PROCESS SAFETY PROGRESS

AN OVERVIEW OF SUPERCHEMS FOR DIERS: A PROGRAM FOR EMERGENCY RELIEF SYSTEM AND EFFLUENT HANDLING DESIGNS

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The Design Institute for Emergency Relief Systems (DI-ERS) Users Group awarded Arthur D. Little, Inc., a contract to provide the next generation computer program for emergency relief system and effluent handling designs.

The new computer program, SuperChems for DIERS, is a dynamic simulator, capable of performing emergency relief system and effluent handling designs for complex geometries and multiphase reaction systems. In addition, SuperChems for DIERS is an equation-of-state based program which provides several benefits over existing non-equation-of-state based methods for systems involving supercritical reactions like polymerizationsof butadiene and acrylonitrile, solution effects such as HCl/Water, and a priori determination of phase splitting.

This new computer program allows the user to dynamically simulate several common configurations for vent containment design. For example, the user is able to simulate a vessel discharging a two-phase mixture into a quench/vent where the catch/vent tank will vent to a stack or a scrubber. Unit operations available include separators (horizontal and vertical), cyclones, etc. The impact of back pressure and continuing reaction in the vent containment system is accounted for in the dynamic simulations.

BACKGROUND

During the 1st quarter of 1996, the Design Institute for Emergency Relief Systems (DIERS) Users Group awarded Arthur D. Little, Inc. a contract to provide the next generation computer program for emergency relief system and effluent handling designs. Highlights of the new computer program as outlined in the request for proposal are summarized below:

1. Provide a general purpose thermodynamic and transport properties generator with implicit corrections for non-ideal behavior in both the liquid and vapor phase. The properties generator should also be able to provide temperature and pressure dependent derivatives for all properties of interest. The generator should be detailed enough so that heat of solution effects and vapor-liquid non-ideal equilibrium are implicit. This generator should also be able to provide all properties and all derivatives required by the computer models. The generator should be equation of state (EOS) based.

2. Create/design an interface allowing the properties generators to access a thermophysical properties database so that properties do not have to be manually added. A databank manager should be provided in order to allow the users to input/modify their own compounds, if needed.

3. Revise all flow models such that the new computer program will address the following items:
   (a) inclined flow
   (b) subcooled flow
   (c) sudden expansion/contraction
   (d) piping segments with varying diameter and orientation
   (e) viscous two-phase flow through safety relief valves and pipes
   (f) continuing chemical reaction in piping and vent containment systems
   (g) detailed energy balances for vessels and piping
   (h) detailed momentum balance for piping
   (i) implicit vapor-liquid equilibrium relations
   (j) the flow models and the vessel balances should be equation oriented.

4. Provide a suitable stiff differential/algebraic (DAE) equation-solver. Proposed schemes should include Gear's or Michelsen's methods.

5. Provide a user-friendly menu-driven interface including graphics plotting capabilities and report generation.

6. Provide required documentation including an Operations Guide, a Users Guide, and a Reference Manual.

7. Validate all new models using experimental data, where available.

Arthur D. Little Inc. (ADL) had already developed a computer program which contained all the above specifications. This program took about five years to develop and is known as SuperChems Expert Version 3. The emergency relief system design portion of SuperChems was customized for the DIERS Users Group and is available for sale from the American Institute of Chemical Engineers (AIChE).

SuperChems for DIERS is an equation-of-state based program which provides several benefits over existing non-equation-of-state based methods for emergency relief system design for systems involving:

1. Reactions with supercritical components such as polymerizations of butadiene, acrylonitrile, etc.
2. Solution effects such as HCl/Water, etc.
3. A priori determination of phase-splitting

SuperChems for DIERS contains a databank of more than 3000 binary systems with equation-of-state binary interaction parameters derived from experimental vapor-liquid and liquid-liquid data. There is also a VLE/VLLE data package. This versatile utility allows the estimation of binary interaction parameters for the equation of state composition dependent mixing rule. The source of data can be one of six data types:

1. Azeotropic data.
2. TPXY measured data (SuperChems for DIERS also includes three thermodynamic consistency utility for X and Y calculations)
3. Mutual solubility data.
4. Henry's law constants (mostly used for gas solubility in liquids)
5. Activity coefficient model parameters
6. Infinite dilution activity coefficients

SuperChems for DIERS has an extensive database with over 1200 chemicals. The database contains 39 thermophysical properties with temperature dependent properties and data quality parameters. The program also has a detailed regression package (linear/non-linear) which allows the reduction of tabular data to equation forms supported by the databanks.

COMPUTER IMPLEMENTATION

Emergency relief system design does not stop at the estimation of the size of the relief device. The effluent must be treated if it is toxic and/or flammable or if it presents an environmental impact. While homogeneous-equilibrium flow (no slip) is typically used for sizing the relief device, slip-equilibrium flow should be used to establish correct pressure drops and safety/environmental impacts.

SuperChems for DIERS is a computer program which allows the integral evaluation of relief dynamics and downstream effects. For example, using SuperChems for DIERS, we can evaluate the time dependent history of pressure, temperature and composition in a reactor vessel as the relief occurs. Simultaneously, the effluent is discharged and handled to meet established (regulatory or internal) criteria. Typically, many options are evaluated before a final design is selected. This includes separation equipment,
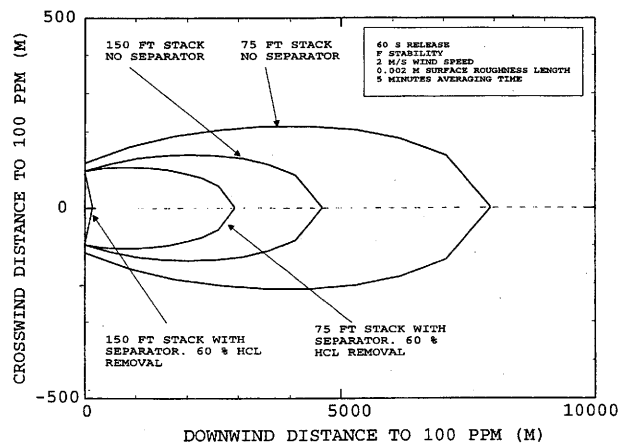
FIGURE 1 ERS/mitigation system effectiveness evaluation using SuperChems for DIERS.

flares, stacks, etc. Figure 1 illustrates the use of SuperChems for DIERS to assess various mitigation measures following an alkyl chloride/water reaction which produces hydrogen chloride.

The most useful aspect of SuperChems for DIERS is its scenario/object driven architecture. Once an object (such as a vessel or piping configuration) is defined, it can be used by one or more scenarios. Once a scenario is defined, it can be duplicated and used to perform what-if or sensitivity analysis.

The detailed algorithms for SuperChems for DIERS are published in references [1] and [2]. This paper will focus on providing examples and benchmarks for SuperChems for DIERS.

QUENCH TANK DESIGN FOR PCL3-WATER

This example deals with a 5,000 gal reactor in which phosphorus trichloride (PCl_3) is used. A scenario was identified where it is possible for a heel of phosphorus trichloride (2,700 kgs) to remain in the reactor undetected (below detection level) at 40 C, and for an operator to attempt to flush the vessel with water. This can lead to the generation of gaseous hydrogen chloride and excessive system pressure.

Water can be introduced into the reactor at the rate of 15 kg/s for 38 seconds. The reactor has a 12-inch rupture disk set at 20 psig. The effluent is discharged into a quench tank.

The quench tank has a volume of 10,000 gal and initially contains 24,000 kgs of water at ambient conditions. The process equipment is illustrated in Figure 2. The reaction rate and characteristics of $PCl_3 - H_2O$ reaction are described by Melhem and Reid in reference [3].

Figure 3 illustrates the calculated time history of pressure, temperature, and individual component flow rates for the reactor and the quench tank. Please note that both HCl and PCl_3 are discharged from the reactor and that PCl_3 reacts with the quench tank water to form phosphorous acid and HCl. One should also note that the temperature and pressure rise in the quench tank are caused primarily by the hydrogen chloride heat of solution.

