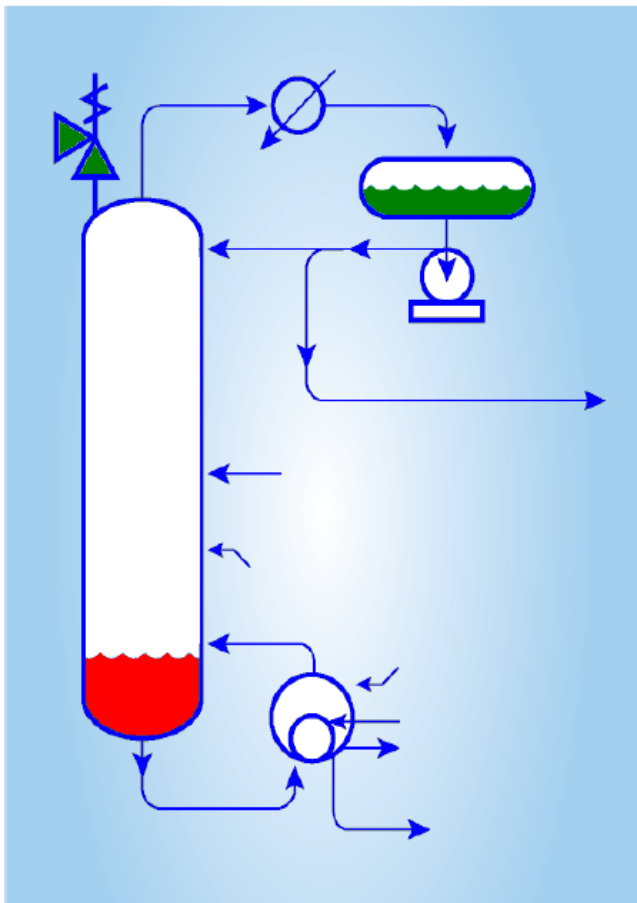# ioMosaic

Retrograde and Phase Change Flow Considerations for Relief and Depressuring Systems

An ioMosaic White Paper

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ioMosaic Corporation

Relief and Depressuring Systems Design and Evaluation Practices

Fluid Flow

Retrograde and Phase Change (RPC) Flow Considerations for Relief and Depressuring Systems

authored by

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Contents

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1 Introduction

Numerous scenarios can lead to retrograde and phase change (RPC) flow [1] in relief and depressuring systems. Potential hazard scenarios considered often include, but are not limited to, depressuring during process upsets (cold depressuring), relief or depressuring under fire exposure, and relief or depressuring under runaway reactions. These scenarios are evaluated to determine relief requirements, the potential for equipment failure due to metal weakening because of increased metal temperatures during fire exposure and/or metal brittle fracture due to the formation of cold liquids in the equipment while depressuring [2]. Time to failure, associated safety and environmental consequences or impacts of relief effluents discharged directly to the atmosphere or vent containment and flare systems, and the effectiveness of any proposed or existing pre or post release mitigation measures represent additional important and required information.

Phase change has to be considered for the vessel contents as well as relief flow conditions. For example, depending on the vessel contents composition and the initial starting conditions of temperature and pressure relative to the contents phase envelope, depressuring might lead to the formation of substantial amounts of cold liquids and/or hydrates. All vapor venting where the vessel contents contain a mixture of vapor and liquid can lead to the formation of two-phase mixture at the discharge of a relief device and as a result the associated choke points and flow rates will be in error if RPC conditions are not considered. Liquid carryover to downstream equipment may need to be considered as a result.

Depending on the scenarios being evaluated and the complexity of the relief/depressuring system, equipment pressures/temperatures may increase or decrease depending on the equipment connectivity and whether or not the equipment is exposed to fire or has ongoing chemical reactions. Chemical compositions can also change over time due to chemical reactions, preferential depletion of light ends, and/or already different starting compositions present in different interconnected equipments. As a result, RPC conditions will dynamically change during the relief/depressuring process. Expected RPC conditions are illustrated and discussed using several case studies. Some of the case studies are simulations of selected actual large scale test data where RPC flow was observed and measured.

# 2 Heat and Mass Transfer Considerations

The calculation of accurate vessel wall temperatures during depressuring and/or pressure relief is challenging. Accurate wall temperatures are required to determine the strength of vessel material of construction, the potential failure pressure, and time to failure. Most detailed dynamic simulation computer codes, such as SuperChems Expert™, use widely published correlations to determine the fluid-wall heat transfer coefficients [1]. For example, a small variation in the natural convection vapor-wall heat transfer coefficient can cause a large variation in the calculated vessel contents temperature and associated wall temperatures. A typical value of the vapor-wall natural convection heat transfer coefficient is approximately $100 \ \mathrm{W/m^2/K}$ and as a result poor heat transfer is experienced during non-condensing all vapor flow. The poor heat transfer can lead to colder

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[1]SuperChems is a trademark of ioMosaic Corporation

vapor temperatures due to expansion cooling and warmer vessel wall temperatures.

Condensation caused by expansion cooling during depressuring can lead to enhanced heat transfer between the vessel walls and the condensing vapor. Condensing liquid film wall heat transfer coefficients can be substantially higher than natural convection coefficients. Nucleate and pool boiling of the liquid in a two-phase system can also enhance heat transfer between the liquid and vessel walls. A typical value of the liquid-wall heat transfer coefficient ranges from 1,000 to 3,000 $\text{W/m}^2\text{/K}$ (see [3]). We note that the calculation of vessel contents pressure during depressuring/pressure relief is less sensitive to variations in heat transfer coefficient values and in general can be very well predicted and calculated as shown below.

Figure 1: Typical user defined wall zones for different vessel geometries as represented by SuperChems Expert
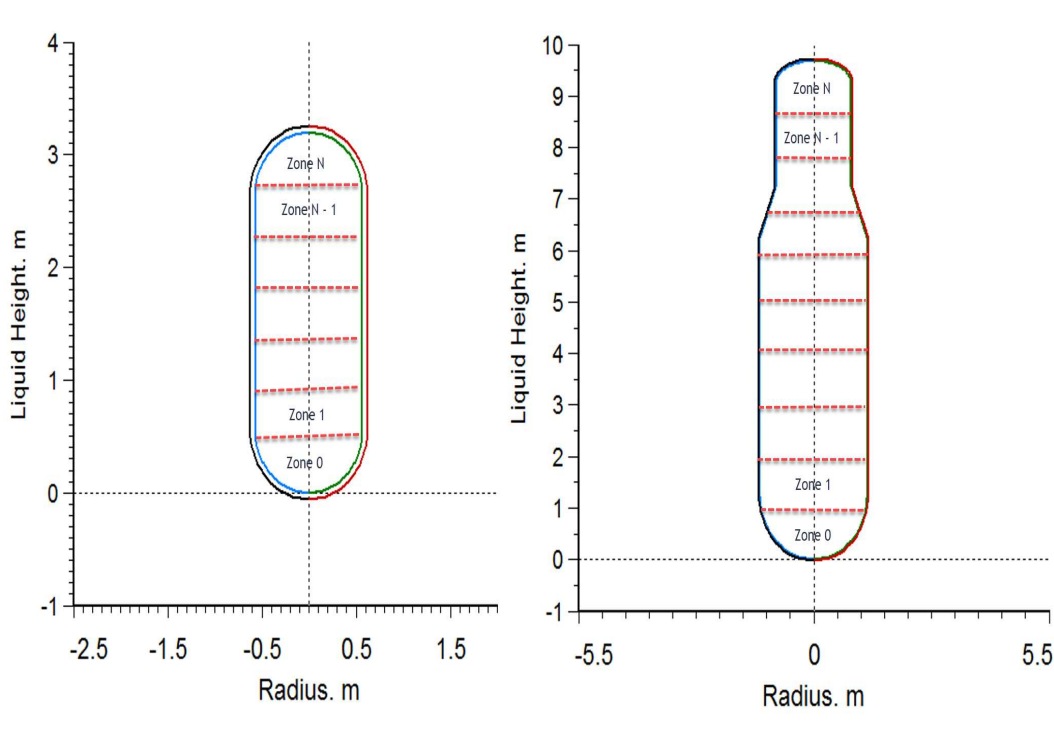
The treatment of mass, flow, and heat transfer dynamics also differs between commercial computer codes. SuperChems Expert assumes the vapor and liquid phases in the vessel are in thermal and physical equilibrium but divides the vessel into many zones (user specified, see Figure 1) to enable better estimates of average wall temperatures for each zone. Heat is transferred between the different wall zones vertically as well as between each wall zone, insulation layer, the vessel contents, and surroundings. This is important when a small amount of liquid is condensed and collects in the bottom of a large vessel or when a specific section of the vessel wall is subjected to intense heating or cooling. SuperChems Expert considers a variety of heat transfer mechanisms including solar heating, water sprays cooling, rain cooling, user defined cooling, user defined heating, jacket heating/cooling, fire exposure, internal chemical runaway reaction, etc. SuperChems Expert also allows the use of insulation and can accurately calculate wetted, flow, and surface areas as a function of liquid level for typical and irregular vessel geometries with a variety of heads (see

Figure 1).

3   Flow Models and Thermodynamics

The flow models in SuperChems Expert consider non-ideal behavior of multi-phase, reacting, and supercritical mixtures using an equation of state [4, 5, 6] with analytic derivatives. Detailed balances are solved in differential form for the vessel contents and flow through nozzles and complex piping using analytic derivatives. Phase change is also automatically detected through nozzle and piping flow. The flow models consider vapor/liquid disengagement using the DIERS coupling equation where two-phase swell is important as well a liquid entrainment due to gas/vapor sparging. The vessel flow dynamics models consider the expansion and contraction of metal due to pressure and temperature change as well, an important consideration for a liquid full vessel under external heating or high pressure depressuring.

