melhem [13] showed that the simple API-521 equation (Equation 1) can be recovered from Equation 2 when the dynamics are properly modeled. Equation 2 can be used to develop both the relief requirements and to assess the failure potential as well as the effectiveness of a variety of potential mitigation options. Melhem [13] also independently demonstrated that Equation 2, when used with Process Safety Office® SuperChems Expert™ vessel and wall dynamics, can accurately reproduce measured large scale [14, 15, 5] fire exposure test data including wall temperatures and vessel failure pressure.

The fire flux provided by Equation 2 is used by detailed dynamic simulation software such as SuperChems Expert to provide time dependent estimates of wall segment temperatures, fluid temperatures and single/multiphase venting rates with and without chemical reactions.

Table 2: Recommended parameter values for Equation 2 for pool fires by API-521 [1] where other data or information are not available



		Pool Fire	
Parameter	Description	Surface Average Heat Flux	Local Peak Heat Flux
ε_f	Flame emissivity	0.75	0.75
ε_w	Equipment emissivity	0.75	0.75
α_w	Equipment absorptivity	0.75	0.75
h	Convective heat transfer coefficient between equipment and surrounding air	20 W/m^2 K	20 W/m^2 K
T_g	Temperature of combustion gases flowing over the surface	873 K (600°C)	1,323 K (1,050°C)
T_f	Fire temperature	1,023 K (750°C)	1,323 K (1,050°C)
q_f	Fire heat flux	60 kW/m^2	150 kW/m^2
q_w	Absorbed heat flux	45 kW/m2	120 kW/m^2

5 Dynamic Modeling of Fire Exposure

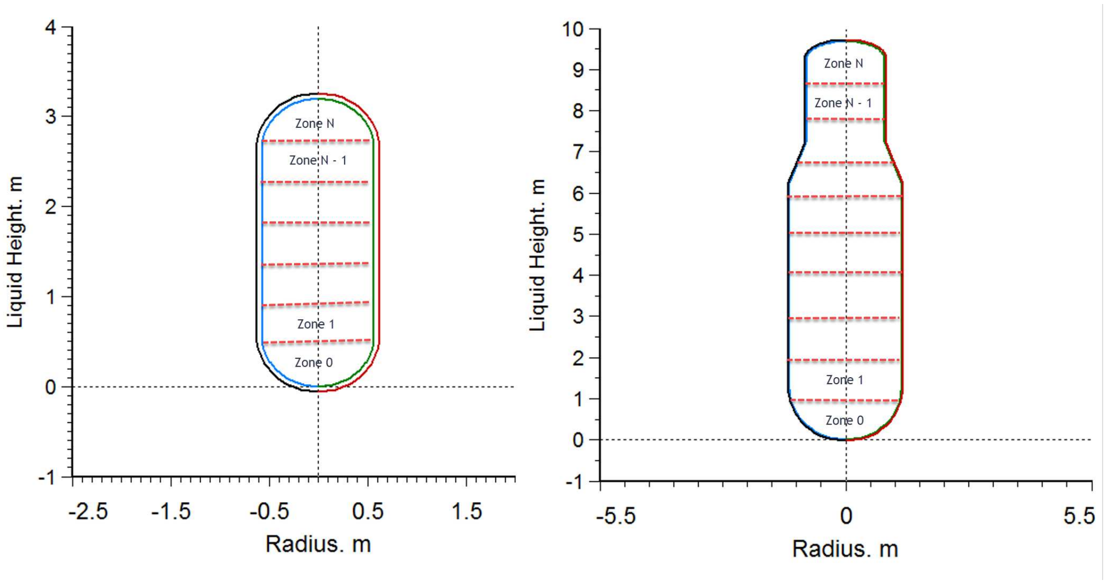
The case studies considered in this paper were modeled using the commercial software package SuperChems Expert , a component of the Process Safety Office® suite. SuperChems Expert solves the time-dependent detailed material, momentum, phase behavior, and energy balances for single and/or multiple interconnected vessels with complex piping for single and multiphase flow. Vapor/liquid disengagement dynamics, as well as reaction systems, are seamlessly handled for vessel and piping flow. The AIChE Design Institute for Emergency Relief Systems (DiERS) markets and sells SuperChems for DiERS (a subset of SuperChems Expert) that is capable of simulating most of the case studies considered in this paper.

A unique feature of SuperChems Expert is how the vessels are segmented and connected (see Figure 3). There is no limit on the number of segments a user can specify. The ability to define multiple segments allows the modeling of flame jet impingement. A wide variety of vessel shapes and heads, including composite vessels, vessel groupings, vessel packings, connectivity options, and relief and mitigation options, are easily represented.

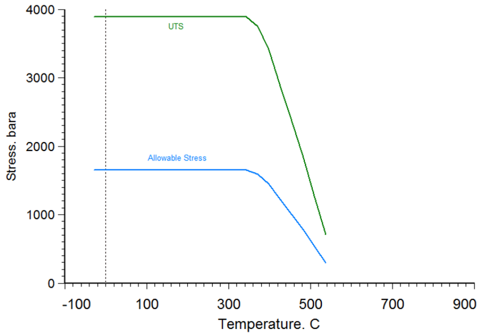
6 Tensile Strength vs. Temperature

For most steels, the ultimate tensile strength (UTS) starts to decrease around 400 °C . As the steel temperature is increased, the strength decreases to less than 10 % of its maximum value starting around 800 °C as shown in Figure 4.

Figure 3: Typical SuperChems Expert representation of vessel segments for dynamic modeling



Source: SuperChems Expert



The allowable stress by industry codes and standards is typically 3 to 4 times lower than the ultimate tensile strength. Steel plates tensile strength data can be obtained from ASME [17], API-579 [18] or other suitable references. Where temperature dependent data is not available for ultimate tensile strength and is available for allowable stress, one can assume that the ultimate tensile strength decreases with temperature in a similar fashion to how the allowable stress decreases with temperature.