FIRE EXPOSURE WITH MULTICOMPONENT VAPOR FLOW

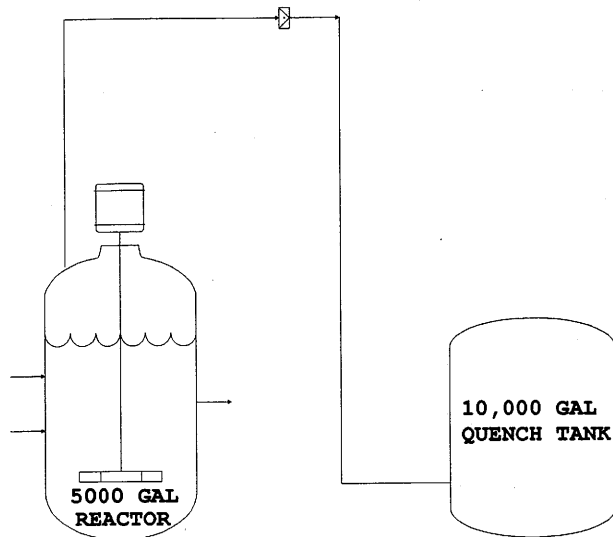The following example illustrates the use of SuperChems

FIGURE 2   A simple reactor/quench tank arrangement.

FIGURE 4   Fire loading on a vessel containing a mixture of acetone, ethanol, and water.

for DIERS to size a safety relief valve for a vessel containing a mixture of acetone, ethanol and water. Important vessel and fire exposure data are summarized in Figure 4 and Table 1. The vessel is a vertical cylinder. Vapor flow is expected. This example illustrates the types of data that can be obtained from SuperChems for DIERS.

SuperChems for DIERS is an equation of state based computer code. The equation of state is used to generate thermodynamic data as well as physical and chemical equilibrium data. Binary interaction parameters (BIPS) for non-ideal systems are either estimated from group contribution methods such as UNIFAC or estimated from experimental vapor-liquid equilibrium data. The binary interaction parameters for the system acetone, ethanol, and water were obtained from the extensive databank provided by SuperChems for DIERS and are based on experimental data. This data is summarized in Table 2. The simulation also in-
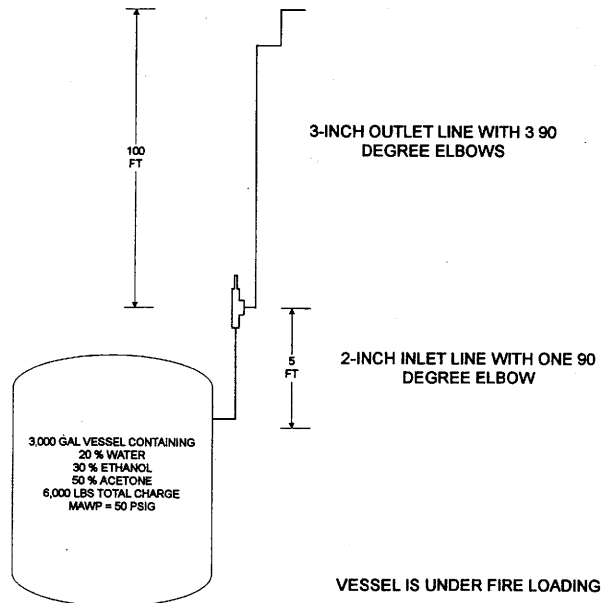
volved the use of nitrogen which was present in the vapor space prior to venting. Binary interaction parameters involving nitrogen were set to zero.

Figures 5 through 10 illustrate the results obtained using SuperChems for DIERS. Two designs using 2J3 and 2H3 conventional safety relief valves were considered. The simulation results show that the 2J3 safety relief valve is slightly oversized (saw tooth response) while the 2H3 safety relief valve produces a vessel pressure which exceeds 1.21 times the MAWP.

Four cases were considered by the computer simulation. These included:

1. 2J3 (1.287 in^2 orifice) safety relief valve with a 2-inch inlet line
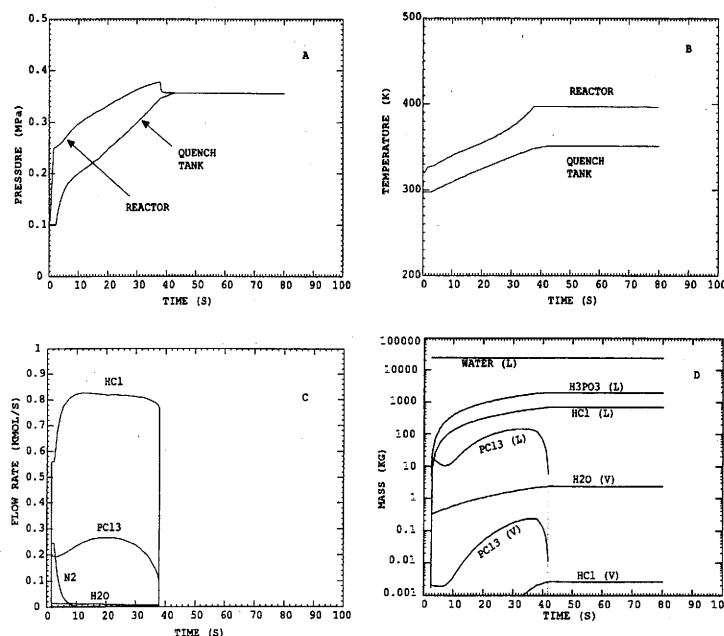

FIGURE 3   Estimated transient profiles for pressure, temperature, mass and flow rate using SuperChems for the PCL3-water quench tank design problem.

TABLE 1. Vessel and Fire Exposure Data

Vessel total charge (kg)	2,722 (6,000 lbs)
Vessel weight fraction water	20%
Vessel weight fraction ethanol	30%
Vessel weight fraction acetone	50%
Vessel metal weight (kg)	2,264
Vessel MAWP (psig)	50
Vessel 1.21 MAWP (psia)	75.2
Vessel type	Vertical cylindrical
Vessel volume (m^3)	11.355
Vessel diameter (m)	2.13
Vessel total surface area (m^2)	28.45
Fire protection	Approved drainage and insulation
Valve type	Conventional, Kd = 0.864
Valve set pressure (psig)	50
Valve piping	2-inch inlet line, 5 ft long with one 90 degree elbow, 3-inch outlet line, 100 ft long, vertical, with three 90 degree elbows
Piping roughness (mm)	0.0457
Fire flux (kW/m^2)	NFPA 30 flux (15,700)
Fire duration (hr)	4

TABLE 2. Binary Interaction Parameters Data for the System Water, Ethanol and Acetone

Binary System	k_{12}	λ_{12}
Water-Ethanol	− 0.08038	0.04809
Water-Acetone	− 0.20594	0.15286
Ethanol-Acetone	0.02586	0.01334

2. 2J3 safety relief valve with a 3-inch inlet line
3. 2H3 (0.785 in^2 orifice) safety relief valve with a 2-inch inlet line
4. 2H3 safety relief valve with a 3-inch inlet line

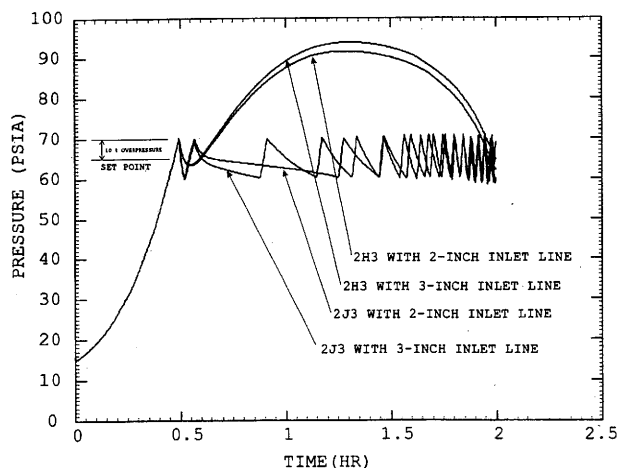Figure 5 illustrates the calculated pressure-time profile