# 4   Case Study 1 - Cold Depressuring, Single Phase Flow

High pressure nitrogen is depressured from 150 bara and 290.15 K through a flow limiting device (choke) that is 6.35 mm in diameter. No phase change is observed during the test as reported by Haque et al. [7, 8] as test I1. The vessel is a vertical cylindrical steel vessel with flat heads, 1.524 m long, 0.273 m in diameter, and has a 2.5 cm wall thickness. The vessel was immersed in stagnant air at 290.15 K to ensure equilibrium conditions before depressuring.

Figure 2 shows excellent agreement between the predicted and measured nitrogen pressure during depressuring. Figure 3 also shows excellent predictions of nitrogen temperature and wall temperature vs. measured values. We note from Figure 4 that condensation did not occur and that natural convection is predicted to dominate the heat transfer between the nitrogen and the vessel wall. The predicted wall temperature values are **average** wall temperature values while the measured values are inside wall temperature values. SuperChems calculates a maximum natural convection heat transfer coefficient value of 130 $\mathrm{W/m^2/K}$. A slightly lower heat transfer coefficient value would have yielded a higher vessel wall temperature and a lower gas temperature.

5   Case Study 2 - Cold Depressuring, Retrograde Flow

This case study is the simulation of another experiment, test I7, performed by Haque et al. [7, 8]. The same test conditions apply as in case study 1 test I1 except the nitrogen is mixed with carbon dioxide (70 mole % nitrogen and 30 mole % carbon dioxide). Measured pressure data was not provided but is expected to be similar to the that of test I1. This is confirmed by the SuperChems Expert simulation. Data for fluid temperatures were provided by [7, 8]. The wall temperature for the gas space is measured while the wall temperature for the liquid space is predicted by [7, 8] and is consistent with their measured liquid temperatures.

Figure 2: Calculated vs. measured nitrogen pressure for Test I1
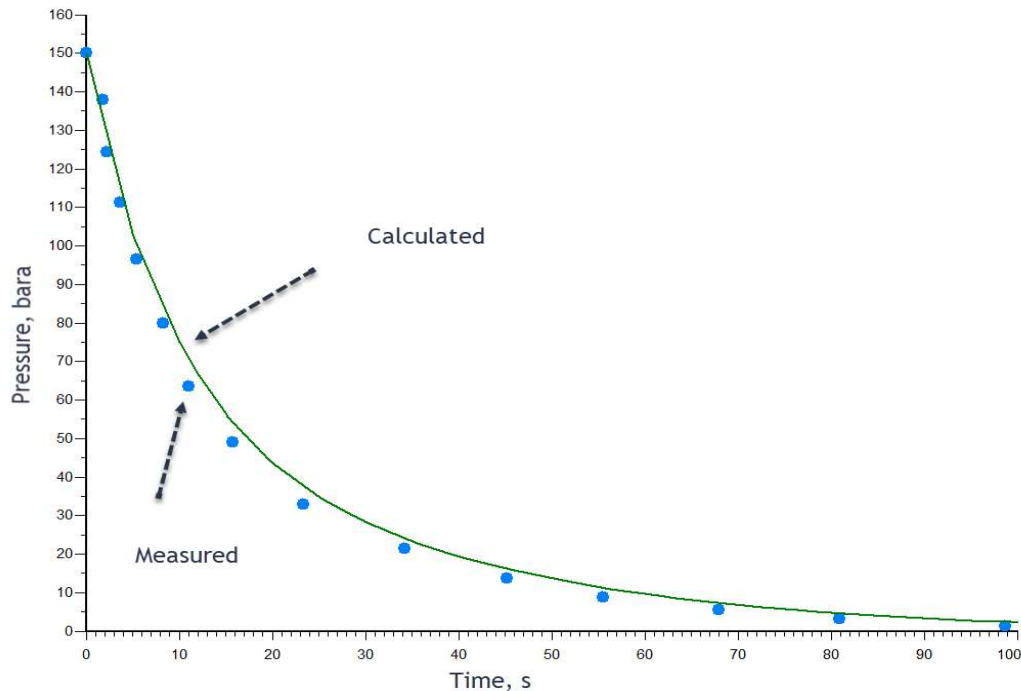
As shown by Figure 5 a small amount of liquid is predicted to form as the pressure crosses the two-phase envelop. SuperChems Expert predicts a liquid level of 0.02 m which occupies the bottom wall zone. The vessel wall was divided into 30 zones in order to capture all the condensed liquid. Where the rate of pressure drop is high enough, it is possible for a delay to occur after the pressure crosses the two-phase envelope in order to allow sufficient time for the condensation process to take place. However, the formation of liquid has to occur if the pressure crossed the limit of mechanical stability without delay.

Test I7 is interesting because the reported measured gas temperature drops below the triple point of carbon dioxide leading to the conclusion that carbon dioxide crystals may have been formed and influenced the fluid-wall heat transfer [2]. This is shown in Figure 6. The wall temperature predictions for the bottom wall zone and the top wall zones are shown in Figure 7. The predictions of wall temperatures in the vapor space are lower than what is measured.

6   Case Study 3 - Cold Depressuring, Retrograde Flow

This case study illustrates the observed behavior of depressuring a large vessel where a small amount of liquid is formed during the pressure reduction process as the pressure crosses the retrograde region of the phase envelope. The depressuring dynamics were modeled using SuperChems Enterprise v8.4 and the actual test data was published by Haque et al. [7, 8].

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[2] An upper bound of $1,000 \mathrm{W/m^2/K}$ was specified in the simulation for the wall-liquid heat transfer coefficient

Figure 3: Calculated vs. measured nitrogen and wall temperatures for Test I1
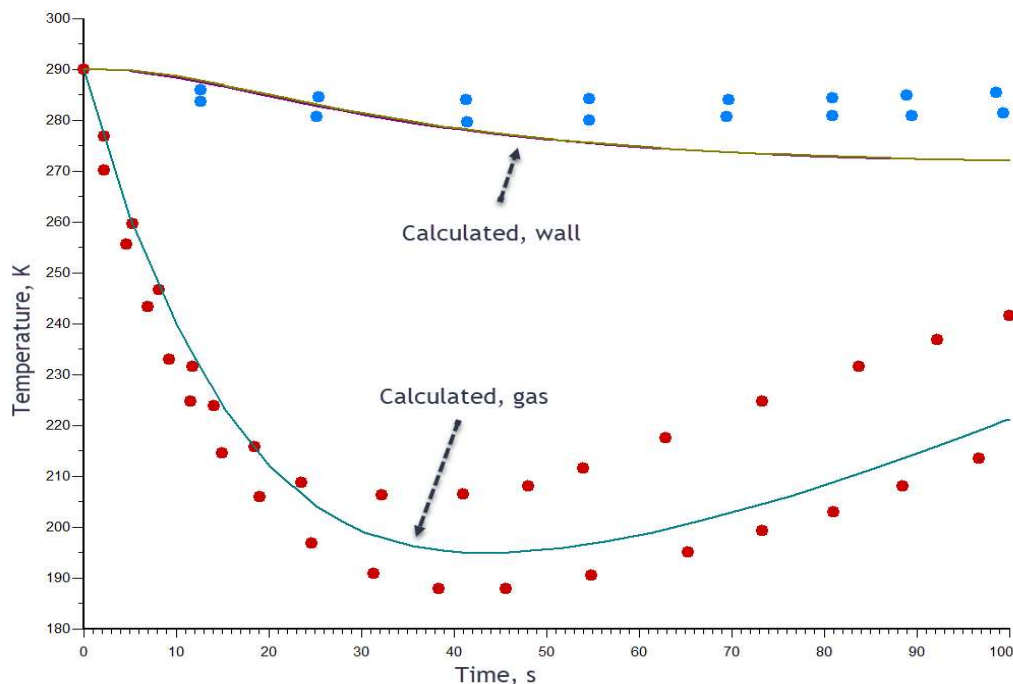
The equipment used is a vertical cylindrical vessel with torisperical heads with a total length of 3.240 m (2.250 tan to tan), an inside diameter of 1.130 m, and a wall thickness of 59 mm. This case study was identified as experiment S9 by Haque et al. [7, 8]. A mixture of 85.5 mole % methane, 4.5 mole % ethane, and 10 mole % propane was vented from the top of the vessel through a 10 mm equivalent diameter flow device. The starting pressure was 120 bara and the starting temperature was approximately 295 K.

Figure 8 shows the SuperChems predictions of fluid pressure/temperature overlayed on the phase envelope of the initial methane/ethane/propane mixture. We note that the pressure drops isentropically and then crosses the phase envelope near the cricondontherm. Two phase condensation occurs in the vessel but the SuperChems dynamic simulation continues to predict all vapor flow entering the flow device according the to DIERS coupling equation with the churn-turbulent vapor-liquid disengagement model.

The observed formation of liquid starts after approximately 100 seconds of flow. Approximately 0.1 m of liquid pooled in the bottom of the vessel. The SuperChems flow dynamics predict a maximum of 0.12 m of liquid formed and the start of liquid formation at 120 seconds approximately. This is shown in Figure 9. The agreement is excellent considering the uncertainties associated with heat transfer [3] between the vessel inner wall and vessel contents.

The pressure predictions are shown in Figure 10 and excellent agreement is predicted. We note that, in general, pressure predictions are less sensitive to uncertainties in the wall/fluid overall heat transfer coefficients. The vessel is divided into 50 sections in the SuperChems simulations.

