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ALERT: Reactive Chemical Storage — How To Determine If Your Insulation Is Going To Work

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Summary

It is a common practice to insulate storage tanks containing reactive chemicals to protect against fire exposure. While this mitigation technique is appropriate for vessels handling non-reactive chemicals, reactive chemicals storage represents a special challenge and must be examined on a case-by-case basis. For certain classes of reactive chemicals, given a sufficiently long hold time, the insulation will always lead to a runaway reaction.

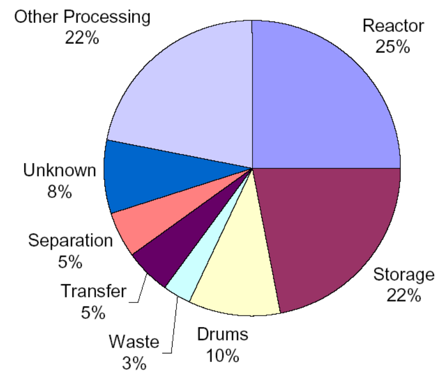
If insulation is to be used, special handling is required in order to insure that after the fire is extinguished, the vessel contents do not reach a temperature that causes a runaway within 48 hours. The 48 hours time limit is selected arbitrarily and should be long enough for most installations to empty the tank contents, inject and circulate additional inhibitor into the tank, cool the tank contents, and/or use the vessel contents in the process.

For vessels containing reactive liquids or non-reactive liquids that are known to be foamers or where two-phase flow is possible due to the disengagement characteristics of the vessel/relief system use the total surface area of the vessel as wetted surface area when estimating heat input into the vessel. Existing guidelines from API and NFPA-30 ignore the impact of two-phase flow on wetted area selection and can lead to non-conservative designs. Assuming a constant heat flux input, a vessel that is 30 % full, for example, will result in a higher reaction rate than a vessel that is 90 % full. This effect has to be established using advanced simulation techniques such as those embodied in SuperChems Expert and SuperChems for DIERS.

In most fixed facilities cases where fire exposure is a credible scenario, the nature of the fuel is known. Use a flame emissive power based on the fuel characteristics, especially if you are dealing with a reactive system.

If you must insulate vessels containing reactive chemicals, a clear understanding of the runaway reactions characteristics should be obtained from adiabatic calorimetry data. Use proven dynamic simulation computer codes such as SuperChems Expert or SuperChems for DIERS to: (a) establish the required relief capacity, (b) establish the time to maximum rate, and (c) establish the required response time for a given insulation thickness.

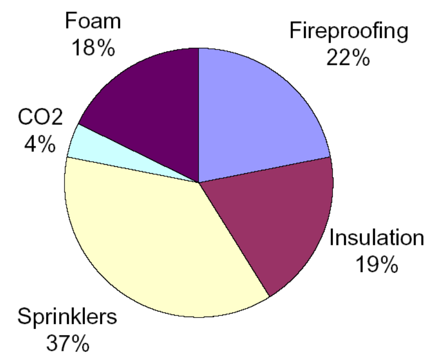
Incident Statistics of Reactive Storage Tanks



According to a survey recently completed by the chemical safety investigation board, 22 % of reactive chemical incidents surveyed occurred in storage equipment, 25 % in reactors, 22 % in other processing equipment, 10 % in storage drums, and the remainder in waste, separation, and transfer equipment. Storage vessels and drums account for 32 % of all accidents surveyed.[1]

Are Reactive Storage Tanks Typically Insulated?

A survey summary reported in the CCPS guideline on the safe storage and handling of reactive chemicals suggests that there is no widely adopted common practice and that practices differ from company to company. 41 % of all respondents to the survey reported that they use insulation and fireproofing while 37 % reported the use of water sprays, and the remainder used other mitigation means.[2]



Insulation Buys Time but Can Lead to a Runaway: How is that possible?