FIGURE 5 Calculated vessel pressure as a function of time for the acetone, ethanol, and water system using 2J3 and 2H3 safety relief valves.
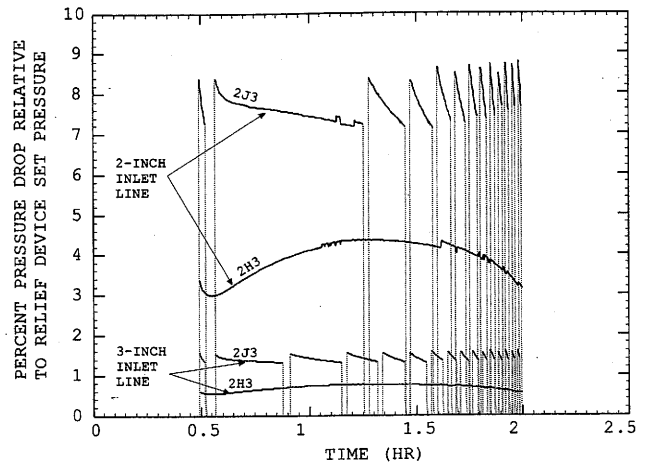

FIGURE 6 Calculated safety relief valve inlet line pressure loss as a function of time for the acetone, ethanol, and water system.
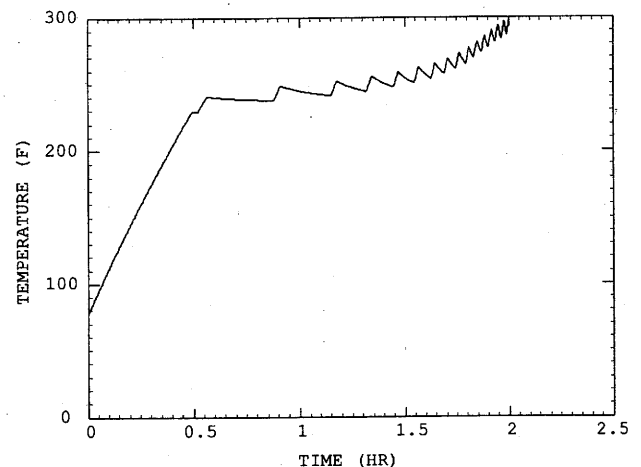

FIGURE 7 Calculated vessel temperature as a function of time for the acetone, ethanol and water system using 2J3 safety relief valve with a 3-inch inlet line.
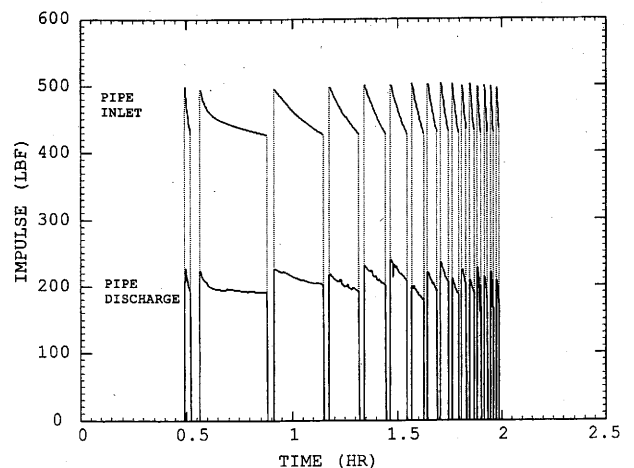

FIGURE 8 Calculated impulse at pipe inlet and pipe outlet as a function of time for the acetone, ethanol and water system using a 2J3 safety relief valve with 3-inch inlet line.
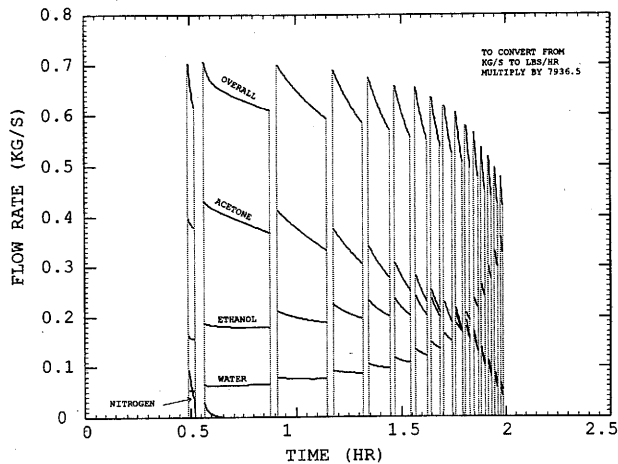
FIGURE 9 Calculated vapor flow rate of the acetone, ethanol, and water system constituents as a function of time using 2J3 safety relief valve with 3-inch inlet line.
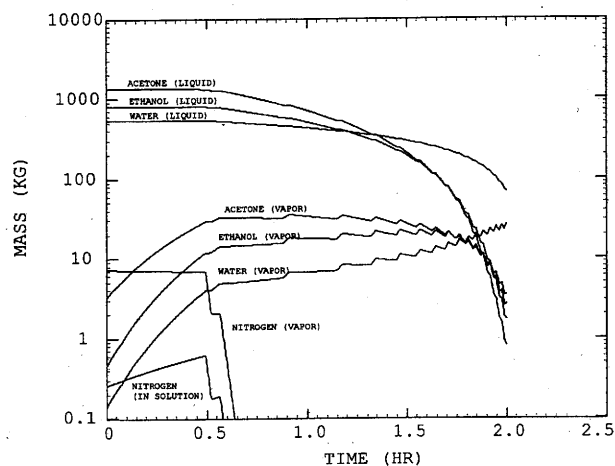

FIGURE 10 Calculated vessel mass of the acetone, ethanol, and water system constituents as a function of time using a 2J3 safety relief valve with a 3-inch inlet line.

calculated by SuperChems for DIERS. All safety relief valves remain closed until 10 percent overpressure is reached in the vessel at which time the valves are fully open. The 2J3 safety relief valve opens and then reseats as nitrogen is discharged from the vapor space of the vessel. The 2H3 safety relief valve opens and remains fully open as the vessel contents are vaporized and discharged.

Figure 5 indicates that while the 2H3 safety relief valve is undersized, the 2J3 safety relief valve should be adequate. SuperChems for DIERS also computes the percent inlet pressure drop with respect to the safety relief valve set pressure. This is illustrated in Figure 6. The percent inlet pressure loss calculated using the 2J3 safety relief valve with a 2-in inlet line exceeds the 3 percent value recommended by the ASME and API. Note that the percent inlet pressure loss reported in Figure 6 includes the accelerational loss as well as the frictional loss. The ASME 3 percent rule applies to irrecoverable frictional pressure losses only.

TABLE 3. Equation of State Binary Interaction Parameters Used to Describe the System Chloroacetyl Chloride, Water, Chloroacetic Acid, Hydrogen Chloride and Nitrogen

Component 1	Component 2	$k_{1,2}$	$\lambda_{1,2}$
Water	Hydrogen chloride	−0.8030	−1.0500
Water	CAC	−0.0513	−0.1950
Water	CAA	−0.1110	0.0417
Water	Nitrogen	0.0000	0.0000
Hydrogen chloride	CAC	0.0021	−0.0081
Hydrogen chloride	CAA	−0.0267	0.0023
Hydrogen chloride	Nitrogen	0.0000	0.0000
CAC	CAA	−0.0135	0.0054
CAC	Nitrogen	0.0000	0.0000

Based on the simulation results, we conclude that a 2J3 safety relief valve with 3-inch inlet line should be adequate for the selected design basis and will also satisfy the recommended 3 percent inlet pressure loss criterion.