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[3]An upper bound of $75\mathrm{W/m^2/K}$ was specified in the simulation for the wall-vapor heat transfer coefficient

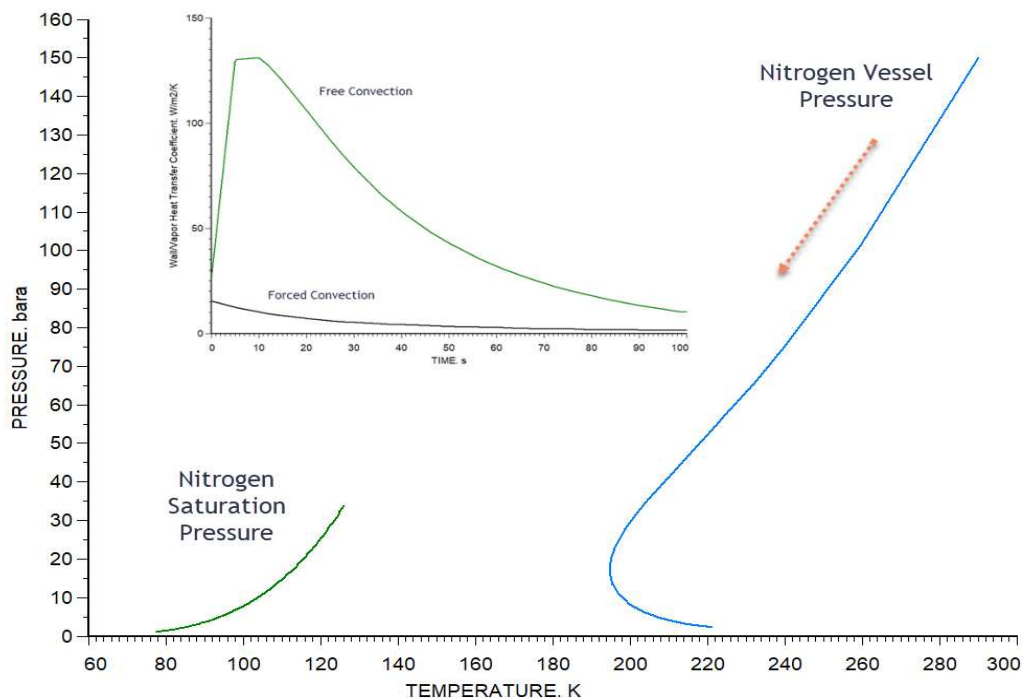Figure 4: Calculated P/T Path for Test I1

Figure 11 shows the predicted vapor fluid temperatures vs. the actual upper and lower bounds of measured values. The measured gas values show some stratification in the vapor space of the vessel because of the poor heat transfer between the inner vessel wall surface and the vapor.

Figure 12 shows the SuperChems predictions for **average** wall temperatures for the bottom and top sections of the vessel. These wall temperatures are compared to the actual measured inside wall temperatures reported by Haque et al. [7, 8] Reasonable agreement is achieved considering that the SuperChems predictions are average values and not inside surface wall temperature values.

7   Case Study 4 - Cold Depressuring, Retrograde Flow

In this case study we simulate another depressuring test reported by Haque et al. [7, 8] where the test data was reported as S12. The same vessel and flow device are reported to be used in S12 as in test S9. The composition of the vapor is changed to include more propane, 66.5 mole % methane, 3.5 mole % ethane, and 30 mole % propane. The increase in propane should and did cause the condensation of more liquid in the vessel and also changes the phase envelope of the mixture.

Figure 13 shows the SuperChems predictions of fluid pressure/temperature superimposed over the phase envelope of the initial methane/ethane/propane mixture. We note that the pressure drops quickly and then crosses the phase envelope near the critical point. Two phase condensation occurs in the vessel but the SuperChems dynamic simulation continues to predict all vapor flow entering the flow device according the to DIERS coupling equation with the churn-turbulent vapor-liquid

Figure 5: Superimposed P/T path over initial N_2/CO_2 mixture phase envelope for Test I7
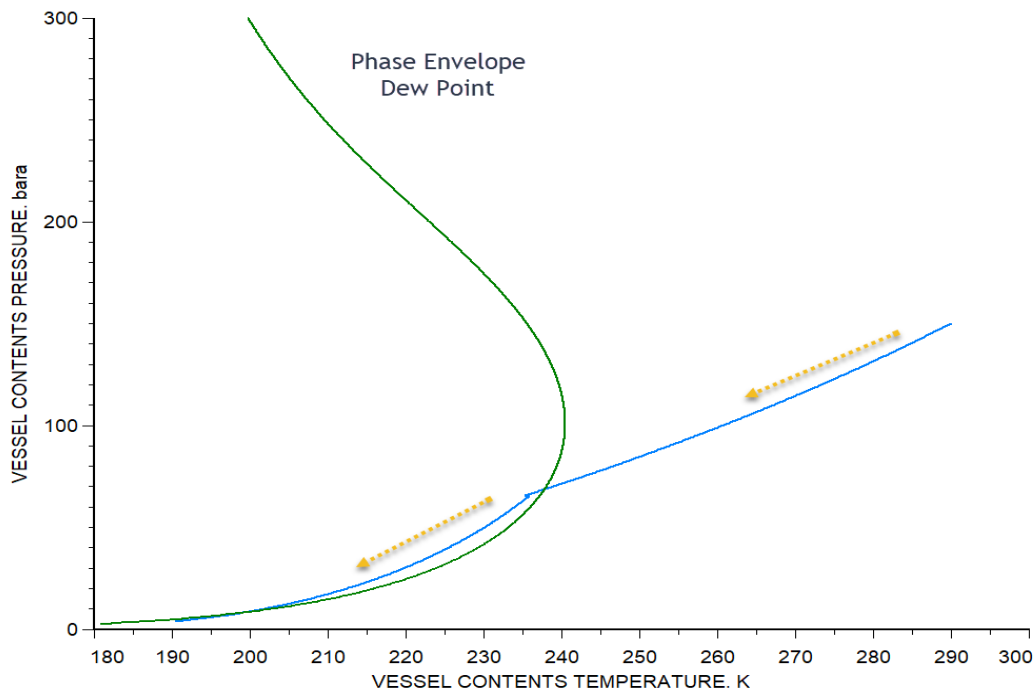

disengagement model. More liquid is formed in Test S12 than in test S9 due to the presence of more propane as evidenced by the P/T path inside the phase envelope. In this particular case SuperChems predicts a maximum liquid level of approximately 2.1 m at 15 seconds while the maximum liquid level reported by Haque et al. [7, 8] is 1.9 m (see Figure 15).

The pressure predictions are shown in Figure 14 and excellent agreement is predicted. As before, we note that, in general, pressure predictions are less sensitive to uncertainties in the wall/fluid overall heat transfer coefficients. The vessel is also divided in 30 sections in the SuperChems simulations and default SuperChems heat transfer correlation values of the wall-vapor and wall-liquid heat transfer coefficients are used.

Figure 16 shows the predicted vapor fluid temperatures vs. the actual upper and lower bounds of measured values. The measured gas values show some stratification in the vapor space of the vessel because of the poor heat transfer between the inner vessel wall surface and the vapor.

Figure 17 shows the SuperChems predictions for **average** wall temperatures for the bottom and top sections of the vessel. These wall temperatures are compared to the actual measured inside wall temperatures reported by Haque et al. [7, 8] Reasonable agreement is achieved considering that the SuperChems predictions are average values and not inside surface wall temperature values.

Figure 6: Calculated vs. measured fluid temperature for Test I7
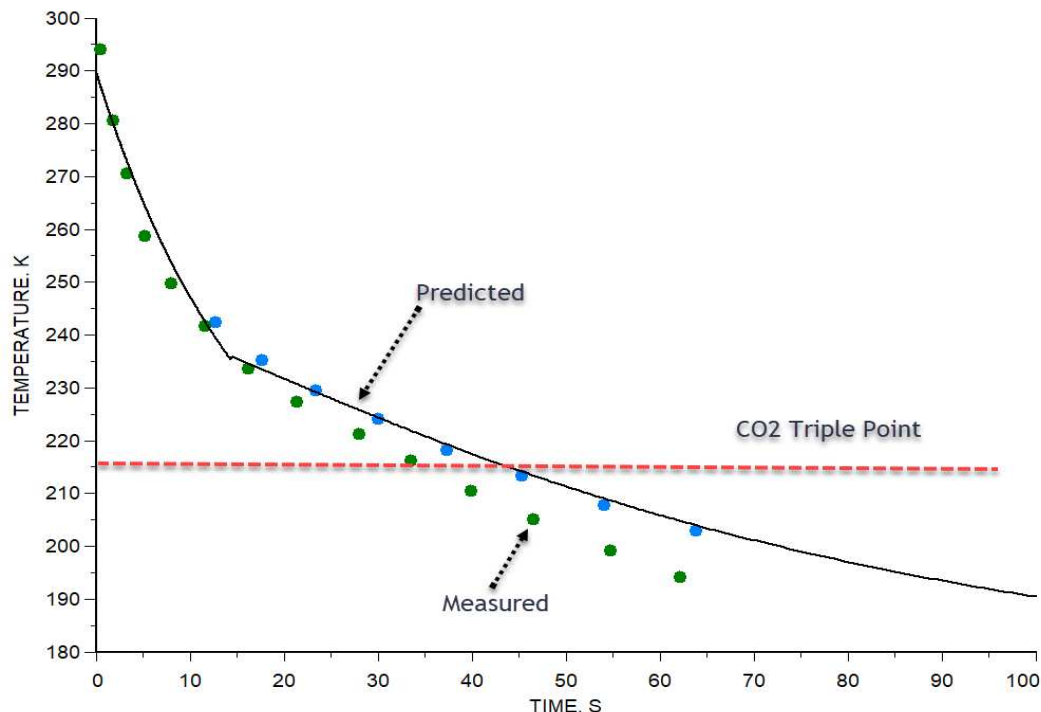
8   Case Study 5 - Fire Exposure, Vessel Failure

In this case study we simulate an actual large scale fire exposure test (fuel oil fire) conducted by the German federal institute for materials research (BAM) [9] on LPG storage vessels. The simulations were conducted using the built-in default SuperChems heat transfer correlations and fire characteristics. The vessel is a large horizontal cylindrical vessel (4.85 m^3 total volume) with a shell wall metal thickness of 6.4 mm and heads metal thickness of 6.8mm. The vessel is constructed from StE 36 unalloyed fine grained steel and is fitted with a 1 inch PSV set at 15.6 barg (capacity of 64 m^3/min air at STP). The test in question is Test 2 referenced in [9]. The vessel was 50 % liquid full of commercial grade propane. The authors report that the vessel was not fully engulfed and only surrounded by the fire. We assumed that the entire vessel is visible to the fire and only half the zones (vessel was segmented into 15 zones for the simulations) were engulfed by the fire. Data pertaining to the actual test is shown in Table 1. The primary objective of this complex simulation is to verify the wall temperature predictions, failure pressure, and time to failure under fire exposure.