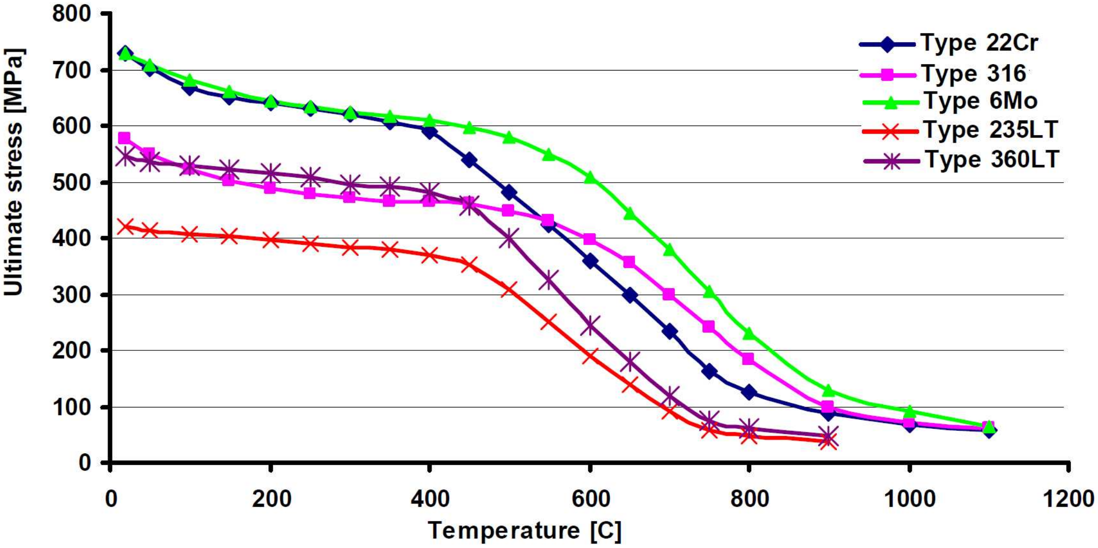
7 Failure Criteria

Commonly used expected failure and deformation criteria compare the equivalent total vessel stress to 2/3 of the ultimate tensile strength or 2/3 of the yield strength [19]. These estimates are dynamic by nature since the wall segments temperature, wall segments strength, and vessel total stress change dynamically with time.

etty is the calculated time at which the total vessel stress exceeds 2/3 of the yield tensile strength. **ettf** is the calculated time at which the total vessel stress exceeds 2/3 of the ultimate tensile strength. A reclosing pressure relief device can only be considered adequate for overtemperature protection if the calculated **ettf** or **etty** exceeds the estimated fire duration or the estimated failure time for vessel structural supports, whichever is less.

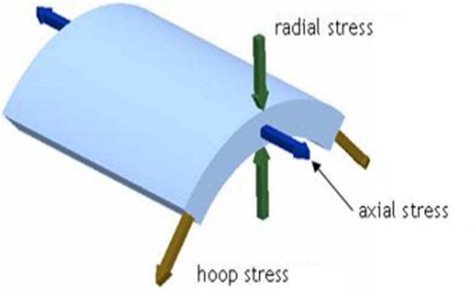
Vacuum protection may also be necessary if a reclosing relief device is the only mean of overpres-

Figure 4: Typical ultimate tensile strength for different steel types [16]



sure and overtemperature protection. Depending on the fire exposure scenario, computer codes such as SuperChems Expert , can be used to characterize flame jet or pool fire flame emissive power, length or height, tilt, geometric view factors, burning rates, atmospheric transmissivity, etc.

Under fire exposure, the total vessel stress resulting from internal pressure and other stresses, σ_e can be approximated using simple cylindrical shell equations [20] as provided in API 521. Longitudinal or axial stresses due to system weight (σ_{ext}) and thermal expansion (σ_{displ}) are less significant and can be ignored.



$$\sigma_e = \sqrt{\sigma_{hoop}^2 + \sigma_{axial}^2 - \sigma_{hoop}\sigma_{axial}} \tag{3}$$

Cylindrical Shape

$$\sigma_{hoop} = \frac{P\left(D_i + 2\delta\right)}{2\delta} \tag{4}$$

$$\sigma_{axial} = \frac{\sigma_{hoop}}{2} + \sigma_{ext} + \sigma_{displ} + \sigma_{other} \tag{5}$$

Spherical Shape

$$\sigma_{hoop} = \frac{P\left(D_i + 2\delta\right)}{4\delta} \tag{6}$$

$$\sigma_{axial} = \sigma_{hoop} + \sigma_{ext} + \sigma_{displ} + \sigma_{other} \tag{7}$$

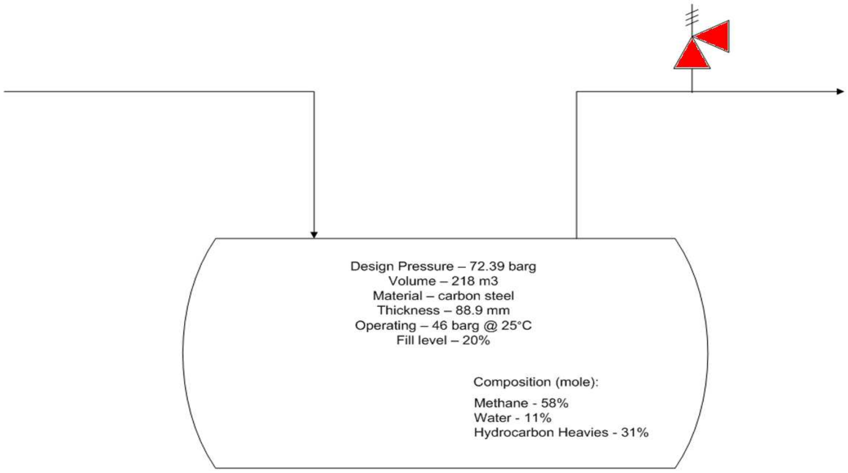
where σ_{other} represents additional stresses except those due to internal pressure or already considered, σ_{ext} is the longitudinal stress due to external loads, σ_{displ} is the longitudinal stress due to thermal expansion and support constraints, σ_e is the equivalent stress (von Mises), δ is the wall thickness, D_i is the inside diameter, P is the internal pressure, σ_{axial} is the axial or longitudinal stress, and σ_{hoop} is the hoop stress. Detailed finite element methods can also be used to estimate **ettf** or **etty** for highly critical installations.

8 Case Study

We consider the case of a process vessel exposed to a hydrocarbons fire (see Figure 5). The pressure relief valve is sized to keep the maximum pressure reached during the fire to less than or equal to 1.21 times the maximum allowable working pressure (1.21 x MAWP).

First, the overpressure relief requirement is established using the heating rate from Equation 1 divided by the latent heat of the contents. We also confirm that the relief requirement is adequate for overpressure protection using SuperChems Expert dynamics.