Figures 7, 8, 9, and 10 illustrate the computed profiles of vessel temperature, inlet and discharge pipe reaction forces, individual component flow rates, and vessel composition as a function of time. The results indicate, as expected, that the vessel mass is preferentially depleted over time, i.e., light components are vaporized first.

DYNAMIC SIMULATION

The following example illustrates the use of SuperChems for DIERS to model the dynamics of pressure relief when multiple vessels are connected. Figure 11 shows the connectivity of the vessels considered in this example.

Vessel A is a 40 liter vessel which contains nitrogen at 414.7 bars (6,000 psig) and 298 K. Vessel A is connected to vessel B via a short 0.25 inch line with an equivalent discharge coefficient of 0.6.

Vessel B is a five liter vessel which contains nitrogen at 298 K and one bar. This vessel is equipped with a rupture disk. The set pressure for the rupture disk is 345.75 bars (5,000 psig). Vessel B is connected to vessel C via a 0.5 inch line with an equivalent discharge coefficient of 0.5.

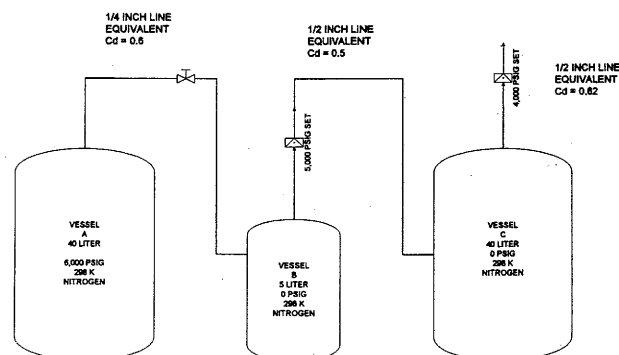Vessel C is a 40 liter vessel which also contains nitrogen at one bar and 298 K. This vessel is equipped with a rup-

FIGURE 11 Dynamic simulation for the nitrogen blow-down example using three connected vessels.

ture disk. The set pressure for this rupture disk is 276.87 bars (4,000 psig). This rupture disk discharges to the atmosphere.

If someone accidently opens the valve between vessels A and B, what will be the final pressure in the system? Will the rupture disk on vessel C burst?

Figures 12 and 13 display the iteration history and how SuperChems for DIERS achieves convergence. It is interesting to note that the rupture disk on Vessel C does not burst for the converged solution while it was predicted to burst in earlier iterations.

NON-IDEAL SOLUTION BEHAVIOR

The constant volume mass and energy balance equations derived in the previous sections are general and implicitly represent fluid non-ideal behavior caused by solution behavior, system pressure and temperature. The partial molar properties are calculated from an equation of state (EOS) with suitable binary interaction parameters (BIPs). BIPs are typically estimated from experimental VLE data or predicted using group contribution methods. Also implicit in the general formulation is the heat generation or removal caused by chemical reaction as the number of moles of reacting species change.

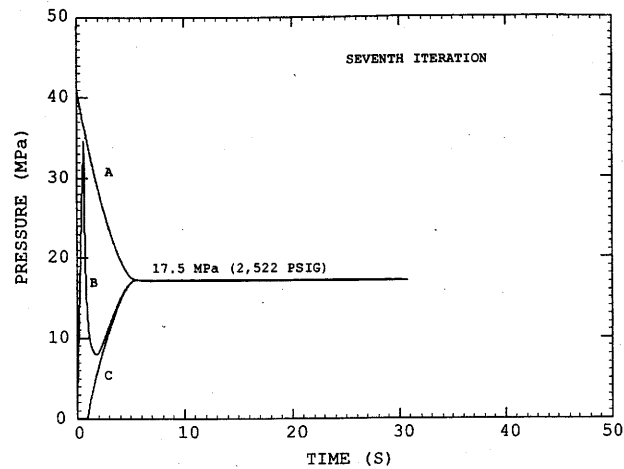We illustrate the use of the EOS approach adopted in the detailed formulation of mass and energy balances on hy-

FIGURE 13 Final pressure profiles in vessels A, B, and C for the nitrogen blowdown example after convergence is achieved.

drogen chloride and water solution behavior. Figure 14 illustrates an enthalpy-concentration diagram estimated using the EOS approach for hydrochloric acid solutions relative to pure hydrogen chloride (gas) and water (liquid) at 273.15 K and one atmosphere. The EOS binary interaction parameters for hydrogen chloride and water were esti-
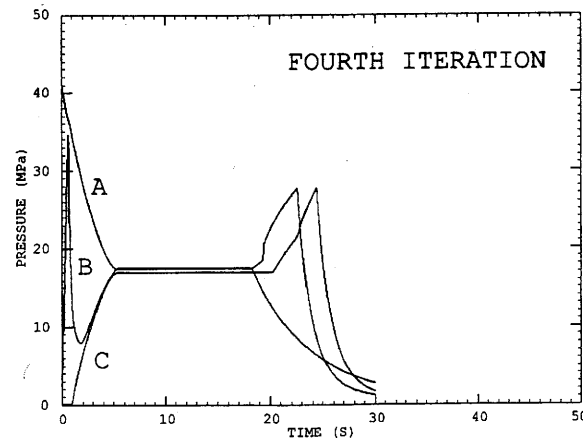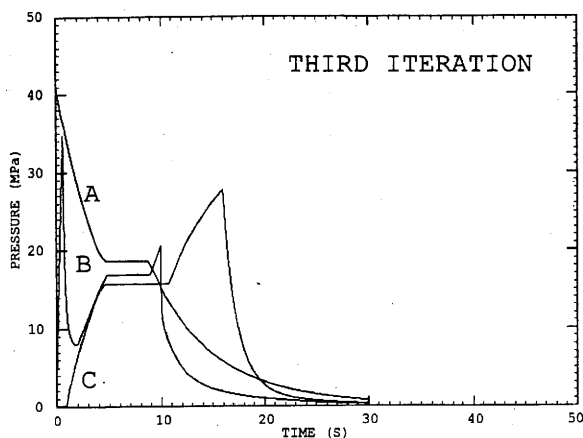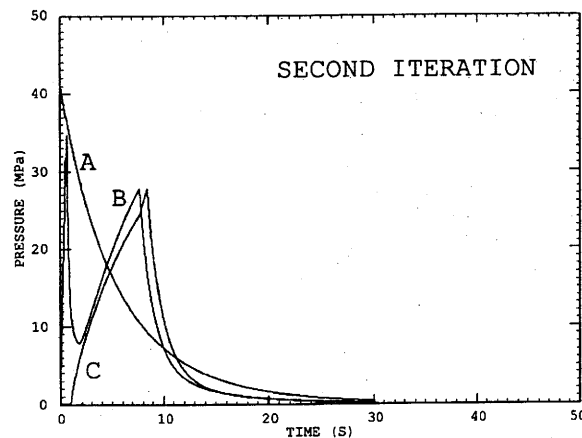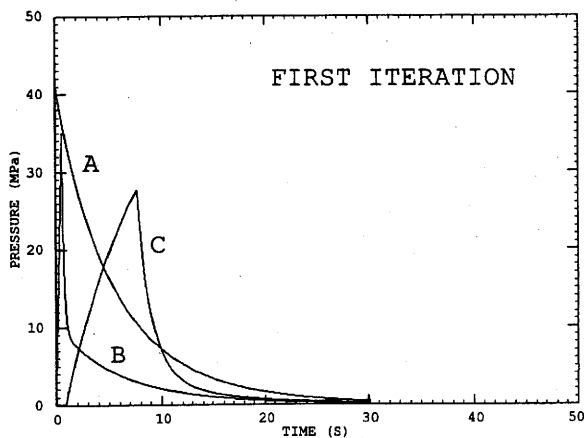
FIGURE 12 SuperChems for DIERS iteration history for the nitrogen blowdown example as the material and energy balance are converged for vessels A, B, and C.
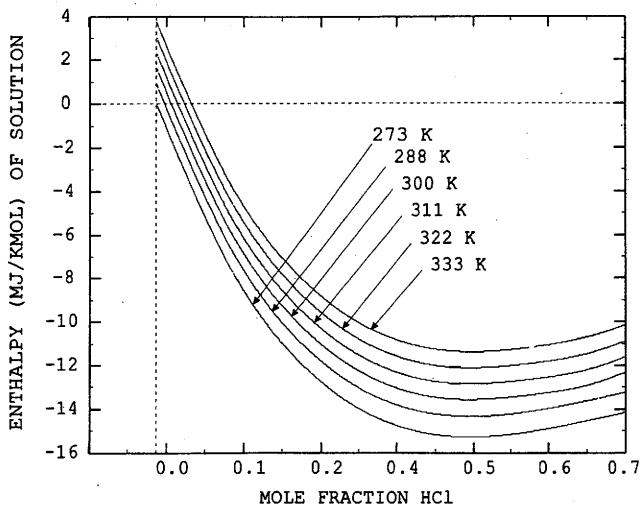
FIGURE 14 Enthalpy-concentration chart of hydrogen-chloride-water solutions relative to pure hydrogen chloride gas and water liquid at 273 K and one atmosphere.