The composition of commercial propane is mostly propane and propylene. Figure 18 illustrates the predicted values of P/T vs. measured values of P/T. The presence of small fractions of butanes could have made the agreement much better because it would depress the vapor pressure at the same temperature.

Figure 19 compares the pressure history predictions with the measured data. Reasonable agreement is obtained. SuperChems predicts the correct PSV opening time and pressure. The reported test

Figure 7: Calculated vs. measured wall temperatures for Test I7
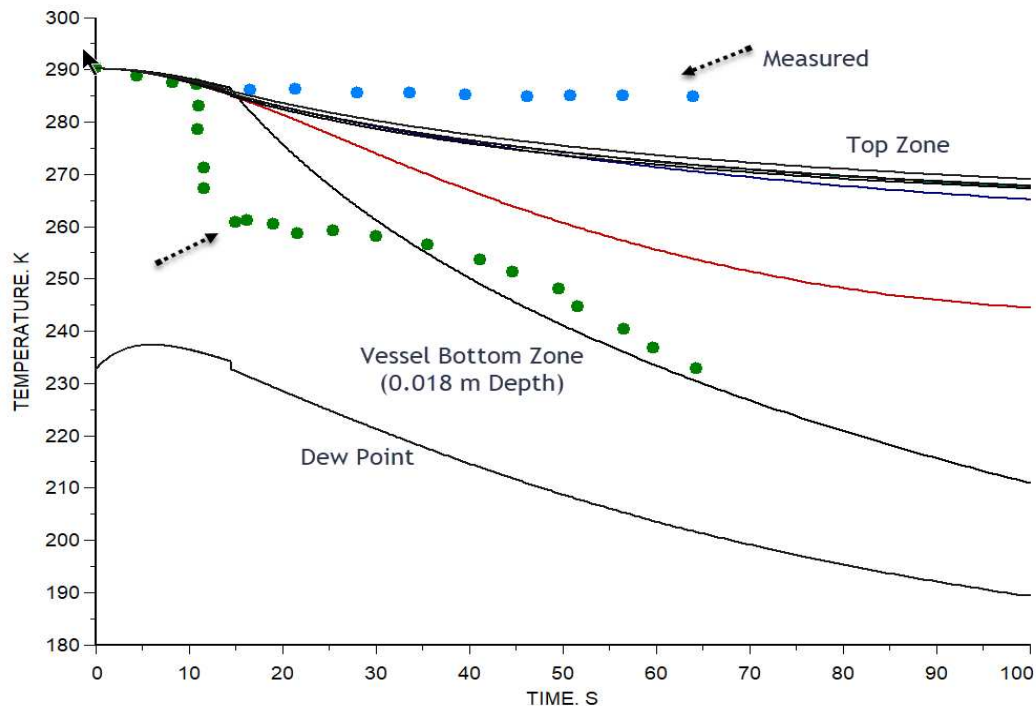
data did not provide a lot of details on the actual PSV other than its reported discharge capacity at NTP of 64 m^3/min. This data was used by SuperChems to specify the size of the PSV.

Figure 20 provides a comparison of SuperChems predictions of average wall temperatures vs. reported maximum external wall temperatures. We would expect the average wall temperatures to be lower as is shown by Figure 20.

Finally, Figure 21 shows the calculated stress due to internal pressure by SuperChems vs. the ultimate tensile strength estimates as a function of average wall temperatures based on the steel type provided in the original test data. The predictions show the internal stress approaching the ultimate tensile strength at approximately 5.3 min. This would be normally used as a failure point prediction due to uncertainties associated with metal strength and the wall temperature predictions. However, even if this was not used as the failure point, Figure 21 shows that the vessel would ultimately fail at the reset pressure of the PSV due to loss of liquid level caused be vapor venting and the substantial increase in wall temperature in the vapor space.

9   Case Study 6 - Fire Exposure, Liquid Full Vessel

Many practical scenarios in overpressure protection require the evaluation of pressure relief for initially liquid full vessels or vessels that become liquid full during relief due to excessive inflow of liquid, liquid swell due fire exposure, and/or liquid swell due to chemical reaction. Because most liquids are slightly compressible, the vessel metal will typically stretch due to rapid pressure

Figure 8: Superimposed P/T path over initial methane/ethane/propane mixture phase envelope for Test S9
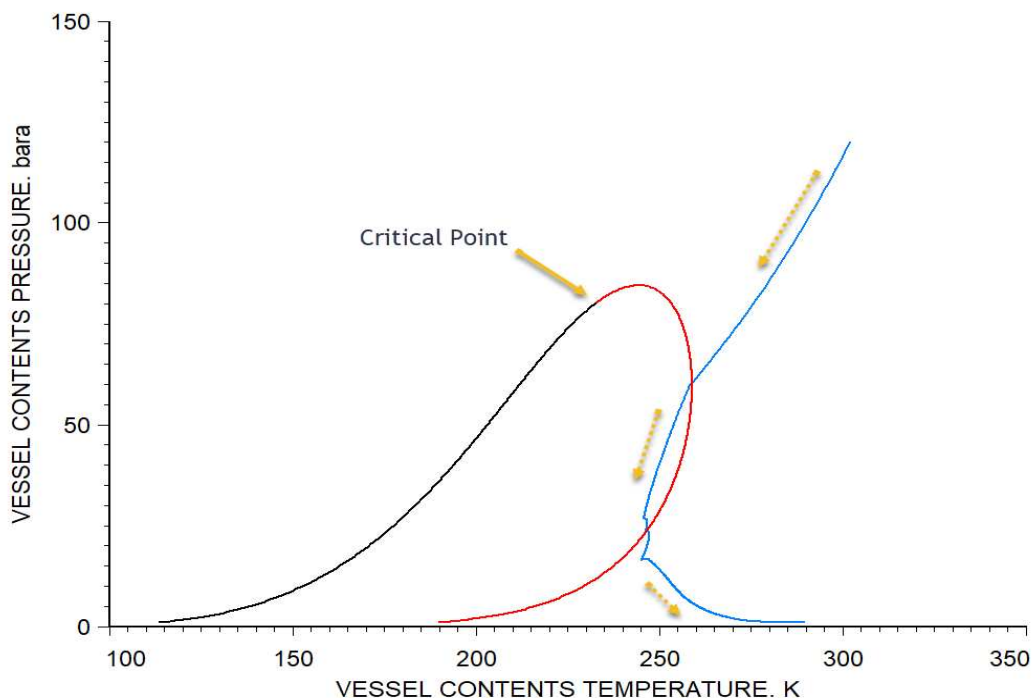

increase or thermal expansion or both. Similarly, the vessel metal will contract upon cooling or decrease in internal pressure.

SuperChems Expert enables calculations for initially liquid full (or vapor full) vessels or vessels that become liquid full (or vapor full) during the relief transient. Figure 22 illustrates the relief transient of a vessel under fire exposure that is initially liquid full where the liquid is a subcooled mixture of 40 % by weight vinyl acetate and 60 % by weight ethylene. The vessel remains liquid full until the rupture disk protecting the vessel bursts leading to initially subcooled liquid flow, followed by flashing flow, followed by all vapor flow after the pressure crosses the two-phase envelope a second time.

10   Case Study 7 - Fire Exposure, Two-Phase to Supercritical Conditions

SuperChems Expert also allows for RPC conditions that result in supercritical flow. This is illustrate in Figure 23. This vessel contains a 50/50 by weight mixture of C_2/C_7 under fire exposure. It is protected from overpressure by a pressure relief valve. The flow conditions transition into supercritical conditions with ease. Ultimately, if the fire exposure is long enough, the vessel will fail at the reset point of the pressure relief valve as shown earlier in case study 5.