Figure 5: Simple fire exposure example of a vessel protected with a single PRV



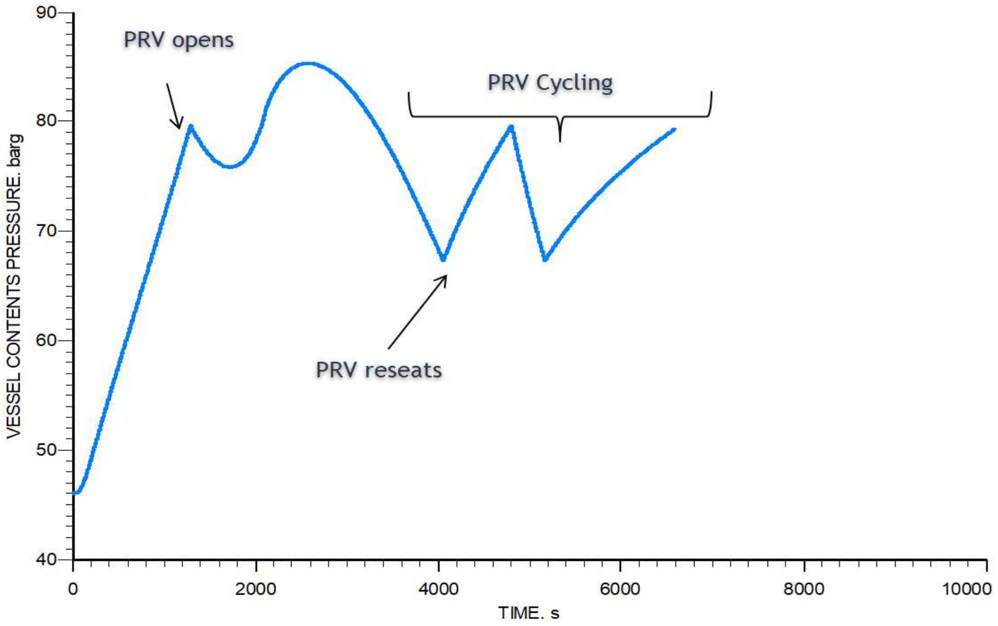
Source: ioMosaic Corporation

While this is currently a common practice, it is well known that a PRV cannot protect a vessel from failure for an extended fire duration. A properly sized PRV has to reseat and, if the fire continues, the vessel will ultimately fail at the reseat pressure of the PRV.

The relief requirement is also established using Equation 2 and the parameters provided by API-521 listed in Table 2. The vessel is divided into five segments. The local peak heat flux of 120 $\mathrm{kW/m^2}$ is used in the simulation since the intent is to calculate the localized maximum wall temperature which affects metal strength.

The pressure time history is illustrated in Figure 6. The dynamic pressure results in Figure 6 confirm that the relief requirement established using the heating rate of Equation 1 appears to be tolerable.

Figure 6: Dynamic pressure profile calculated using SuperChems Expert



Source: SuperChems Expert

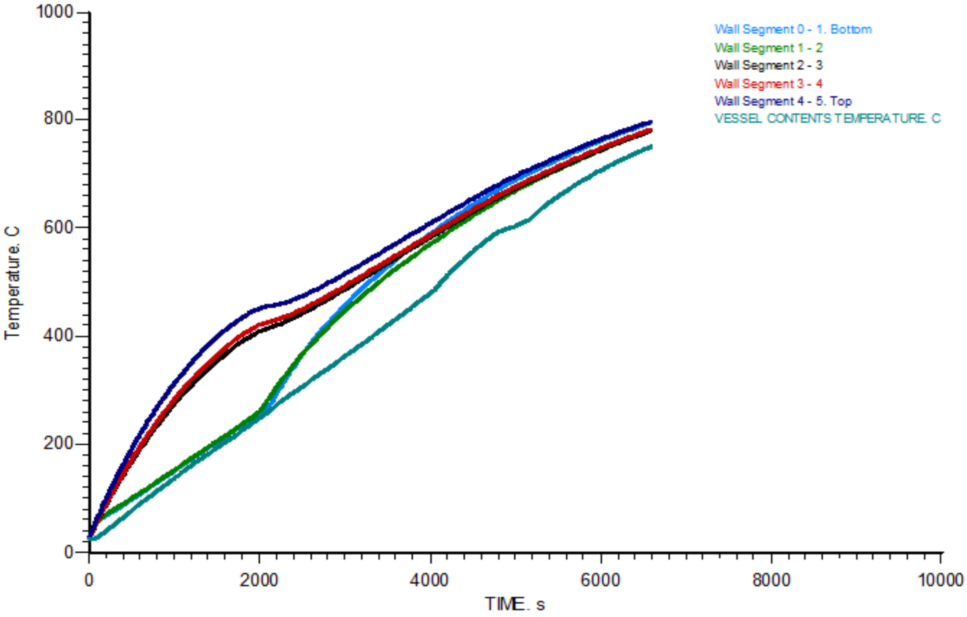
The temperature profiles for all five vessel wall metal segments are shown in Figure 7. As expected, the walls in contact with the vapor space heat up faster and become hotter than the walls in contact with the liquid space. We note that the liquid level is ultimately depleted (vaporized), and once the liquid level is depleted, the metal segments that become dry are heated more quickly.

We also need to consider the impact of the onset of two-phase flow from a relief device and/or a depressuring valve when they are actuated. The heat stored in the vapor walls can ultimately be recovered by the vessel contents during two-phase swell and/or flow since the vapor walls will get coated with a two-phase mixture.

Since we know the metal wall segment temperatures and we also know the pressure history as a function of time, we can estimate the internal equivalent stress the metal segments are exposed to and decide if the metal is likely to fail. We consider 2/3 of the ultimate tensile strength to be the failure boundary. A 2/3 safety factor is normally recommended (see NFPA 68 [19]) to account for uncertainties associated with metal properties, defects, and calculation methods.