mated from experimental VLE data to be:

$$k_{1,2} = -0.803 = k_{2,1} \qquad (1)$$

$$\lambda_{1,2} = 1.05 = -\lambda_{2,1} \qquad (2)$$

The predicted data·shown in Figure 14 is in excellent agreement with the experimental data on heat of solution for hydrogen chloride-water mixture reported by Hougen and Watson in reference [4].

Figure 14 is useful for the estimation of final temperature when mixing solutions of varying hydrogen chloride composition. For example, if we were to mix 0.263 kmol of a 10 percent by weight (5.26 mol percent) mixture of hydrogen chloride and water at 288 K with a mixture containing 30 percent by weight (17.6 mol percent) hydrogen chloride and water, what would be the final mixture temperature?

The enthalpy of each of the two solution mixes is read from Figure 14. The 10 percent solution enthalpy is −3.5 MJ/kmol or −0.92 MJ and the 30 percent solution enthalpy is −8.00 MJ/kmol or −3.024 MJ. The mixture enthalpy is calculated to be −3.944 MJ or −6.15 MJ/kmol. Upon mixing, the final mixture composition would be 12.53 mol percent hydrogen chloride. Using a mole fraction of 12.53 percent and a molar enthalpy of −6.15 MJ/kmol, we can read from Figure 14 a temperature of 305.5 K or 89.9 F. Hougen and Watson [4] report a temperature of 90 F for the same problem.

We consider another example to illustrate how non-ideal solution behavior can alter the pressure-temperature behavior of systems where hydrogen chloride and water are generated by a chemical reaction. Two cases are considered:

1. A vessel initially contains 1000 kg of water (55.5 kmol) at 300 K and one bar. The total vessel volume is 9.2 m³. The vessel vapor space contains nitrogen. 622 kg (5.5 kmol) of liquid chloroacetyl chloride (CAC) is pumped into the vessel at 0.00925 kmol/s. The CAC entering the vessel is at 300 K and one bar and is immediately mixed with the water due to the action of an agitator. Mixing is

sufficient to cause an immediate reaction between CAC and water to generate hydrogen chloride and chloroacetic acid:

$$C_2H_2Cl_2O + H_2O \rightarrow C_2H_3ClO_2 + HCl \qquad (3)$$
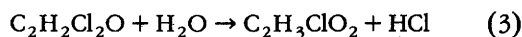
2. This case is similar to case one. The vessel initially contains 622 kg of CAC and water is pumped into the vessel at the rate of 0.00925 kmol/s.

Figure 15 illustrates the pressure-temperature behavior for both cases. For case one, as CAC is pumped into the vessel, it mixes with water and immediately reacts to generate hydrogen chloride which goes into solution as the ratio of water to CAC is 10:1. A peak pressure of 2.2 bar is reached at 100 C. For case two, water is pumped into the vessel, mixes with CAC and generates hydrogen chloride which has a limited solubility in chloroacetyl chloride and CAA. As a result, the pressure and temperature increase steadily. As the CAC is depleted and more water is added, the hydrogen chloride goes into solution. The final vessel conditions are the same as in case one with a peak pressure of 20.2 bar. Figure 16 shows a similar behavior for the same system at one bar. Figure 16a illustrates the effect of water to CAC molar ratio on the combined net heat of solution and reaction. At a molar ratio of one, the heat of reaction is −25 MJ/kmol. Figure 16b indicates that all evolved hydrogen chloride is gaseous when the molar ratio of water to CAC is less or equal to one, i.e., CAC is in excess or stoichiometric. As excess water is added, the hydrogen chloride goes into solution. At a molar ratio of water to CAC greater or equal to four, all evolved hydrogen chloride is retained in the liquid phase. The heat of solution effects are shown in Figure 16.

The pressure-temperature behavior is a key relation for pressure relief design. Non-ideal solution behavior plays a key role in the interpretation of experimental data and scale-up. This is similar to concepts taught in general chemistry about adding acid to water!

PEAK LIQUID AND VAPOR FLOW DURING RELIEF
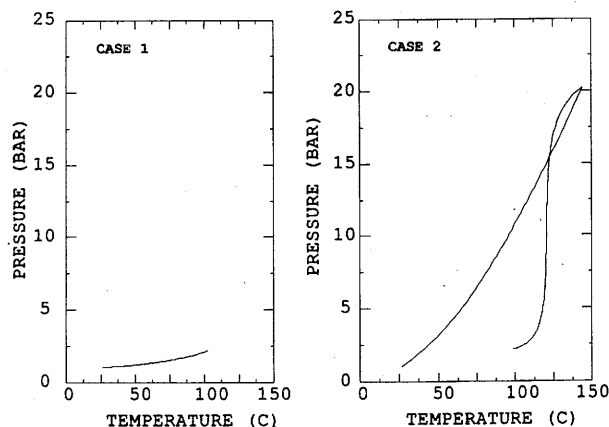
The design of separation equipment for two-phase flow

FIGURE 15 Non-ideal solution behavior impact on closed vessel pressure-temperature behavior for chloroacetyl chloride-water system.
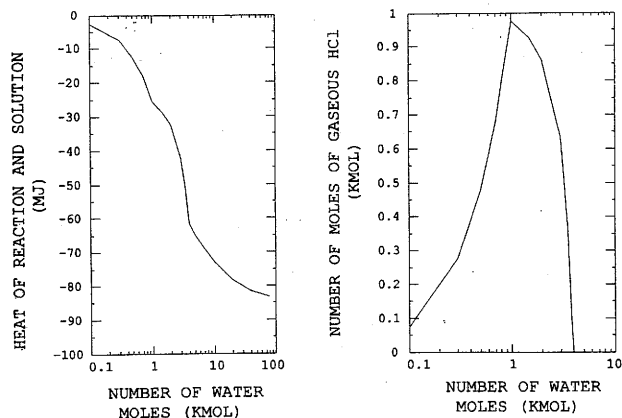
FIGURE 16 Non-ideal solution thermodynamics for the system chloroacetyl chloride, water, chloroacetic acid and hydrogen chloride. Basis = 1 kmol of chloroacetyl chloride, 298 K, one bar, open volume.

requires the specification of a peak vapor flow rate [5]. For many reactive systems, the peak vapor-liquid flow occurs at an intermediate point during the relief transient. Figure 17 illustrates this point by using SuperChems for DIERS to simulate the relief transient of the decomposition of $C_9H_{13}N$. As shown by Figure 17 at the start of relief, the cumulative (all mixture components are included) liquid flow rate is around 250 kg/s and the cumulative vapor flow rate is around one kg/s. The peak vapor flow takes place at 240 s during relief and is around five kg/s with a corresponding liquid rate of 100 kg/s. The peak vapor flow value should be used as input for design and not the initial value. Most simplified/shortcut methods are not capable of providing such data.