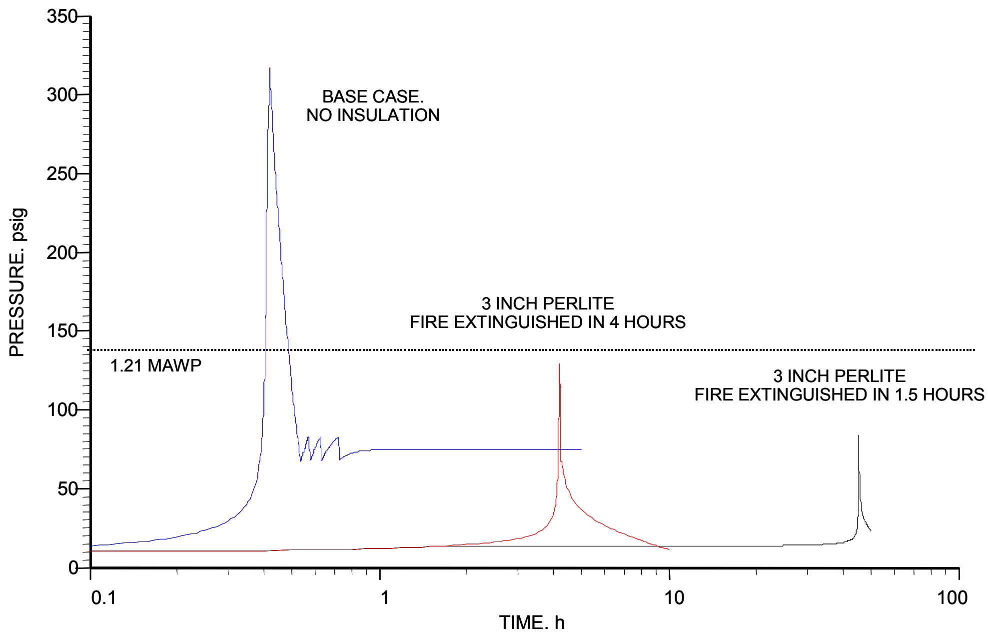
The addition of insulation to a vessel containing a reactive chemical transforms the vessel into a near adiabatic environment. Natural heat loss from the vessel is greatly minimized. Given a sufficiently long hold time, reactions will initiate and runaway without the aid of internal cooling. This problem can be further exacerbated if the stored material is contaminated or is a peroxide former.

This is best illustrated using an example. Consider a small storage vessel containing a reactive monomer. The vessel is equipped with a safety relief valve. The monomer is flammable and the vessel is also located in a common area with other flammable materials storage and processing vessels. As a result, a fire exposure scenario is considered to be credible and must be accounted for in the relief design. A combination of insulation, lower relief device set point, and a larger relief area, as limited by the existing vessel nozzle, are considered as possible mitigation.

[1] J. Murphy, CSIB Public Hearing Staff Preliminary Conclusions, May 2002, Paterson, New Jersey.

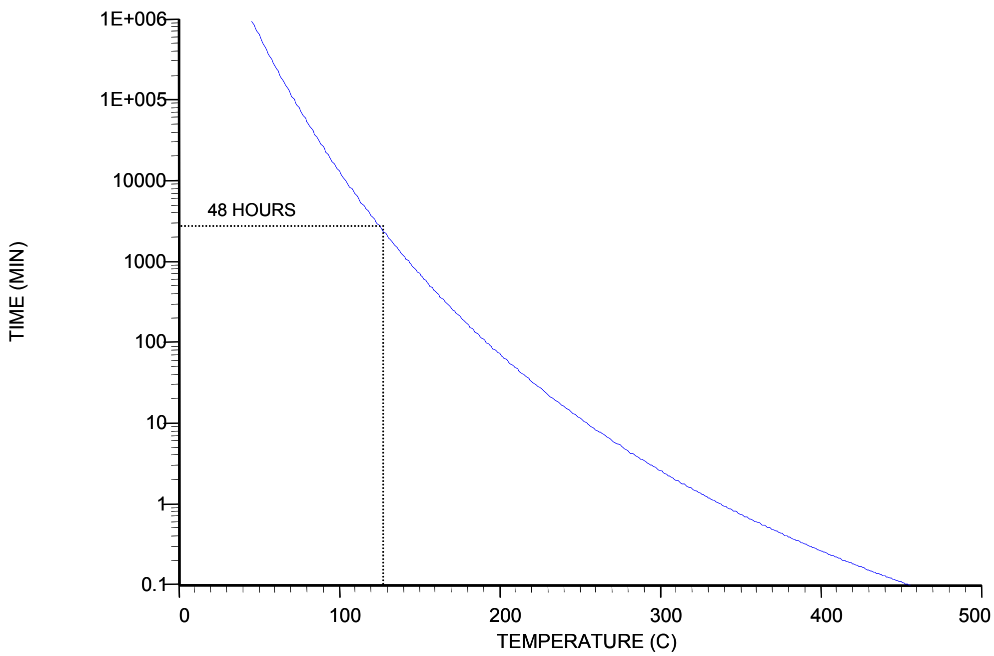
[2] CCPS, Guidelines for the Safe Storage and Handling of Reactive Materials, 1995