Figure 9: SuperChems liquid level predictions for Test S9
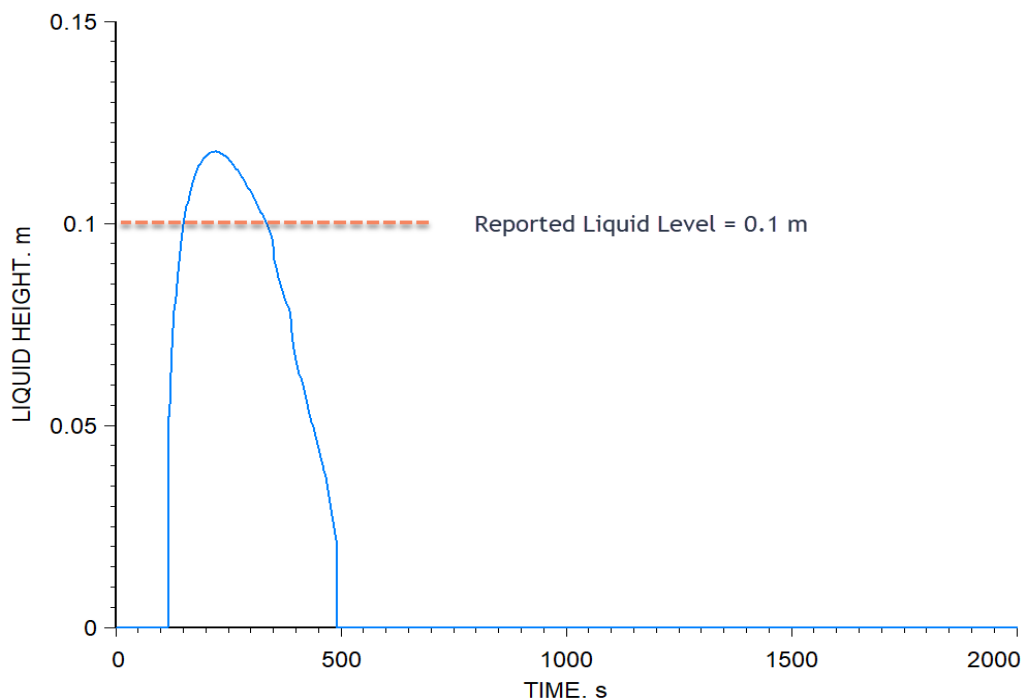
11 Conclusions

This paper demonstrates that the general vessel flow dynamics models available in SuperChems Expert can provide accurate data for the design and evaluation of relief and depressuring systems during fire exposure, liquid full, and/or retrograde and phase change conditions. Predictions of best value estimates for minimum and maximum wall/fluid temperatures, liquid or hydrate formation, time to failure due to brittle fracture, overpressure, and/or overtemperature are possible. This information can be obtained quickly and easily for more informed risk reduction and mitigation strategies. Depending on the system considered and study objectives, one can also define simulation parameters that can bias the predictions to enable the selection of conservative estimates instead of best value estimates of temperatures, liquid levels, and/or relief requirements.

12 Attachments

SuperChems Expert project files RPC-1, RPC-2, and RPC-3 are provided to enable users to reproduce all the case studies and benchmarks described in this paper.

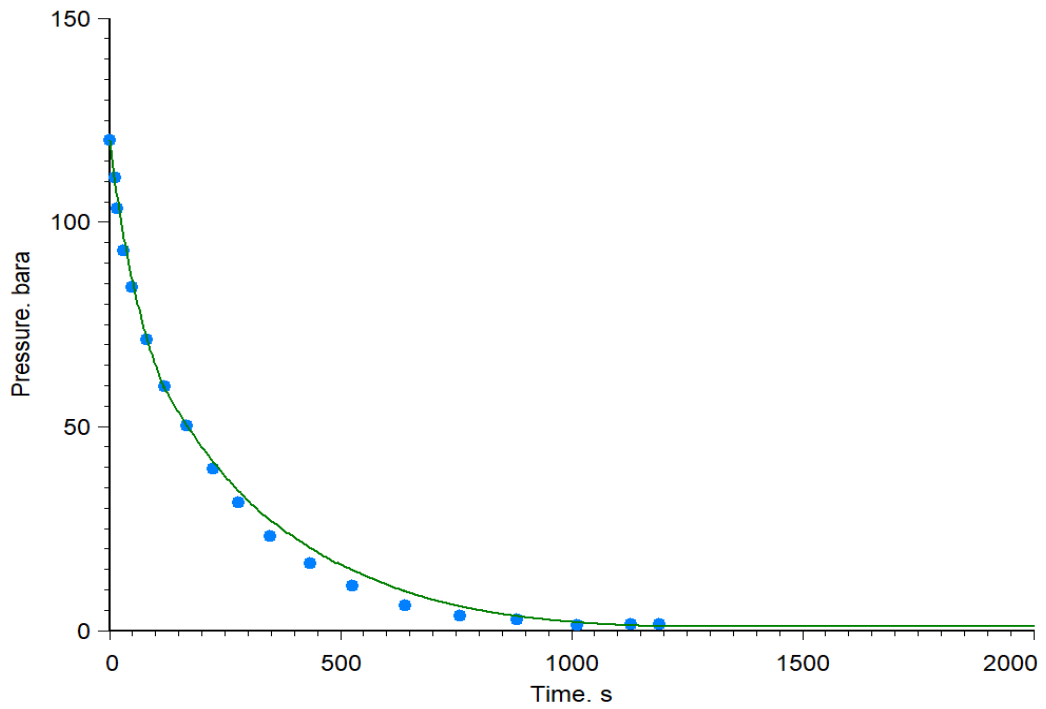Figure 10: SuperChems pressure predictions for Test S9

Figure 11: SuperChems fluid contents temperature predictions for Test S9
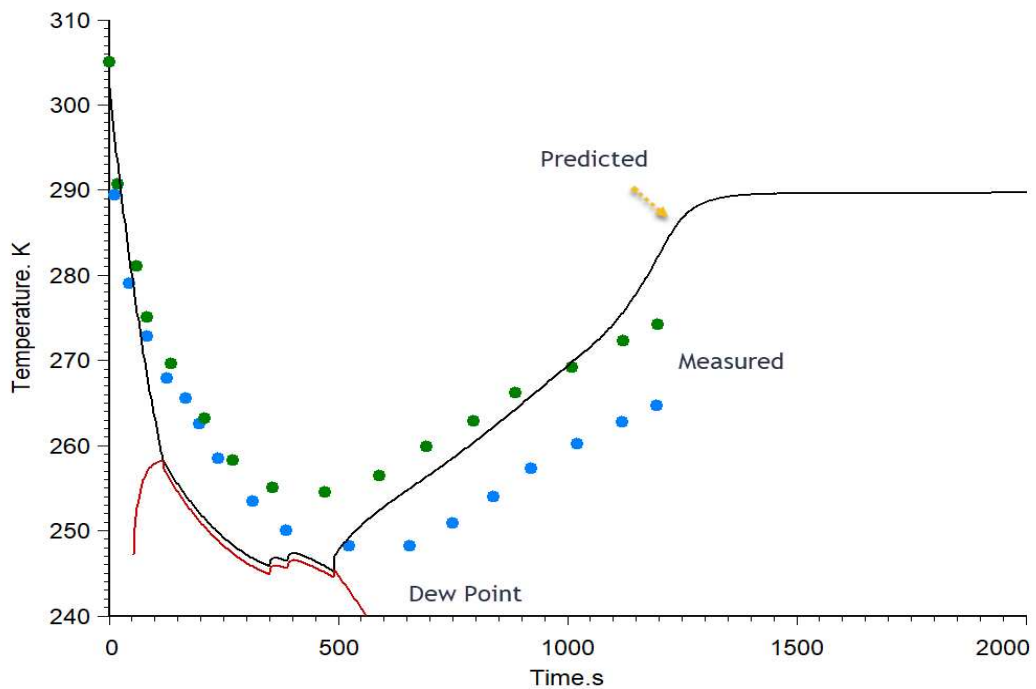
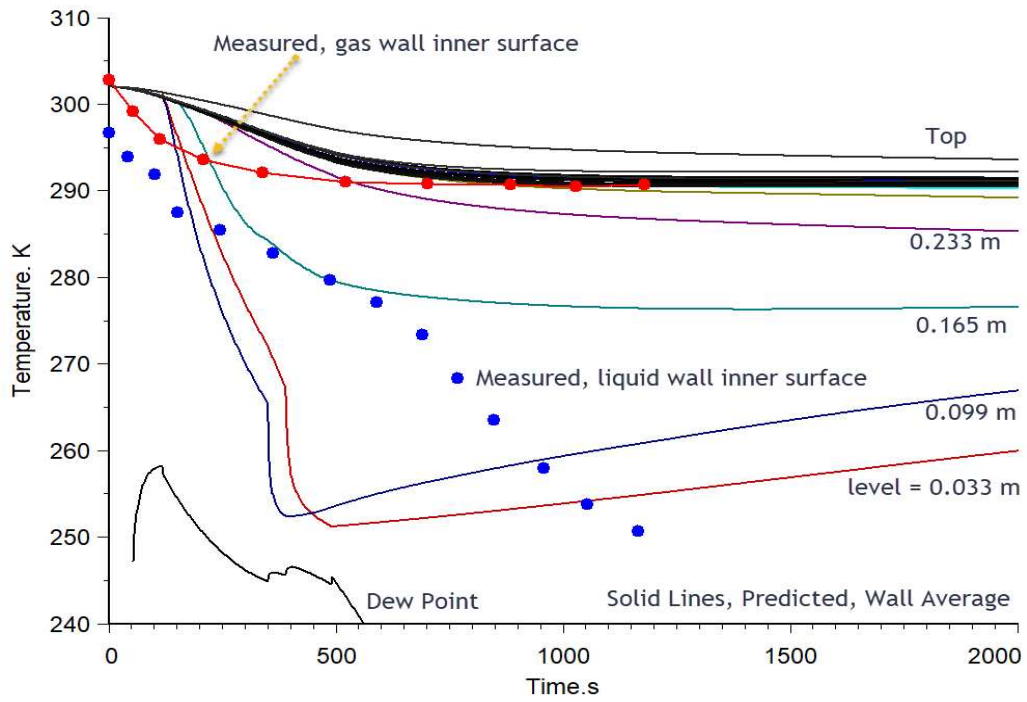Figure 12: SuperChems vessel wall temperature predictions for Test S9