IMPACT OF PIPING ORIENTATION ON FLOW

In order to illustrate how piping orientation might impact the flow capacity of a relief line, we consider a simple example involving saturated water. Two-phase homogeneous-equilibrium flow occurs in a piping configuration
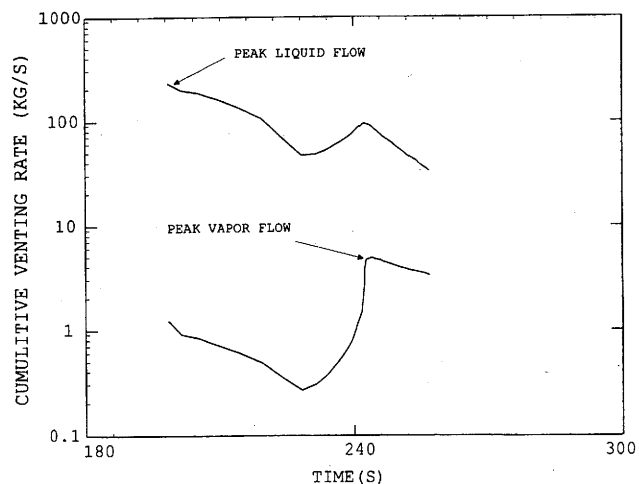
TABLE 4. Impact of Piping Orientation on Flow Capacity

Seg. 1 Angle (deg)	Seg. 2 Angle (deg)	Seg. 1 Length (m)	Seg. 2 Length (m)	Flow Rate (kg/s)
0	90	2.5	2.5	5.547
90	0	2.5	2.5	5.410
0	90	24.45	24.45	2.973
90	0	24.45	24.45	2.529
0	90	244.0	244.0	0.864
90	0	244.0	244.0	0.540

consisting of two equal length segments having the same diameter (2 inch). The pipe inlet conditions are as follows:

- Temperature = 151.9 C
- Pressure (saturation) = 500000 Pa
- Vapor quality = 0.001
- Pipe roughness = 4.57×10^{-5} m

Two pipe orientations are considered:

1. The pipe consists of a horizontal segment followed by a vertical segment
2. The pipe consists of a vertical segment followed by a horizontal segment

Table 4 summarizes the computed flow rates obtained by SuperChems for DIERS for both cases one and two for different pipe lengths. More flow is predicted for case one than for case two. A flow method that does not account for the gravity term in the momentum equation would predict the same flow rate for both cases.

The case one orientation should lead to more flow because less pressure drop is exhibited in the horizontal segment without much change in the vapor quality. For case two, however, the vapor quality increases faster in the first segment (90 deg orientation) due to more pressure drop and thus leads to less flow. Figures 18 and 19 illustrate the pressure and vapor fraction profiles for a 244-m long pipe.

SUBCOOLED LPG FLOW

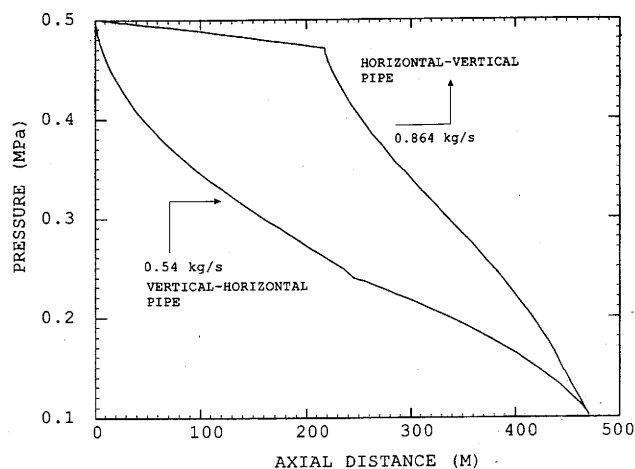Figure 20 illustrates an experimental setup used by Shell

FIGURE 17 A typical vapor-liquid discharge profile during a process induced $C_9H_{13}N$ decomposition.

FIGURE 18 Impact of piping orientation on pressure.
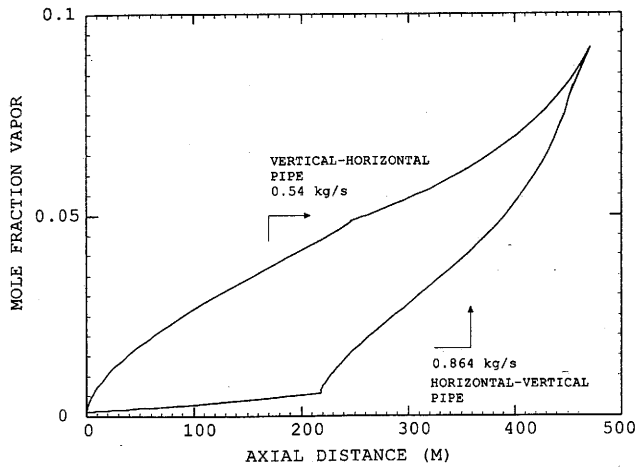
FIGURE 19 Impact of piping orientation on vapor quality.

Tank is 3/4 full
Pipe roughness is 1.5E-06 m

LPG Composition (mol %)

propane	97.4 %
iso-butane	1.6 %
n-butane	0.8 %
ethane	0.2 %
propylene	<0.1 %

FIGURE 20 Subcooled LPG flow experimental setup.

FIGURE 21 Calculated pressure profile in piping during LPG blowdown.
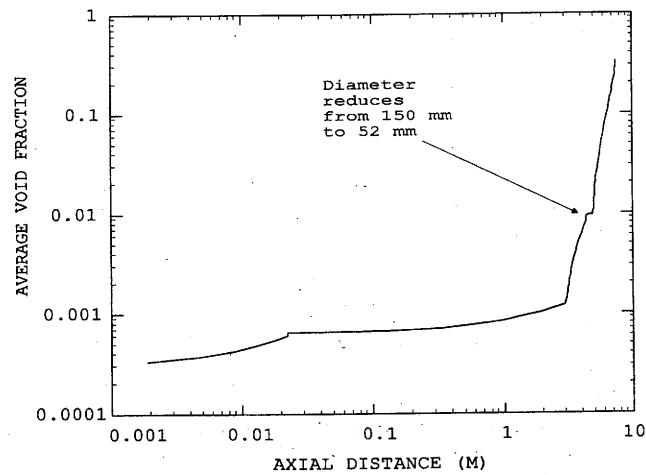

FIGURE 22 Calculated void fraction profile in piping during LPG blowdown.

TABLE 5. Comparison Between Calculated Subcooled LPG Flows by SuperChems for DIERS and Experimental Data

Flow Method	Flow Rate (kg/s) $\epsilon = 1.5 \times 10^{-6}$ m	Flow Rate (kg/s) $\epsilon = 2.5 \times 10^{-5}$ m
Experimental	21.4	
Homogeneous	14.5	13.8
Moody slip	19.2	18.0
Theoretical	28.2	28.2

Research [6] for the estimation of subcooled LPG flow. Pressure in the vapor space is maintained at 880,000 Pa by using a nitrogen pad. The vessel and piping dimensions are also shown in Figure 20. SuperChems for DIERS was used to calculate the flow rate and pressure-void fraction profile in the piping. Table 5 illustrates the calculated flows using both homogeneous-equilibrium and Moody slip models. The reported experimental flow value is closer to that predicted using slip-equilibrium flow. The same behavior is observed for subcooled water flow illustrated in the example based on the experiments of Nielsen [7].