Figure 1: Pressure History as a Function of Insulation Thickness and Relief Area



Source: SuperChems Expert 5.0

Figure 2: A Typical Time to Maximum Rate Dependence on Storage Temperature



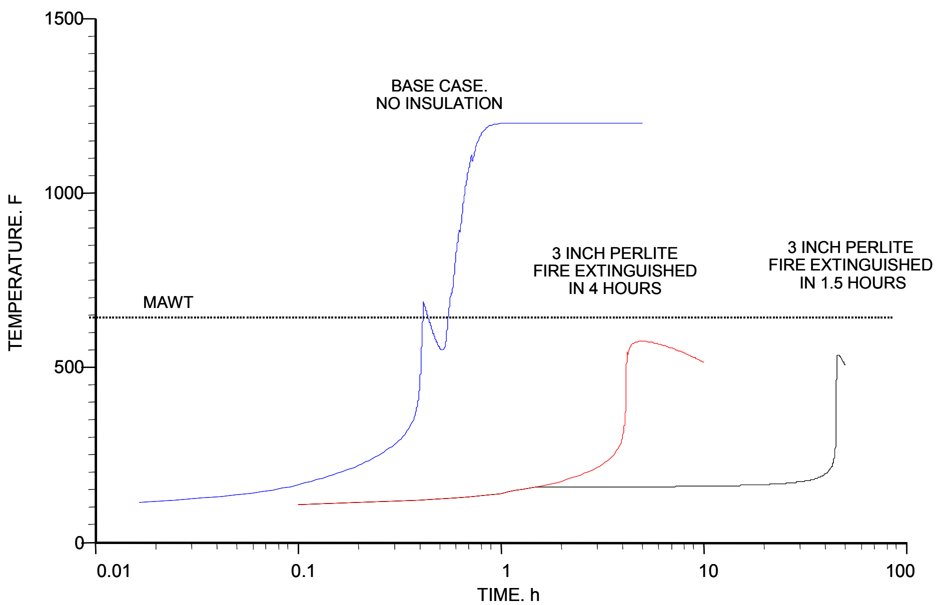
Source: SuperChems Expert Version 5.0

Figure 1 illustrates the impact of insulation and a larger relief area on the pressure in the vessel. A longer fire exposure time is required to reach the polymerization onset temperature with more insulation. If the fire is extinguished in four hours, the storage vessels contents temperature is high enough to cause a self-accelerating runaway in less than one hour after the fire is extinguished. If the fire is extinguished in 1.5 hours, a self-accelerating runaway will occur 48 hours later.

The impact of temperature on time-to-maximum rate is implicitly accounted for in the simulation. However, one can establish a simple time-to-maximum-rate from limited data such as the heat of reaction, heat capacity, and activation energy. These diagrams are often constructed assuming a zero order reaction. Figure 2 illustrates the typical impact of temperature on time to maximum rate. The relationship is established from adiabatic calorimetry and/or well characterized runaway reaction data.

Figure 3 illustrates the estimated temperature history in the vessel as a function of insulation thickness and compares it to the maximum allowable working temperature of the vessel metal. The data indicates that with 3 inches of fireproof insulation, the fire would have to be extinguished in less than four hours. One should note that extended fire exposure would ultimately result in failure of the metal. As the temperature of the metal increases, the yield strength of the metal decreases, ultimately leading to the failure of the metal. Loss of metal yield strength is a serious issue where flame jet

Figure 3: Temperature History as a Function of Insulation Thickness and Relief Area