The failure stress of each metal segment is shown in Figure 8 as is the overall internal stress. The wall segments failure stresses reduce rapidly after 2000 - 3000 seconds when the wall temperatures reach 450 - 500 °C . This vessel is predicted to fail in approximately one hour, or (**ettf**= 1 hour). If there is sufficient fuel inventory to sustain a fire for an hour, the PRV is not going to protect the

Figure 7: Dynamic temperature profiles for vessel contents and wall segments calculated using SuperChems Expert



Source: SuperChems Expert

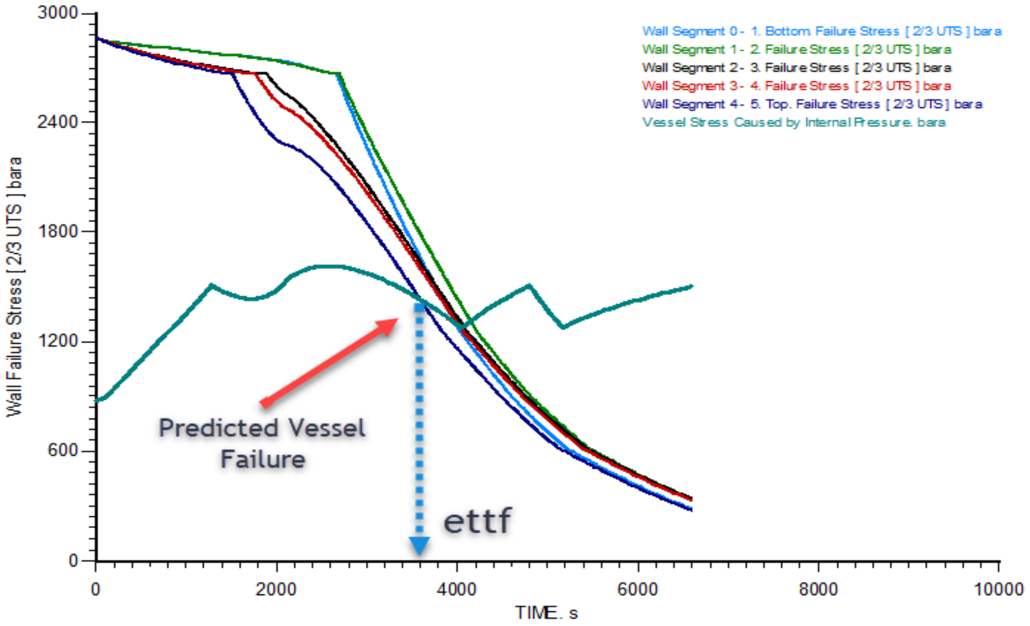
vessel from failure.

9 Piping Components Exposed to Fire

Piping components heat up faster than vessels because they have a larger surface to volume ratio. It is a common practice to add an additional piping allowance of 10 % to the wetted surface area when using Equation 1 to determine the heating rate which is used to determine the overpressure relief requirements only.

Under fire exposure, piping components containing liquid and connected to the bottom of vessels tend to track liquid temperatures due to gravity flow driven by density stratification during heating. Piping components connected to the vapor space or piping components that do not contain liquids are more likely to fail first. Piping components containing vapor are good candidates for fire proof insulation in order to minimize failure risk from excessive temperatures during fire exposure.

Figure 8: Dynamic stress profiles for vessel contents and wall segments calculated using SuperChems Expert



Source: SuperChems Expert

10 Vessel Jackets Exposed to Fire

Vessel jackets present another extreme relief design case under fire exposure [21]. Vessel jackets have a small volume and a very large surface area, or a high surface to volume ratio like piping components.

Cooling jackets are usually run liquid full where the liquid is pumped at a pressure well above its saturation point, i.e. the liquid is subcooled at the jacket operating temperature. As the liquid in the jacket is heated by external fire, the liquid expands and liquid thermal relief occurs through the relief device. Liquid thermal relief continues until the liquid in the jacket reaches its bubble point at a pressure where the relief device is fully open (usually at 10 % over the set point for pressure relief valves). After the bubble point of the liquid is reached, twophase flow will occur until the jacket is emptied through the relief device.

The geometry of vessel jackets in not favorable for vapor/liquid disengagement [22, 23, 24]. Because of the jacket large surface to volume ratio and very poor vapor/liquid disengagement characteristics, fire exposure leads to high heating rates and homogeneous two-phase flow during venting. As a result, nozzles on vessel jackets are usually too small to meet two-phase flow requirements. In most cases, it is not practical or feasible to install a large PRV on a vessel jacket. Fire proof insulation and/or the use of fusible plugs are options that are often used to reduce failure risks and relief requirements. Jackets are often equipped with small PRVs for liquid thermal relief only.

11 Multiphase Flow Considerations

Most legacy relief sizing calculations for fire exposure used Equation 1 and assumed all vapor flow with heating rates based on wetted surface area only. As discussed earlier, twophase flow can cause the entire vessel surface area to be wetted and can result in a much larger relief requirement. Even in the case of large storage vessels where bulk heating of the liquid content does not occur, twophase flow can still occur. A variety of scenarios can lead to twophase flow under relief conditions.

In general, two-phase flow during relief can occur because of flow hydrodynamics and poor vapor/liquid disengagement where (a) the liquid swells due to generation of vapor bubbles in the liquid [1], (b) fluid expansion occurs due to heating, and/or (c) the superficial vapor velocity is high enough through the pressure relief device. Oversized relief devices can induce two-phase flow because a large relief flow area yields a higher superficial vapor velocity. Runaway chemical reactions and/or chemical systems that are viscous and/or foamy almost always lead to homogeneous two-phase flow.

Two-phase flow can also occur by entrainment, for example, where gas is sparged at a high enough rate in the liquid. In some systems, condensation leading to two-phase flow in the discharge piping can also occur due to expansion cooling caused by pressure reduction through a control valve or a pressure relief device.

It is preferred to eliminate or significantly reduce the potential for two-phase flow. This can be accomplished by either (a) reducing the risk/likelihood of the scenarios that can lead to two-phase flow to a tolerable level and/or (b) specific relief and effluent handling systems design considerations and implementations [2].

More mass is vented from a vessel during two-phase flow than during all vapor flow. During all vapor flow, the liquid has to make up the lost vapor and beneficial energy tempering occurs. This helps to reduce the relief requirements for fire exposure scenarios for example.

As a result of more mass being discharged due to two-phase flow, potential dispersion, fire, and explosion hazard footprints can become significantly larger. Vent containment and/or flow separation are often required to reduce the risks of two-phase flow. When homogeneous two-phase flow occurs, the specific ratio of vapor to liquid does not change in the vessel during venting and as result beneficial energy tempering does not occur. When more vapor is vented relative to liquid, beneficial energy tempering occurs because the liquid has to make up the lost vapor. This is one of the primary reasons why homogeneous two-phase flow results in large relief requirements for vessels exposed to external fire, external or internal heating, and/or where chemical runaway reactions are the cause of the homogeneous two-phase flow.