Figures 21 and 22 illustrate pressure and void fraction profiles during vessel blowdown. It is apparent from these

TABLE 6. Propane Cylinder Experimental Data Summary

| Variable	Value
Cylinder weight (empty) (kg)	30.4
Cylinder volume (m³)	0.102
Cylinder charge (kg)	43.7
Initial temperature (K)	308
Initial pressure (bar)	16
Propane mole fraction	97.3
Butane mole fraction	1.7
Other	1.0
Release orifice size (in)	3/8 ID
Release piping (ft)	50 (copper tubing)
Copper roughness (m)	0.0000457 (assumed)
Ambient temperature (F)	103
Relative humidity (percent)	95
Date	July 15, 1991 at 2:00 pm
Flow phase	Gas flow only
Total mass vented (kg)	8.0 in 180 s
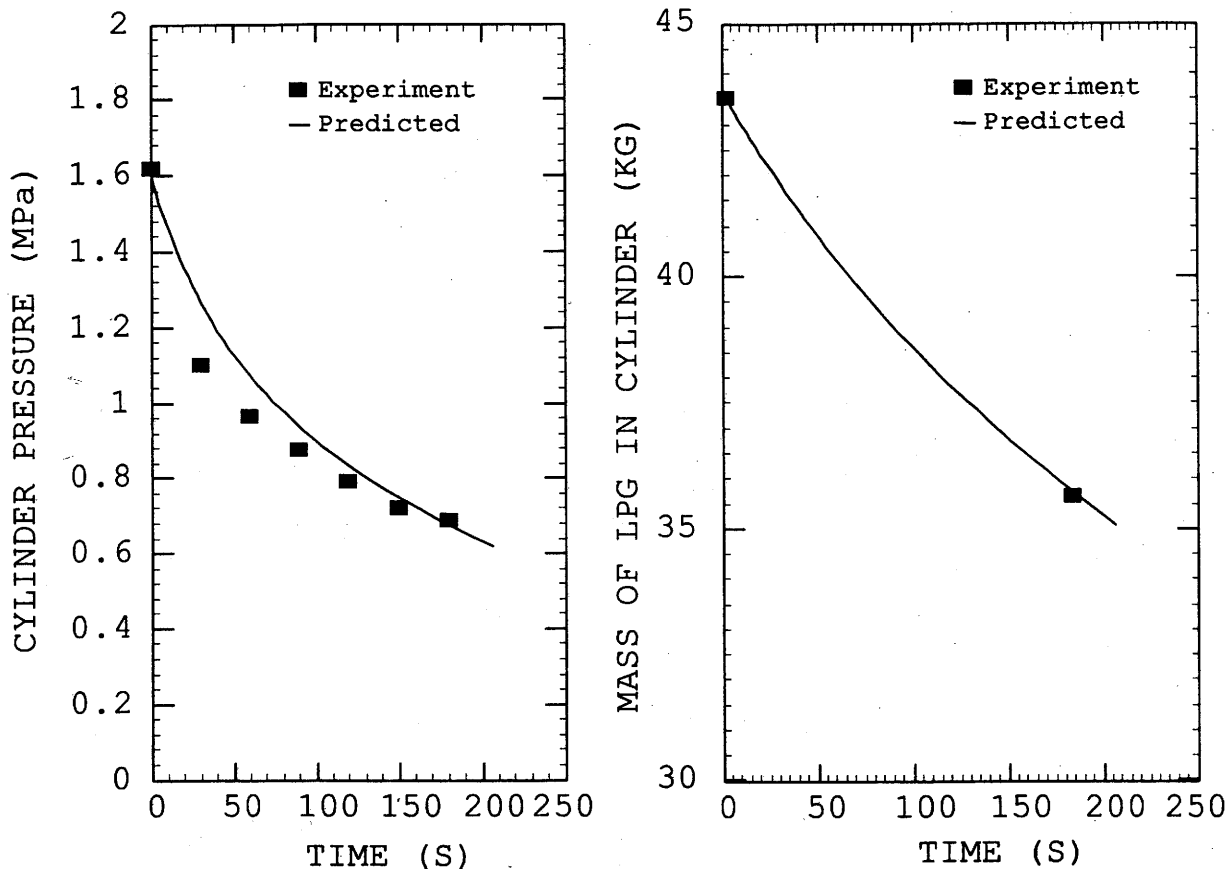
FIGURE 23 Propane cylinder blowdown: comparison of experimental data and model predictions for pressure profile and total mass vented.

graphs that large changes in pressure and void fraction occur at the point at which the pipe diameter reduces from 150 mm to 52 mm.

LPG CYLINDER BLOWDOWN

This benchmark deals with the blowdown of a cylinder containing propane. The experimental was conducted by Melhem *et al.* in 1991 [*8*]. The pressure profile in the cylinder was recorded as a function of time. The total mass of propane remaining in the vessel was measured at 180 seconds. Table 6 summarizes data pertinent to the test.

Model results are summarized in Figures 23 and 24. The data shows excellent agreement between measured and predicted data.

NIELSEN'S SUBCOOLED / FLASHING WATER FLOW

SuperChems for DIERS was used to predict subcooled/water flow data experimentally measured by Nielsen [7]. A 1.98 cubic meter, vertical cylindrical vessel having diameter of 1.078 m and two ASME 2:1 elliptical heads contains water at a temperature of 176.1 C. The total (water vapor plus hydrostatic) pressure in the vessel is (9.3 bara) 930,000 Pa. Horizontal pipes having square-cut entrances and the internal diameters, lengths and pipe roughness values shown in Table 7 drain the vessel.

These drain pipes are side-mounted at 0.1 m above the tangent line of the bottom head. The 1145.4 kgs of water

above the drain pipe result in the initial hydrostatic head of 0.131 bara. Assuming both homogeneous-equilibrium and slip-equilibrium flow, the initial flow rates were calculated by SuperChems for DIERS and are tabulated in Table 8. Again, this data indicates that some degree of slip is present during discharge.

INCLINED PIPE FLOW

Consider the following problem involving an inclined pipe with all liquid flow. The following assumptions are made:

- Both temperatures and density are constant.
- Flow reaches steady state, i.e., initial transients following flow actuation are not accounted for.
- Pipe area is constant.
- Pipe discharges to atmosphere with no exit losses.

Starting with a differential momentum balance for a single-phase flow, we can show that pressure drop in the pipe has three components: accelerational, frictional, and gravitational:

$$\frac{1}{\rho}\frac{dP}{dz} = -u\frac{du}{dz} - \frac{2u^2f}{D} - g\sin\theta \qquad (4)$$