Source: SuperChems Expert Version 5.0

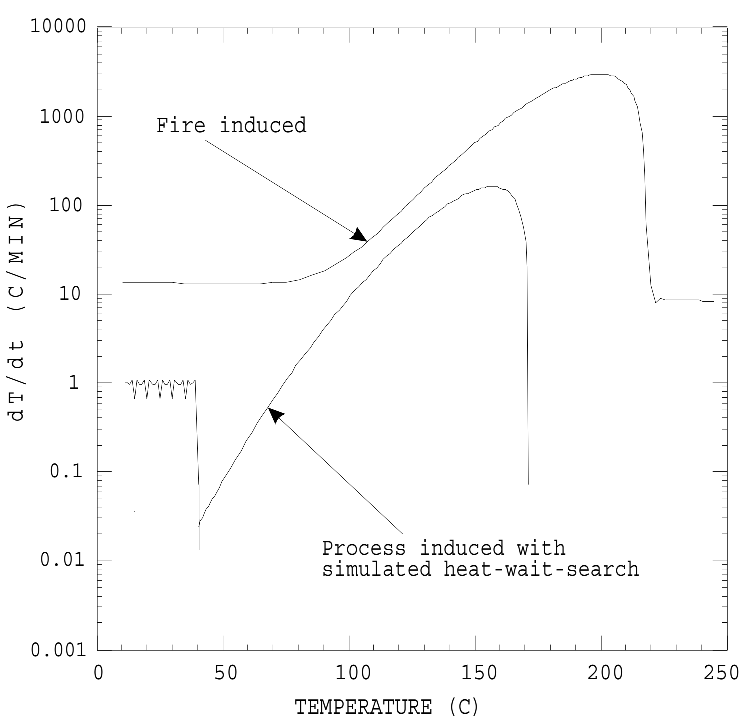
impingement is possible on the vapor space of vessel. In such situations, failure of the metal is likely to occur in a short duration (minutes). Relief devices protect against over-pressure rather than over-temperature.

For reactive chemicals, a runaway reaction induced by an external source of heat, such as a fire, produces a significantly higher relief requirement than a process-induced runaway reaction. With an external heating source, less reactant is consumed by the reaction to reach the onset temperature. An external heating source also leads to additional liquid vaporization and vapor/liquid expansion. This effect is highly non-linear and is illustrated in Figure 4.

Assuming a constant heat flux input, a vessel that is 30 % full, for example, will result in a higher reaction rate than a vessel that is 90 % full. This effect has to be established using advanced simulation techniques such as those embodied in SuperChems Expert and SuperChems for DIERS.

If fire exposure represents a credible scenario, the estimation of an accurate rate of heat input into the storage vessel is essential to the development of a safe design. Runaway reaction characterization under adiabatic conditions must also be well quantified (calorimetry data from an adiabatic device such as an ARC or APTAC is highly recommended).

Figure 4: Impact of Fire Exposure on Reaction Rates
Data is for hydrogen peroxide/water system



Source: SuperChems Expert Version 5.0

For storage vessels containing large quantities of reactive chemicals, a fire-induced runaway may result in large relief requirements that may not always be practical. In such situations, insulation can be used as a mitigation measure, if the proper analysis is conducted with proper data and tools.

The addition of insulation transforms the storage vessel into an adiabatic environment. The relationship of time to runaway (or time to maximum rate) and temperature is logarithmic as shown in Figure 2 for the example discussed earlier.

Insulation for fire protection can be effective if it is rated for fire exposure and is mechanically secure. As illustrated in the monomer example earlier, the insulation does buy time until the fire is extinguished. Depending on the activation energy for the chemical in question, its heat of reaction, the size and shape of the storage vessel, and the expected hold time, insulation may be the wrong thing to do without careful analysis.

The final temperature in the vessel must be low enough to prevent a runaway after the fire is extinguished. Autocatalytic systems and systems with inhibitors should be examined with great care.

Heat Transfer To Vessel Contents

A vessel either partially or totally engulfed in fire receives both radiant heat from the flames and convective heat from the hot combustion products. The magnitude of these two components depends on the fuel characteristics, combustion process, ambient conditions, and fire geometry, optical thickness of the flame, tank geometry and thermal properties.

Heat is transferred by conduction, convection and radiation to the liquid and vapor contents of a tank. Radiative heat transfer occurs as heat is transmitted through the hot vessel walls in the vapor space to the vapor. A large fraction of the heat received by the vapor is then transmitted through the vapor to the liquid surface because of the transparent nature of the vapor.