It is therefore important to be able to determine:

(a) what configurations and/or process conditions can lead to two-phase flow,

---

[1] Generation of bubbles can occur due to mechanical means and/or chemical reactions including decomposition reactions.

[2] This includes the use of quenching systems that suppress chemical reactions that can cause two-phase flow, such as the introduction of a quench fluid, and/or the quick injection of an inhibitor or a neutralizing agent.

(b) the vapor quality entering the vent, and

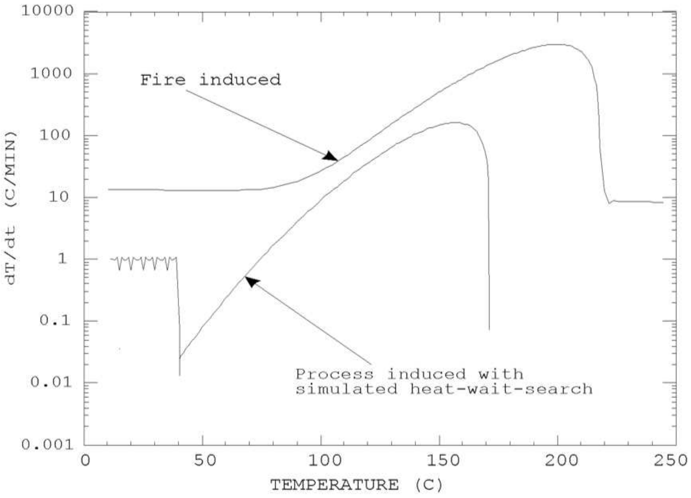
(c) the rate at which two-phase flow occurs.

Undoubtedly, one of the most important contributions of the American Institute of Chemical Engineers (AIChE) design institute of emergency relief systems (DIERS) to chemical process safety is the development of the coupling equation which can be used to determine if and when two-phase will occur and what the vapor quality entering the vent will be [22, 23, 24]. DIERS also published methods for the estimation of two-phase flow rates.

The DIERS coupling equation should be used in all fire exposure scenarios to determined if twophase flow will occur.

12 Special Considerations for Reactive Systems

Fire induced runaway reactions often result in significant relief requirements and twophase flow. Heating induced by fire increases the reaction rates exponentially and causes higher vessel pressure and temperature levels. A fire can generate more vapor, causes thermal expansion, and allows the vessel pressure to reach the set point of the relief device with less reactant consumption and more reactant mass at time of relief. The effect of fire on reaction rates in highly non-linear, involves complex analysis and requires rate expressions [25].



If inhibitors are used, a fire can cause an inhibitor to be depleted at high temperatures causing spontaneous reactions at elevated temperatures in excess of the normal reaction onset temperatures [26].

Fire exposure scenarios where reactive chemicals are present require special care [27]. In some instances, when all vapor flow occurs, preferential depletion of light ends can lead to concentrating of active ingredients leading to more violent reactions and possible spontaneous decompositions and deflagrations. This is especially important where solvents are used and the solvent boiling point is less then the onset temperature of the undesired reaction. In some systems, the undesired reactions may be autocatalytic. Fire exposure increases the bulk liquid temperature and as a result decreases the induction time to runaway.

13 Vessels Containing Mixtures and Heavy Hydrocarbons

Fire exposure on vessels containing mixtures with heavy components, where all vapor flow is possible, can cause excessive wall temperatures due to preferential boil off and depletion of lights and concentrating of heavy components. In some cases the coincident temperature with the pressure relief valve set point can be very high depending on the physical properties of the heavy components present.

In some heavy hydrocarbon systems thermal cracking can take place at these elevated temperatures [28]. Even though the thermal cracking reactions are mostly endothermic, higher volumetric flows are produced due to the formation of smaller molecules which may lead to higher relief requirements if the vessel can survive the high wall temperatures. Depending on the set point, a pressure relief valve may not offer any protection at all. Recent test data and research by DIERS [29] indicates an endothermic heat of cracking of approximately $100\ \mathrm{BTU/lb}$.

14 Fire Exposure Mitigation Measures

There are many strategies and methods that can be used to mitigate fire exposure risks. These strategies and methods include but are not limited to the use of (a) depressuring valves, dump valves, or depressuring systems, (b) fire proof insulation, (c) water sprays or sprinklers, (d) fusible plugs, (e) earth coverage and other forms of shielding from thermal radiation such as walls, and (f) drainage and sloping.

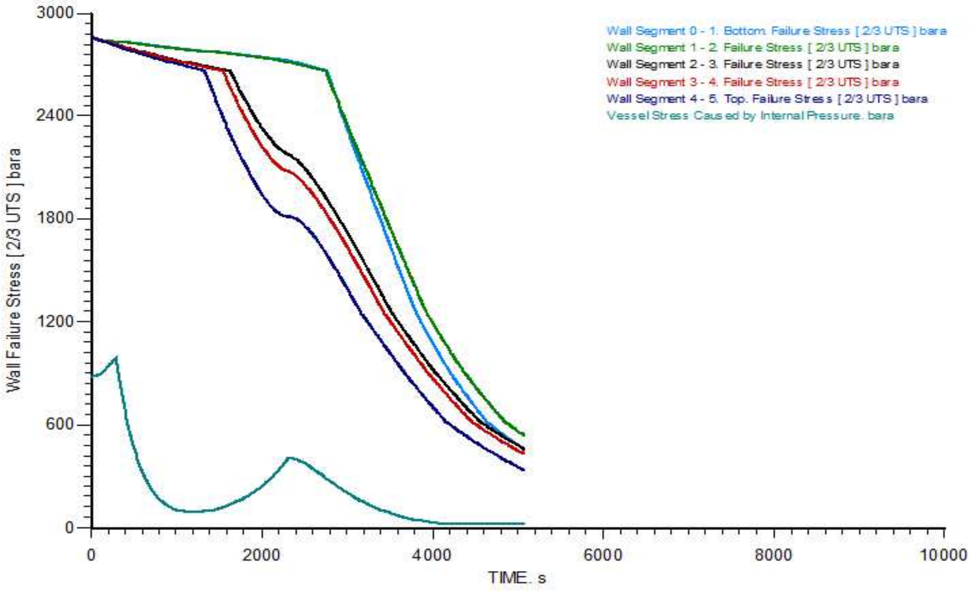
14.1 Depressuring Systems

The primary objective of a depressuring system is to decrease the pressure faster than the decline of the coincident metal strength. A properly sized depressuring valve can reduce the pressure (stress) in the vessel faster than the reduction of tensile strength caused by fire heating. In the absence of detailed modeling tools that consider the wall temperature dynamics, API-521 [1] recommends reducing the internal pressure to 50 % of the design pressure within 15 minutes of the fire scenario. Note that this criterion is for 1 inch thick steel only. Stainless steel vessels may sustain higher pressures than specified and vessels with wall thickness that is less than 1 inch may fail at lower pressures than specified.