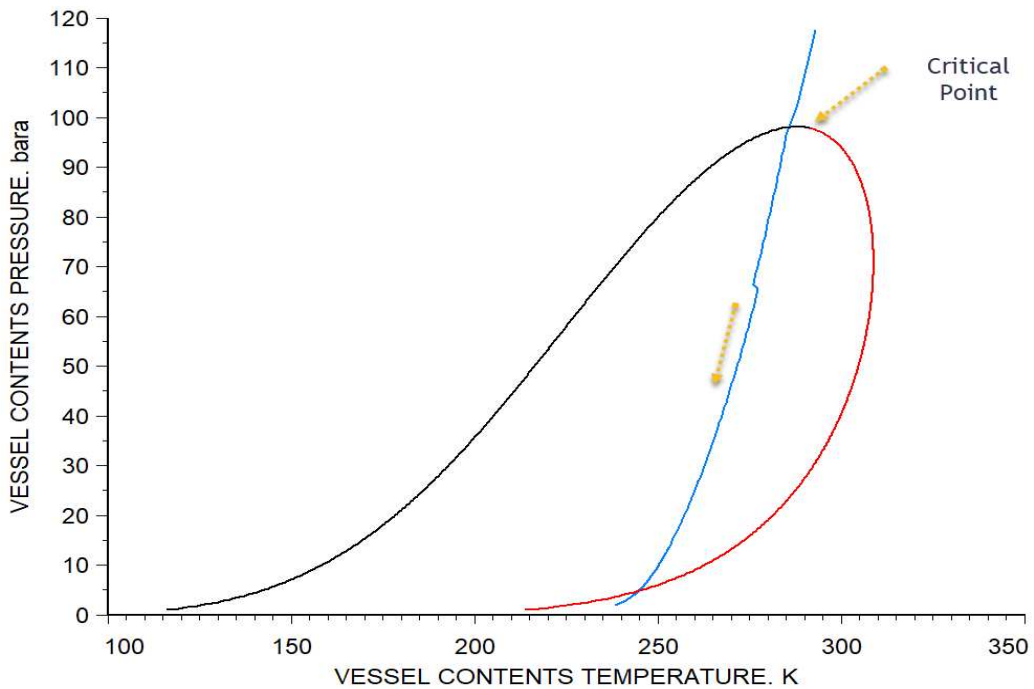Figure 13: Superimposed P/T path over initial methane/ethane/propane mixture phase envelope for Test S12

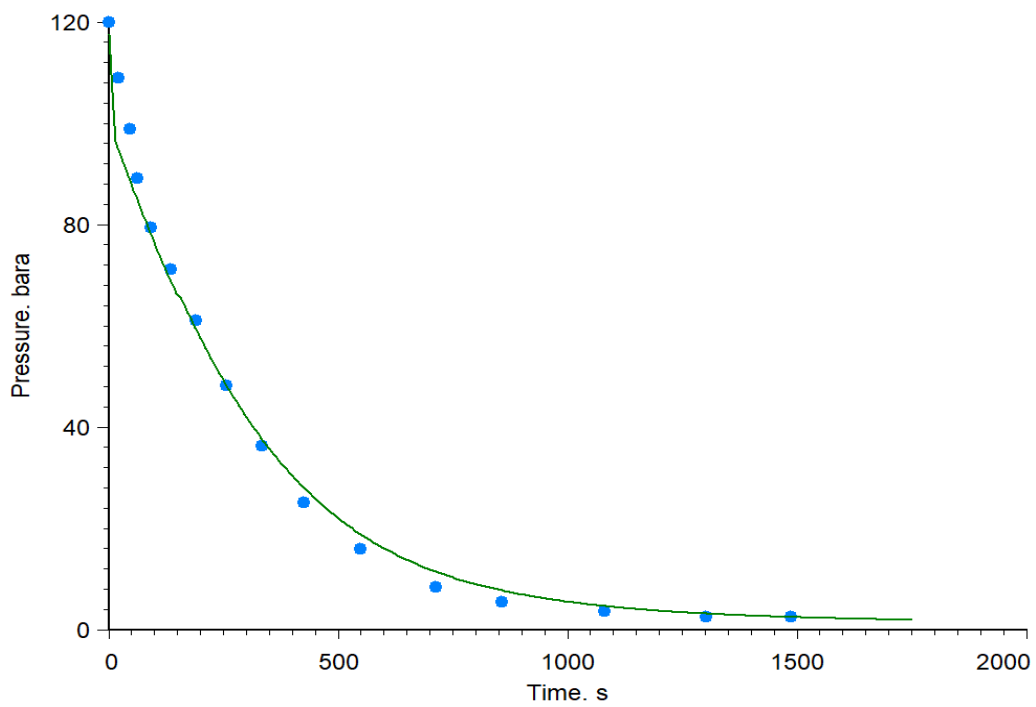Figure 14: SuperChems pressure predictions for Test S12

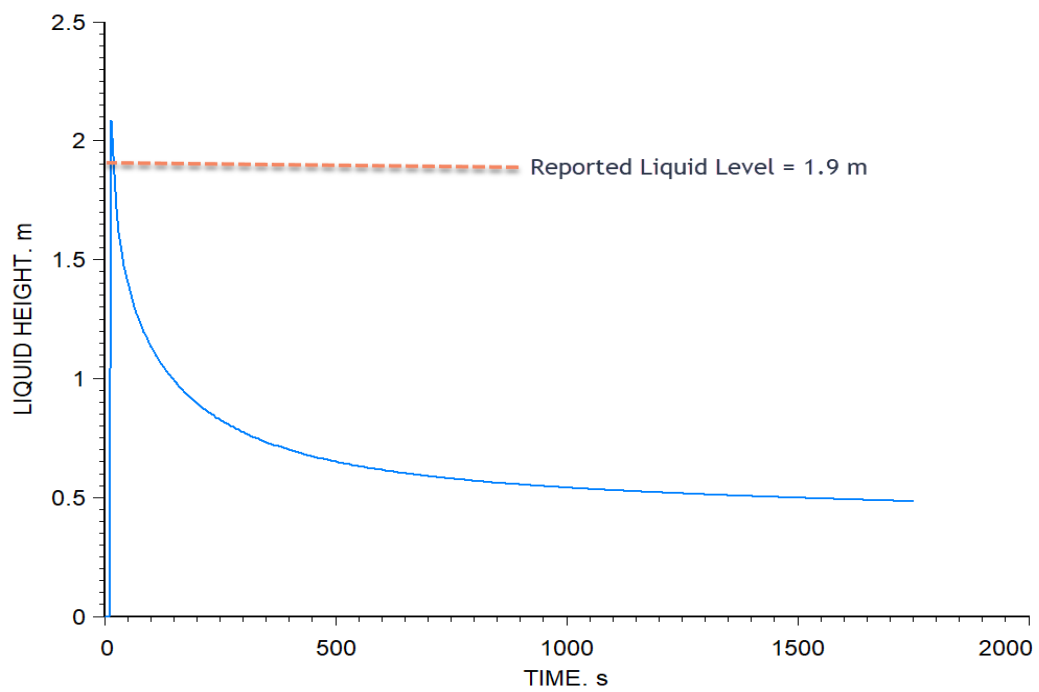Figure 15: SuperChems liquid level predictions for Test S12

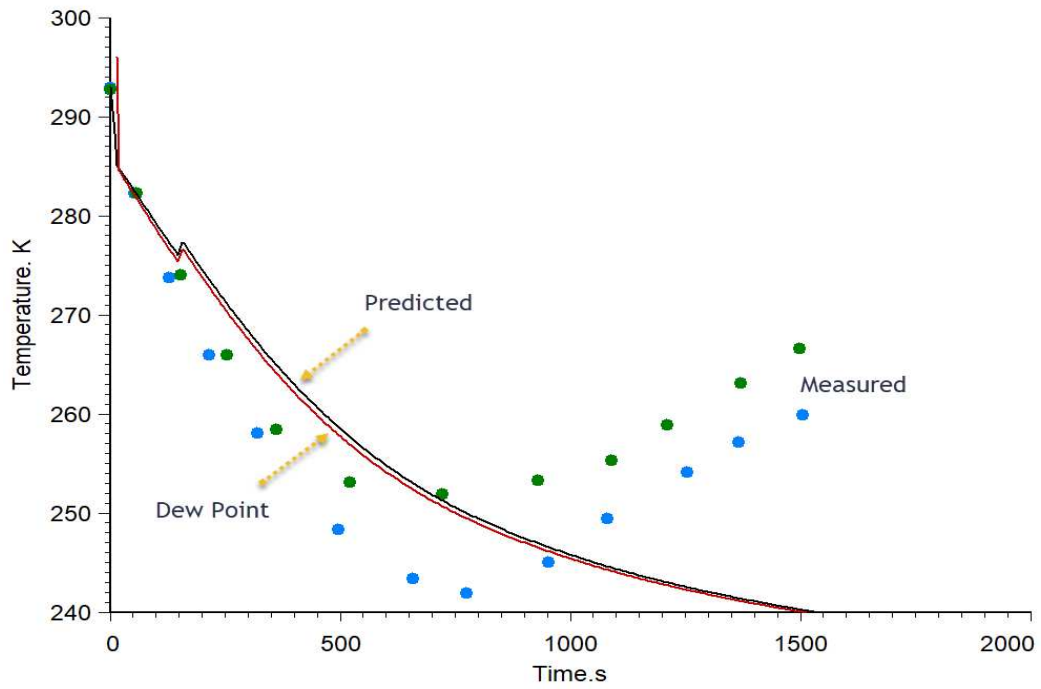Figure 16: SuperChems fluid contents temperature predictions for Test S12