The initial mode of heat transfer to the liquid is conduction. This occurs over a short period of time after which buoyancy forces dominate and convection becomes the principal mode of heat transfer. Buoyancy driven flows are created near the inner walls of the vessel by convective heating and nucleate boiling. This can lead to thermal stratification in both the liquid and vapor.

Depending on the difference between wall and bulk liquid temperatures, the heat transfer mechanisms are natural convection, sub-cooled/saturated nucleate boiling, or film boiling.

Fire Flux Estimation

Fire exposure heating rates are estimated using well-established standards and recommended practices including NFPA-30/ANSI-2000, OSHA 1910.106, API-520/521, and API-2000. There are specific details associated with the estimation of the heating rate from each of these methods. These details pertain to the selection of heat transfer surface area (often referred to as wetted surface area), the vessel type (vertical, spherical, or horizontal), the normal vessel liquid level, and the use of mitigation techniques such as insulation, drainage, and water sprays.

All of these methods represent the heat input into the vessel using an equation of the form:

$$Q = q\, A_w^a = E_p\, F\, A_w^a$$

Where E_p is the fire heat flux, F is a mitigation protection fire flux derating factor (environmental factor), A_w^a is the vessel wetted surface area available for heat transfer, and a is a parameter that is fitted from experimental data that depends on the vessel wetted surface area/total exposed area used in the experiments. Table 3 and 4 show a summary of how the wetted surface area and the fire mitigation protection (environmental) factor are used in API and NFPA-30.

Emissive Power Issues

The heating rates estimated from these techniques are not always conservative. In 1997, experiments conducted by NFPA showed that the heating rate estimated by API is underestimated by a factor of 3 for hexane and overestimated by a factor of 1.8 for ethanol (see Table 1).

Table 1: Large scale fire test data conducted by NRC of Canada

Fuel	Qtest (BTU/hr)	Qtest/QAPI
Ethanol	2,620,000	0.56
Hexane	14,436,000	3.06

Source: NRC, Canada (see NFPA 30, A93 TCR); QAPI = 4,703,480 BTU/hr

The fuel type, burning rate, flame drag, pool fire diameter, geometric view factors (fraction of the vessel surface visible to flame), and atmospheric conditions will influence the flame emissive power and how much heat is conducted or radiated to the vessel surface.

The methods outlined by NFPA, OSHA, and API are somewhat outdated and based on limited test data. Since the 1940s, major advancements have occurred in fire research and many large-scale pool fire experiments were conducted by NFPA, the US DOT, the gas research institute (GRI), Shell Research, and the American Gas Association (AGA) to name a few. Research findings helped to experimentally establish the flame emissive power of many hydrocarbon fuels and helped validate correlations for flame height, burning rates, and flame drag. SuperChems Expert implements the best established correlations for establishing pool fire and flame characteristics, including geometric view factors and atmospheric transmissivity estimates for cases where the vessel may not be engulfed in flame but is exposed to flame radiation.

the flame surface into different zones with different luminosity and radiation characteristics. Simple expressions for estimating the heat input from a flame radiating to a vessel have long been established:

$$q = E_p \tau F_m$$

Where q is the incident flux in kW/m2, E_p is the flame emissive power, τ is the atmospheric transmissivity coefficient, and F_m is the geometric view factor. The view factor and atmospheric transmissivity values range between 0 and 1. For direct flame impingement, a good first approximation of the heat flux can be obtained by setting the values of both the geometric view factor and atmospheric transmissivity to 1. For hydrocarbon fuels, and based on large-scale experimental test data, Arthur D. Little Inc. established a simple correlation for the estimation of flame emissive power from the normal boiling point:

$$E_p = 117 - 0.313\, NBP \; or \; 20, \;\; whichever \;\; is \;\; greater$$

Where NBP is the normal boiling point/bubble point of the fuel in F. Table 2 illustrates the impact of boiling point (number of carbons) on the flame emissive power.