Reduction in pressure to 100 psig is suggested in API-521 [1] for vessel leaks. 15 minutes is recommended in the current version of API-521 [1]. The criteria recommended by API-521 are not effective for flame jet impingement. A depressuring time of five minutes or less is more appropriate and needs to be confirmed using dynamics.

It can be demonstrated for our example case study discussed earlier that equipping our process vessel with a properly sized depressuring valve to reduce the pressure to 100 psig in 15 minutes will protect the vessel from failure during an extended fire exposure as shown in Figure 9. Other mitigation measures that can be explored are the use of fire proof insulation, fixed water sprays, etc.

Figure 9: Dynamic stress profiles for vessel contents and wall segments calculated using SuperChems Expert using a properly sized depressuring valve



Source: SuperChems Expert

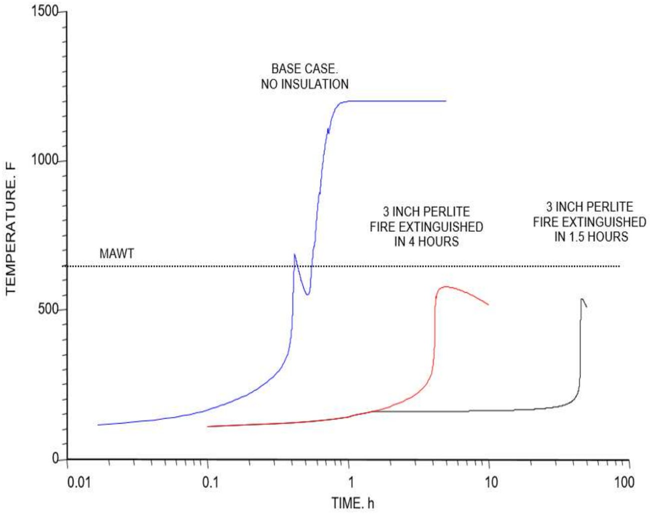
Depressuring systems have to be sized properly [30, 31]. An overly sized depressuring valve or system can cause cold fluid and metal temperatures during rapid depressuring. Cold temperatures can lead to metal embrittlement and/or the formation or the carryover of liquids or hydrates downstream of the vessel(s) begin depressured.

14.2 Fire Proof Insulation

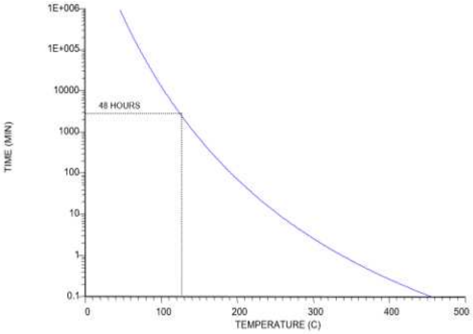
The use of fire proof insulation is a possible mitigation measure that can provide protection and risk reduction. When a sufficient thickness of insulation is used, a longer fire duration is needed to heat the metal to excessive temperatures. The rate of heating to the vessel walls and contents can be substantially reduced, which reduces relief requirements and in many cases can buy sufficient response time to either outlast or extinguish the fire. Insulation of vessels may not be a preferred choice due to the potential of corrosion under insulation (CUI).

In order for insulation to be considered fire proof (see API 521, NFPA 30), it must be able to effectively function up to 1,660 °F for up to two hours. The insulation must retain its shape, most of its integrity in covering the vessel, and its insulating value. Fire proof insulation cannot be dislodged when exposed to high pressure water systems used in fire fighting. Stainless steel jacketing is necessary because moist or wet insulation can lose its effectiveness. Jacketing must also be anchored on vertical structures because it can slide due to expansion under fire exposure.

Fire proof insulation may not be an optimal solution for systems containing reactive chemicals [32]. Insulating a vessel containing a reactive chemical can reduce the heat input from an external fire, but it will also reduce the heat loss from the vessel to the surroundings after the fire is extinguished. A heavily insulated vessel can become a near adiabatic system which can enable a chemical reaction to runaway. If insulation is used for fire exposure mitigation for vessel containing reactive chemicals, a reliable estimation of time to runaway is needed (by measurement or dynamic modeling) after the fire is extinguished. Typically, 48 hours can provide enough time for site operations to either bring additional cooling or to pump out the vessel contents.



For reactive systems we need to determine if there is adequate protection even after the fire is extinguished. The time to maximum rate yielding 24 or 48 (tmr_{24} or tmr_{48}) hours will require a minimum insulation thickness. This can be calculated using the methods described by Melhem in references [33, 25, 26] and may require small scale calorimetry measurements.



14.3 Water Sprays or Sprinklers

The primary function of water sprays is to cool the metal surface to approximately 100 °C and to outlast the fire. In order for water sprays to be effective, enough water flow rate must be provided for coverage, i.e. no bare metal spots can be developed or exposed during the fire. Other considerations include time-lag for activation of the sprinkler system and availability of water over the entire fire exposure duration. In addition, water sprays may not be effective for jet fire exposure and may not protect against runaway reactions with onset temperatures less than 100 °C .

14.4 Fusible Plugs

The use of fusible plugs presents an effective strategy for protecting vessel jackets under fire exposure and in some unique high hazard systems, where rapid or spontaneous decompositions are possible, the main vessel [21, 34] itself. The cost of using one or more large fusible plugs to reduce pressure relief valve flow requirements may be less expensive than changing the valve as well as the inlet and/or discharge piping. In general, the use of fusible plugs is often limited to water and water glycol systems (unless you can establish that corrosion is not an issue). Fusible plugs should not be used to vent toxic and/or flammable material and should be directed away from walkways and operating personnel to a safe discharge location [35].