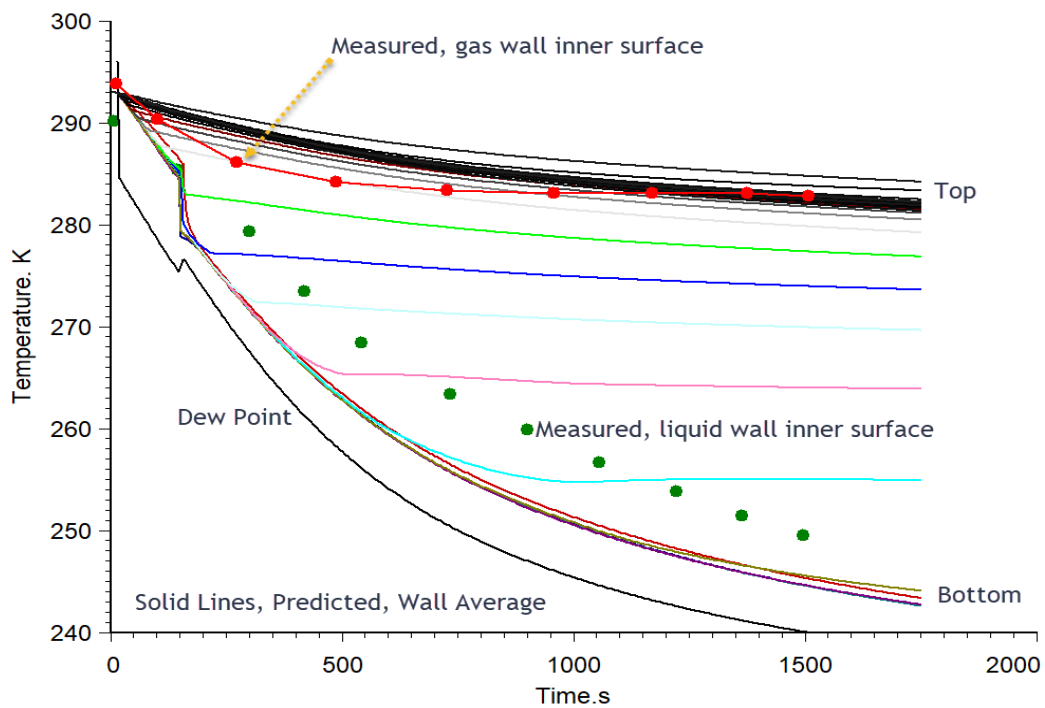Figure 17: SuperChems vessel wall temperature predictions for Test S12

Table 1: BAM fire exposure Test 2 conditions

Conditions	Actual	Predicted
Ambient temperature, C	2	
Propane temperature prior to testing, C	37	41
propane pressure prior to testing, bara	14.5	14.7
Time to start of PSV discharge, min	2.41	1.54
Start of discharge of PSV, bara	18.3	18.2
Time to vessel failure, min	8.1	5.3 to 8.4
Liquid propane temperature when rupture occurs, C	84 - 87	93 - 105
Rupture pressure, bara	40	43.5
Top outer wall temperature at rupture time, C	420	
Outer wall temperature at the vapor space at 45 degree position at rupture time, C	300	
Outer wall temperature at the liquid space at rupture time, C	90	

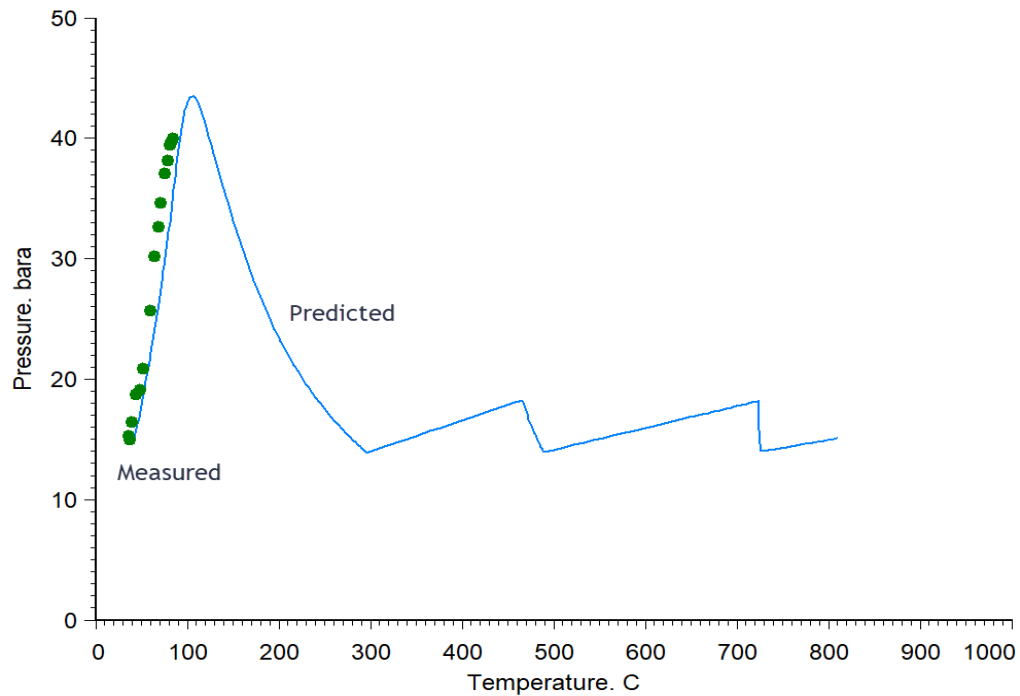Figure 18: Calculated vs. measured P/T for BAM Test 2

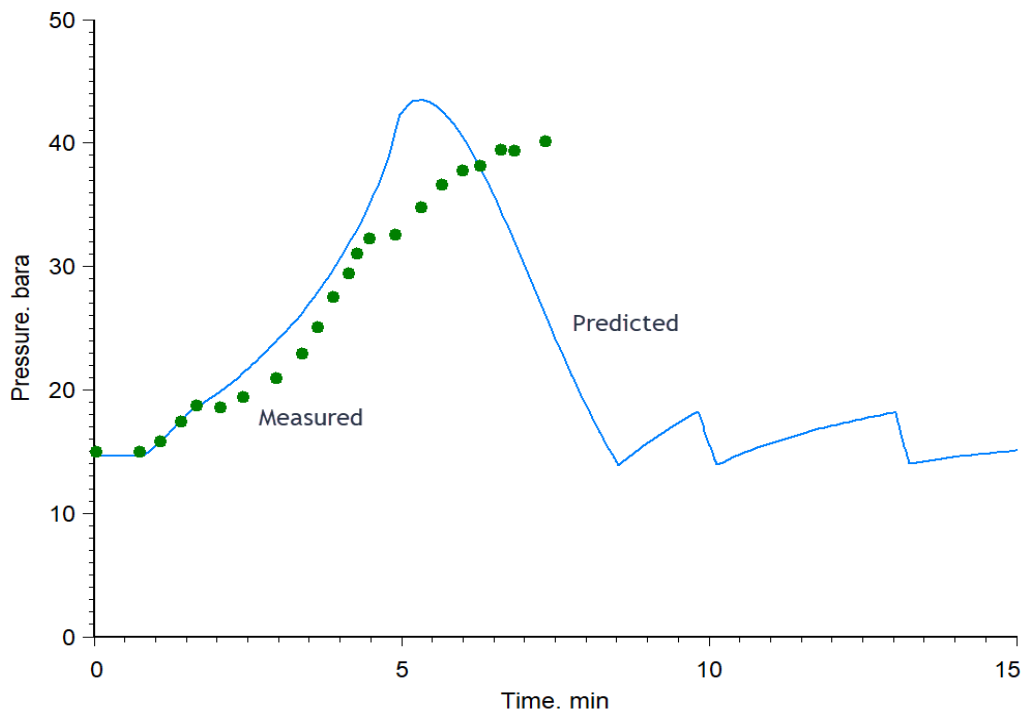Figure 19: Calculated vs. measured pressure history for BAM Test 2

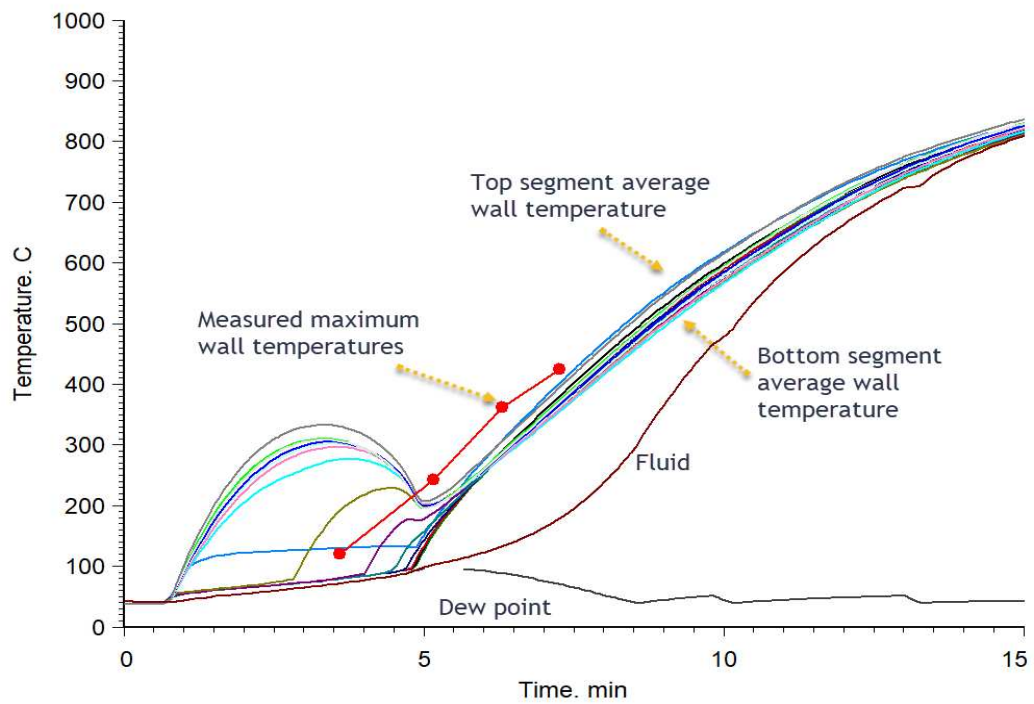Figure 20: Calculated vs. measured wall temperatures for BAM Test 2