Table 2: Flame emissive power from SuperChems Expert Correlation

Fuel	Normal Boiling Point (F)	Estimated Flame Emissive Power (kW/m2)
Methane	-258.68	198
Ethane	-127.48	157
Propane	-43.67	131
Butane	31.10	107
Pentane	96.92	87
Hexane	155.71	68
Heptane	209.17	52

Source: Arthur D. Little

Heat Transfer Area (Wetted Area) Issues

A more important issue to consider when using the standard heating rate equations established by NFPA/API/OSHA is the use of wetted surface area and how that applies to the case of reactive storage.

API 520/521, for example, allow for the derating of the heat input into the vessel based on normal fill level. This means that a storage vessel that is 25 % full will get a smaller heating input than a vessel that is 50 or 90 % full. For non-reactive and non-foamy systems, and where two-phase flow does not occur, the use of wetted surface area to estimate the heat input into the vessel is warranted. Less heat is radiated through the vapor space of the vessel to the liquid surface than what is conducted through the vessel walls in contact with the liquid contents.

The majority of reactive systems will result in two-phase flow upon actuation of the relief device. Two-phase flow is feasible when the material is known to be a foamer or when the relief system/vessel disengagement characteristics favor two-phase flow (high vessel superficial vapor velocity). As a result, liquid contacts the vapor space walls and the total exposed surface area of the vessel should be used, regardless of fill level. Literal interpretation of the recommend heating rates/wetted surface area used by API-520/521 will result in underestimating the heat input into the vessel and consequently will lead to a non-conservative design.

The experimental data used to establish the API/NFPA curves did not exhibit two-phase flow. As a result, those curves should only be applied to non-reactive systems, where two-phase flow does not occur.

Recommendations

For vessels containing reactive liquids or non-reactive liquids that are know to be foamers or where two-phase flow is possible due to the disengagement characteristics of the vessel/relief system, use the total surface area of the vessel as wetted surface area.

In most fixed facilities cases where the fire exposure is a credible scenario, the nature of the fuel is known. Use a flame emissive power based on the fuel characteristics, especially if you are dealing with a reactive system.

If you must insulate vessels containing reactive chemicals, a clear understanding of the runaway reactions characteristics should be obtained from adiabatic calorimetry data. Use proven dynamic simulation computer codes such as SuperChems Expert or SuperChems for DIERS to: (a) establish relief requirements, (b) establish the time to maximum rate, and (c) establish the required response time for a given insulation thickness.

Refer to Appendix A for a checklist of design solutions/actions to consider for minimizing the risk of fire exposure.

Table 3: Wetted Area Estimation Methods

Storage / Vessel Class	API-520/521	API-2000	NFPA-30/ANSI-2000/OSHA1910.106
Liquid Full	All up to 25 ft	N/A	N/A
Storage drums, knockout drums, process vessels	Normal operating liquid level up to a height of 25 ft	75 % of total surface area, or the surface area to a height of 30 ft above grade, whichever is greater	75 % of total exposed area
Fractionating columns	Normal level in bottom plus liquid holdup from all trays; total wetted surface area up to a height of 25 ft	N/A	N/A
Working storage	Average inventory up to a height of 25 ft	N/A	N/A
Vertical tanks	N/A	Total surface area of the vertical shell up to height of 30 ft above grade. For a vertical tank supported on the ground, the bottom head/plate is not included. For elevated vertical tanks, a portion of the bottom head/plate is to be included as additional wetted area	First 30 ft above grade of the exposed shell area.
Spheres and Spheroids	Up to the maximum horizontal diameter or up to a height of 25 ft, whichever is greater	55 % of the total surface area, or the surface area to a height of 30 ft above grade, whichever is greater	55 % of the total exposed area

Table 4: Recommended Fire Environmental Factor Values

Condition	API-520/521	API-2000	NFPA-30/ANSI-2000/OSHA
Insulation	0.3 to 0.026 depending on conductance	0.3 to 0.025 depending on conductance	0.3 for a minimum conductance of 4
Drainage	Included in heat rate expression	0.5	0.3 with good drainage. 0.15 with insulation and good drainage
Drainage and prompt fire fighting resources	Heat rate expression reduced by a factor of 0.6		
Underground or earth covered		0 or 0.03	0
Depressuring and emptying facilities	1.0		

Appendix A: Multi-Step Fire Exposure Mitigation Options

1. *Identify / Prevent (Reduce)*

    a. Loss of Containment

    b. Ignition Sources for Fires

2. *Prevent Emergency Venting During a Fire*

    a. Limit Fire Duration (No Fuel – No (Limited) Fire)

        i. Diking / Curbing (Isolate Reactive Chemicals)