The primary objective of a fusible plug is to drain the liquid in the jacket before the liquid temperature reaches the bubble point at relief pressure. As a result, a small or smaller pressure relief valve to protect the vessel jacket from liquid thermal relief and/or partial two-phase flow can be used. The melting temperature of a fusible plug should be selected high enough (a minimum of 30 °C above the maximum expected operating temperature is recommended) to prevent spurious opening from process temperature excursions, steam cleaning, etc. Fusible plugs should not be covered with insulation. Install fusible plugs near (not at) the lowest point of the jacket. Install fusible plugs at a low enough point (within 12 inches from the jacket) to discharge the maximum possible amount of liquid. Avoid locations where the fusible plug may become inoperable due to build up of dirt, scale/silt over the inlet.

Fusible plugs should be treated like any other relief device for record keeping, inspections, and maintenance. Fusible plugs are relatively inexpensive. Replace fusible plugs periodically (determine a suitable frequency based on your maintenance program). Fusible plugs should be removed prior to any chemical cleaning of vessel jackets.

15 Conclusions

Where fire exposure scenarios are used for the development of relief requirements for emergency relief systems, reasonable estimates of **etty** or **ettf** are required for strict OSHA compliance. They are also necessary for effective risk management as well as effective emergency response and fire protection.

This is particularly important for systems that contain reactive chemicals, chemicals with high boiling points, and process equipment that are gas filled or process equipment containing liquids where the vapor space can be engulfed/impinged by fire or exposed to flame thermal radiation.

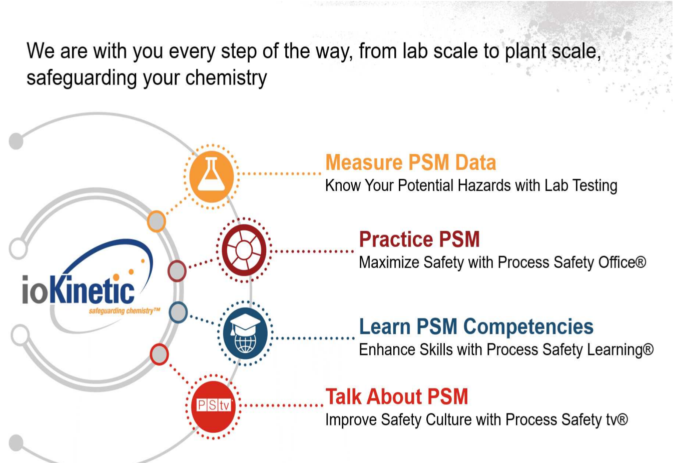
Modeling system dynamics using SuperChems Expert can be very useful and can provide insight into the proper selection of insulation thickness, actuation time of the depressuring system, water spray density requirements, etc. More importantly, dynamics are very useful to study the sensitivity of the final design to key mitigation parameters or system characteristics.

How can we help?

In addition to our deep experience in process safety management (PSM) and the conduct of large-scale site wide relief systems evaluations by both static and dynamic methods, we understand the many non-technical and subtle aspects of regulatory compliance and legal requirements. When you work with ioMosaic you have a trusted ISO certified partner that you can rely on for assistance and support with the lifecycle costs of relief systems to achieve optimal risk reduction and PSM compliance that you can evergreen. We invite you to connect the dots with ioMosaic.


We are with you every step of the way for the long haul as you journey to PSM excellence and shareholder value

We also offer laboratory testing services through ioKinetic for the characterization of chemical reactivity and dust/flammability hazards. ioKinetic is an ISO accredited, ultra-modern testing facility that can assist in minimizing operational risks. Our experienced professionals will help you define what you need, conduct the testing, interpret the data, and conduct detailed analysis. All with the goal of helping you identify your hazards, define and control your risk.


We are with you every step of the way, from lab scale to plant scale, safeguarding your chemistry

Please visit `www.iomosaic.com` and `www.iokinetic.com` to preview numerous publications on process safety management, chemical reactivity and dust hazards characterization, safety moments, video papers, software solutions, and online training.

References

[1] API. *API Standard 521 - Pressure Relieving and Depressuring Systems*. American Petroleum Institute, 7th edition, 2020.

[2] API 520. Sizing, selection and installation of pressure-relieving devices in refineries. Parts I and II, March 2020.

[3] NFPA 30. Flammable and combustible liquids code, 2015.

[4] G. A. Melhem and D. Gaydos. Properly calculate vessel and piping wall temepratures during depressuring and relief. *Process Safety Progress*, 34(1):64–71, 2015.

[5] G. A. Melhem, P. A. Croce, and H. Abraham. Data summary and analysis of NFPA's BLEVE tests. *Process Safety Progress*, 12(2):76–82, 1993.

[6] G. A. Melhem, H. Ozog, and S. Saraf. Understand LNG rapid phase transitions - (with RPT test data appendices). *ioMosaic Corporation White Paper*, 2006.

[7] G. A. Melhem. Quantify non-equilibrium flow and rapid phase transitions (RPT). *ioMosaic Corporation White Paper*, 2020.

[8] G. A. Melhem. Non-equilibrium flow and rapid phase transitions (RPT). In *DIERS Spring Virtual Meeting*. AIChE, March 2021.

[9] API. *API Recommended Practice 581 - Risk Based Inspection Methodology*. American Petroleum Institute, 3rd edition, 2016.

[10] G. A. Melhem. Reducing uncertainty in LNG fire exposure modeling. In *LNG Topical Conference*. AIChE/CSChE, August 2009.

[11] G. A. Melhem. Are pool fires only 25 ft high? In *DIERS Users Group Meeting*. AIChE, Spring 2008.

[12] G. A. Melhem and J. Dunjo. A risk-based approach for predicting domino effects due to fires. In *13th Global Congress on Process Safety*. AIChE, March 2017.

[13] G. A. Melhem. Proper calculations of pipe and vessel wall temperatures during relief and/or depressurization. In *78th API Fall Refining and Equipment Standards Meeting*, pages 221–226, November 2013.

[14] B. Droste and W. Schoen. Full-scale fire tests with unprotected and thermal insulated LPG storage tanks. *Journal of Hazardous Materials*, 20:41–53, 1988.

[15] W. Schoen and B. Droste. Investigation of water spraying systems for LPG storage tanks by full-scale fire tests. *Journal of Hazardous Materials*, 20:73–82, 1988.

[16] Scandpower. Guidelines for the protection of pressurised systems exposed to fire. Technical Report 27.207.291/R1, Statoil, March 2004.

[17] ASME. Boiler and pressure vessel code. section VIII, rules for construction of pressure vessels, 2019.

[18] API. Standard 579 - fitness-for-service, 2016.

[19] NFPA 68. Standard on explosion protection by deflagration venting, 2018.