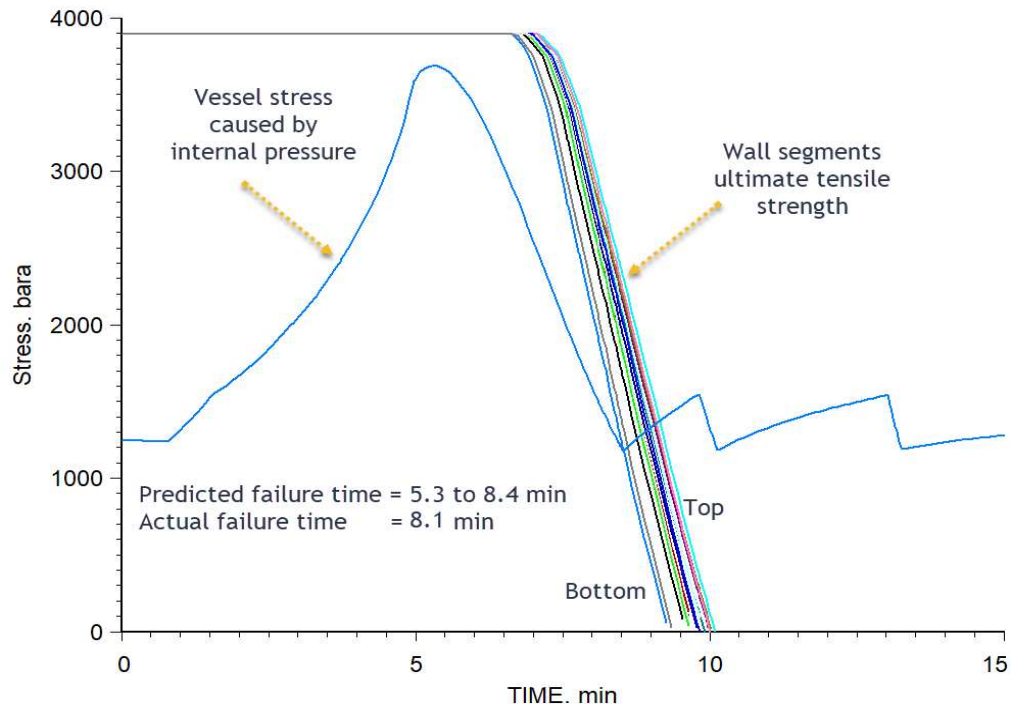Figure 21: Calculated vs. measured failure time for BAM Test 2

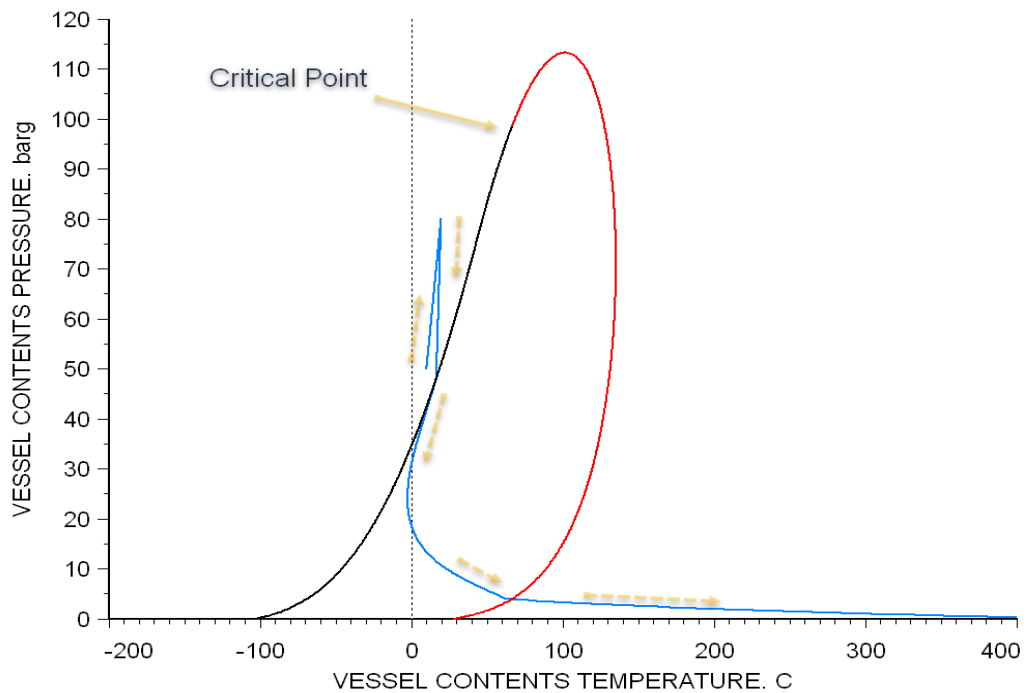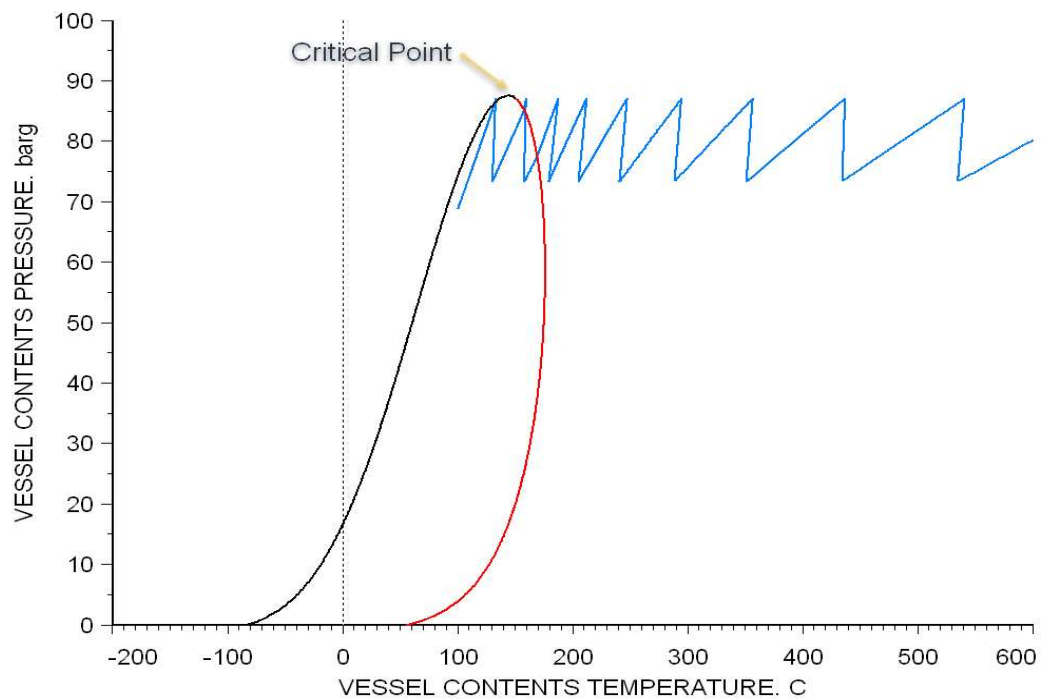Figure 22: Calculated relief transient for an initially liquid full vessel under fire exposure

Figure 23: Calculated relief transient for an initially two-phase vessel under fire exposure that reaches supercritical conditions

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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).

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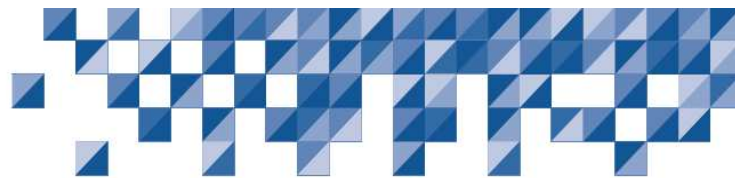E-mail. melhem@iomosaic.com

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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.

ioMosaic is an integrated process safety and risk management consulting firm focused on helping you manage and reduce episodic risk. Because when safety, efficiency, and compliance are improved, you can sleep better at night. Our over 300 years of combined industry expertise allow 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. For more information on ioMosaic, please visit: **www.ioMosaic.com**.

Consulting Services

- Auditing and Due Diligence
- Chemical reactivity management
- Combustible dust hazard analysis (DHA) and testing
- Due diligence support
- Effluent handling design
- Pressure relief and flare systems design
- Facility siting
- Fault Tree/SIL/SIS Analysis
- Fire and explosion dynamics
- Incident investigation, litigation support, and expert testimony
- Liquefied natural gas (LNG) safety
- Pipeline safety
- Process engineering design and support
- Process hazard analysis (PHA)
- Process safety management (PSM)
- Quantitative risk assessment (QRA)
- Risk management program development
- Structural dynamics
- Training

Laboratory Testing Services

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

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