            1. Requires Leakage (Inventory Reduction) to Provide Fuel

        ii. Drainage

        iii. Water Spray (Wash Fuel Away)

    b. Extinguish Fire (Fire Duration)

        i. Trained Responders

        ii. Proper / Sufficient Equipment

        iii. Water Supply

        iv. Foam Supply / Availability / Special Equipment

3. *Prevent Two-Phase Flow During A Fire (Atmospheric Vessels) – Vessel Collapse*

    a. Initial Fill Level

        i. Thermal Expansion

        ii. Level Swell

            1. DIERS Wall-Heated Model

            2. DIERS Non-Boiling Height Model

            3. DIERS Entrainment Model

4. ***Prevent Runaway Reaction During a Fire – Worst Case Scenario***

    a. Limit Tank Contents Temperature During Fire

        i. Water Spray (Maximum Temperature Due to Water Spray)

        ii. Insulation (Thickness vs. Thermal Conductivity Considerations)

5. ***Prevent Runaway Reaction for 48 Hours After a Fire Is Extinguished – Worst Credible Scenario***

    a. Emergency Action Plan – Restore Safe Condition

    b. Consider Time vs. Temperature (Time to Maximum Rate)

    c. Inhibitor Effectiveness Calculations

6. ***Consider Normal Storage***

    a. Continuous Temperature Monitoring (All Reactive Chemicals)

    b. Preplanned Alarm / Emergency Action / Evacuation Temperatures

    c. Preplanned Mitigation Measures

        i. Community Notification

        ii. Shelter in Place

        iii. Evacuation Plan / Methodology

About the Authors

Dr. Georges Melhem is managing general partner of ioMosaic Corporation. Prior to 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 and managing director of Arthur D. Little's Global Safety and Risk Management Practice and its Process Safety and Reaction Engineering Laboratory.

Dr. Melhem is an internationally known pressure relief design, chemical reaction systems, and fire and explosion dynamics expert. In this regard he has provided consulting and design services, expert testimony and incident investigation support and reconstruction for a large number of clients.

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.

Harold G. Fisher retired as a Principal Engineer from the Process Safety Technology Group of Union Carbide Corporation after 40 years of service following the acquisition by the Dow Chemical Company. He has over 11 years of production engineering experience and 27 years reaction safety engineering / emergency relief system design experience. He earned a BSChE from Syracuse University in 1961 and MSChE, MSE (IE) and MBA degrees from West Virginia University in 1968, 1971 and 1974, respectively.

Harold has been involved with the Design Institute for Emergency Relief Systems (DIERS) since 1976 having served as Technical Chairman from 1982-1984 and Chairman of the DIERS Users Group since 1985. He is a lecturer for the AIChE Continuing Education Courses "Emergency Relief System Design Using DIERS Technology" and "Methods for Sizing Pressure Relief Vents". He was the editor and contributing author of the AIChE / DIERS Project Manual and co-editor and contributing author of two AIChE / DIERS “International Symposia on Runaway Reactions, Pressure Relief and Effluent Handling” books.

He is a Fellow of the AIChE. Upon his retirement, Mr. Fisher opened a consultancy and has entered into an exclusive alliance with Fauske & Associates of Burr Ridge, IL.

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About Us

ioMosaic Corporation is a leading provider of safety and risk technology consulting services and software solutions. Our areas of expertise include runaway reactions and pressure relief design, consequence and risk analysis, fire and explosion dynamics, incident investigation, litigation support, training, mitigation design, hazard evaluation, and model development.

What is ioMosaic?

ioMosaic is a combination of two terms. io is the standard industry acronym for input (i) output (o). In any problem solving activity there is data that must be gathered and analyzed, the input. Usually the solution to a problem involves many pieces of data all of which are important, but none of which alone can solve the problem. It is up to the analyst to find each relevant piece of data and then arrange the pieces to form the solution, just like looking at a mosaic. Once all the pieces are in place, the solution is apparent!

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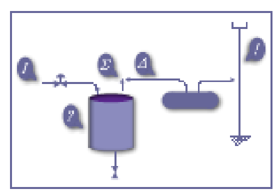

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