[20] P. Salater, S. Overaa, and E. Kjensjord. Size depressurization and relief devices for pressurized segments exposed to fire. *Chemical Engineering Magazine*, pages 23–28, September 2002.

[21] G. A. Melhem. Pressure relief design for vessel jackets under fire exposure using fusible plugs. *ioMosaic Corporation White Paper*, Novemeber 2004.

[22] G. A. Melhem. Eliminate the DIERS coupling equation singularity. In *DIERS Users Group Meeting*. AIChE, Fall 2008.

[23] M. Grolmes and H. Fisher. Vapor liquid onset/disengagement modeling for emergency relief dishcharge evaluation. In *AIChE Summer National Meeting*, 1994.

[24] G. A. Melhem. Two-phase flow onset and disengagement methods. *ioMosaic Corporation White Paper*, Novemeber 2020.

[25] G. A. Melhem. Polymerization modeling for emergency relief systems. *ioMosaic Corporation White Paper*, 2020.

[26] G. A. Melhem, James Close, and Ying Zhang. Polymerization reactions inhibitor modeling - styrene and butyl acrylates incidents case studies. *ioMosaic Corporation White Paper*, 2020.

[27] G. A. Melhem and P. Howell. Designing emergency relief systems for runaway reactions. *Chemical Engineering Progress*, pages 23–28, September 2005.

[28] F. Self, G. Arora, D. Sielegar, and V. Quiroga. Craking of petroleum resid - model development. In *Joint US and European DIERS meeting*. AIChE, May 2019.

[29] J. Hauser, D. Smith, D. Smith, G. Hendrickson, and M. Levin. Diers research report - external fire case - low volatility fluids. In *DIERS meeting*. AIChE, October 2018.

[30] G. A. Melhem. Retrograde and phase change RPC flow considerations for relief and flare systems. *ioMosaic Corporation White Paper*, 2018.

[31] G. A. Melhem. Retrograde and phase change RPC flow considerations for relief and depressuring systems. *ioMosaic Corporation White Paper*, 2018.

[32] G. A. Melhem and H. G. Fisher. Reactive storage vessels - how to determine if your insulation is going to work. In *DIERS Users Group Meeting*. AIChE, Fall 2002.

[33] G. A. Melhem, S. Grenier, and L. Ding. Thermal stability indicators. *ioMosaic Corporation White Paper*, 2020.

[34] D. K. Winegardner. Pressure relief systems for vessel jackets exposed to fire. In *DIERS Users Group Meeting*. AIChE, October 1992.

[35] G. A. Melhem. What is a safe discharge location? In *AIChE Webinar Series*. AIChE, March 2020.

About the Author

Dr. Melhem is an internationally known pressure relief and flare systems, chemical reaction systems, process safety, and risk analysis expert. In this regard he has provided consulting, design services, expert testimony, incident investigation, and incident reconstruction for a large number of clients. Since 1988, he has conducted and participated in numerous studies focused on the risks associated with process industries fixed facilities, facility siting, business interruption, and transportation.

Prior to founding ioMosaic Corporation, Dr. Melhem was president of Pyxsys Corporation; a technology subsidiary of Arthur D. Little Inc. Prior to Pyxsys and during his twelve years tenure at Arthur D. Little, Dr. Melhem was a vice president of Arthur D. Little and managing director of its Global Safety and Risk Management Practice and Process Safety and Reaction Engineering Laboratories.

Dr. Melhem holds a Ph.D. and an M.S. in Chemical Engineering, as well as a B.S. in Chemical Engineering with a minor in Industrial Engineering, all from Northeastern University. In addition, he has completed executive training in the areas of Finance and Strategic Sales Management at the Harvard Business School. Dr. Melhem is a Fellow of the American Institute of Chemical Engineers (AIChE) and Vice Chair of the AIChE Design Institute for Emergency Relief Systems (DiERS).

Contact Information

Georges. A. Melhem, Ph.D., FAIChE
E-mail. melhem@iomosaic.com

ioMosaic Corporation
93 Stiles Road
Salem, New Hampshire 03079
Tel. 603.893.7009, x 1001
Fax. 603.251.8384
web. www.iomosaic.com

Index

ioMosaic®

Minimizing risk. Maximizing potential.®

US Offices

New Hampshire (Salem) – *Headquarters*
Texas (Houston)
Minnesota (Minneapolis)
California (Berkeley)

International Offices

Kingdom of Bahrain (Al Seef)
United Kingdom (Bath)

Software Solutions

Process Safety Enterprise®

Centralize the process safety management lifecycle to accelerate business goals

Process Safety Office®

Identify, evaluate, and control process hazards with tools used by process safety consultants

Process Safety Learning®

Build your process safety competencies incrementally with online training

Process Safety tv®

View, share, and discuss PSM worldwide on a secure platform

Contact Us

www.ioMosaic.com
sales@ioMosaic.com
1.844.ioMosaic

About ioMosaic Corporation

Through innovation and dedication to continual improvement, ioMosaic has become a leading provider of integrated process safety and risk management solutions. ioMosaic has expertise in a wide variety of areas, including pressure relief systems design, process safety management, expert litigation support, laboratory services, training and software development.

As a certified ISO 9001:2015 Quality Management System (QMS) company, ioMosaic offers integrated process safety and risk management services to help you manage and reduce episodic risk. Because when safety, efficiency, and compliance are improved, you can sleep better at night. Our extensive expertise allows us the flexibility, resources, and capabilities to determine what you need to reduce and manage episodic risk, maintain compliance, and prevent injuries and catastrophic incidents.

Our mission is to help you protect your people, plant, stakeholder value, and our planet.

Consulting Services

- Asset Integrity
- Auditing and Due Diligence
- Combustible Dust Hazard Analysis and Testing
- Facility Siting
- Fault Tree/SIL/SIS Analysis
- Fire and Explosion Dynamics
- Incident Investigation, Litigation Support and Expert Testimony
- Liquefied Natural Gas Safety
- Pipeline Safety
- Process Engineering Design and Support
- Process Hazards Analysis (PHA)
- Process Safety Management (PSM)
- Reactive Chemicals Evaluation and Testing
- Relief and Flare Systems Design and Evaluations
- Risk Management Program Development
- Quantitative Risk Assessments (QRA)
- Software Solutions
- Structural Dynamics
- Training

Laboratory Testing Services (ISO accredited)

- Chemical Reactivity
- Combustible Dust
- Battery Safety
- Specialized Testing