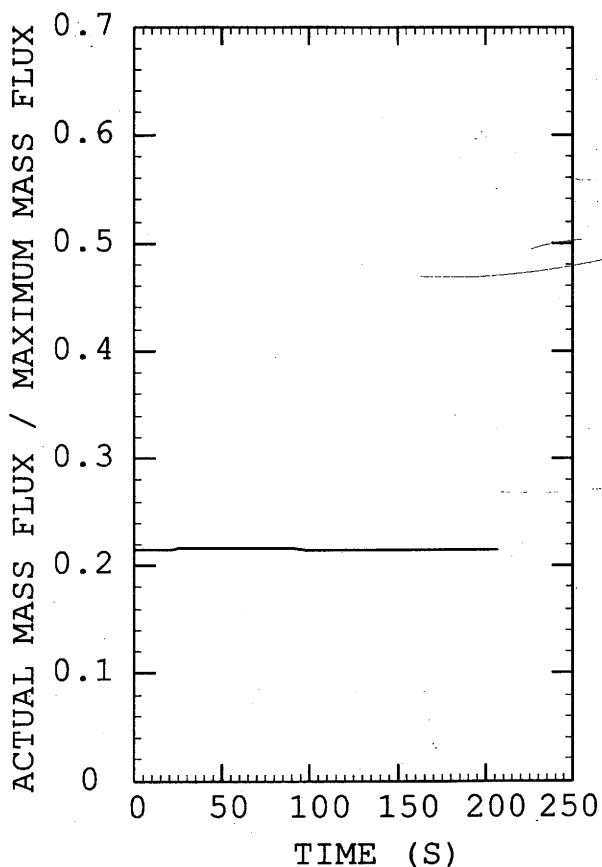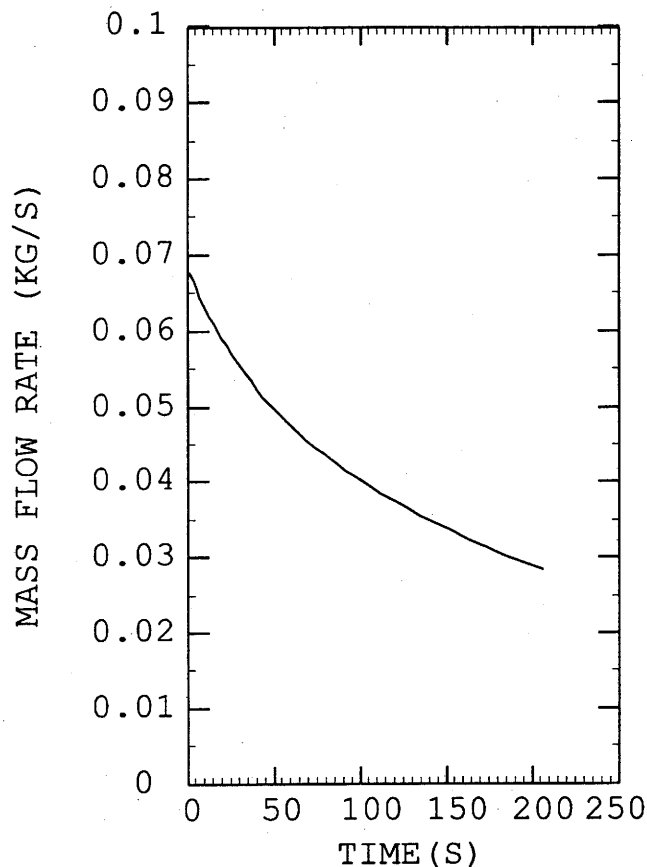For most liquid flows, the term du/dz is small and can be

FIGURE 24 Propane cylinder blowdown: model predictions of venting rate and flow reduction due to the presence of copper tubing.

TABLE 7. Summary of Pipe Data for Nielsen's Water Flow Experiments

Pipe Number	Pipe Diameter (mm)	Pipe Length (mm)	Pipe L/D	Pipe Roughness (mm)
1	79.9	1840	23	0.024
2	32.8	2000	61	0.013
3	10.6	1870	176.4	0.013

TABLE 8. Comparison Between Calculated Subcooled/Saturated Water Flows by SuperChems for DIERS and the Nielsen Experimental Data

Flow (kg/s)	Pipe 1	Pipe 2	Pipe 3
Experimental	33.1	5.23	0.44
Homogeneous	27.6	4.20	0.330
Moody slip	45.0	6.45	0.43

ignored for illustration purposes. The term dP/dz must be less or equal to zero in order for flow to occur. At the limit:

$$\frac{dP}{dz} = 0 = -\frac{2u^2 f}{D} - g\sin\theta \qquad (5)$$

where θ is the pipe angle with respect to the horizontal. For small diameters, the first term dominates and dP/dz is always negative. For large diameters, dP/dz can reach zero at a mass flux of:

$$G = \rho\sqrt{\frac{-gD\sin\theta}{2f}} \qquad (6)$$

Integrating the mechanical energy balance without constraining the sign of dP/dz will lead to an integral balance

that can be used for inclined flow with diameters large enough to cause a positive dP/dz term. The integral balance will lead to an overall pressure drop but will fail to elucidate the pressure behavior between the inlet and the outlet points. The integral balance will only indicate that flow will increase as pipe length increases.

The system will maximize mass flow such that the Gibbs free energy is minimized between the inlet and the outlet point. This will require that the overall pressure drop be negative and will allow pressure to increase in order to satisfy the pressure drop constraint.

We will illustrate this using an actual example. Consider water flow at 298 K and two bars in an inclined pipe. Several cases are considered with pipe diameters ranging from two to eight inches and pipe inclination ranging from -45 to -90 degrees (downward). An entrance loss equivalent to 1.5 velocity heads is assumed.
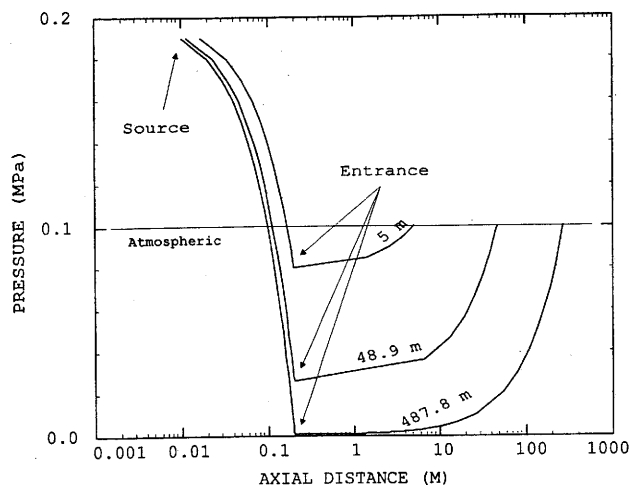
FIGURE 25 Calculated pressure profiles for inclined (downflow) water flow pipe.

Table 9 illustrates maximum flow capacity of the pipe for various conditions. Figure 25 illustrates the pressure profile along the pipe axis and shows that while the overall pressure drop is negative, the pressure across the pipe entrance is allowed to decrease and then increase to ambient pressure at the outlet. Clearly, this indicates the pressure will fall below the bubble point and will lead to the formation of an unstable flow regime with continuing bubble formation and collapse as flow occurs. This might present several implications for bottom venting with reactive chemicals such as peroxides unless sufficient nitrogen makeup and/or vapor pressure generation takes place during flow.

SENSITIVITY TO FIRE LOADING

The following example illustrates the use of SuperChems for DIERS to establish the sensitivity of both reactive and non-reactive systems to fire exposure.

To illustrate the impact of fire loading on emergency relief system design for a non-reactive system, consider a propane storage vessel which initially contains 600 kgs of propane at 292 K and 7.985 bars. The vessel characteristics are shown in Table 10. The pressure history is estimated for three external heat flux values of 5, 25, and 100 kW/m².

TABLE 10. Propane Storage Tank Characteristics

|	
Volume (m³)	1.893
Length (m)	3.023
Outside diameter (m)	0.950
Shell thickness (m)	0.0063
Head thickness (m)	0.00533
Maximum allowable working pressure at 611 K (MPa)	1.724
Hydrostatic test pressure (MPa)	2.58
Relief valve setting (MPa)	1.724
Relief valve diameter (m)	0.0254
Relief valve area (m²)	0.000425

Flow from the safety relief valve is assumed to be homogeneous two-phase without slip.

As shown by Figure 26, the safety relief valve is oversized for a five kW/m² heat flux value. This is apparent due to valve cycling. Under a 100 kW/m² heat flux the pressure level in the tank reaches two times MAWP. Valve cycling occurs when the vessel contents are completely vaporized. For the high fire flux case, the relief valve is undersized; however, vessel integrity is not seriously compromised.

For vessels containing reactive chemicals the rate of energy/pressure accumulation is significantly increased because the reaction temperature reaches onset with less reactant consumption. The effect of fire on reaction rates is highly nonlinear.

To illustrate this highly nonlinear effect of fire loading on vessel temperature and pressure behaviors we consider a steel storage vessel containing a hydrogen peroxide-water solution that is exposed to an external heat flux varying between five and 100 kW/m². The vessel is equipped with a rupture disk (3-inches in diameter) at a set pressure of three bars. We assume that no piping is attached to the rupture disk. The vessel volume is one m³ and has an MAWP of 10.34 bars.

The peroxide-water solution consists of 159 kg of hydrogen peroxide and 716 kgs of water. The vessel initial temperature and pressure are 10 C and one bar respectively. Hydrogen peroxide decomposes in the liquid phase and forms oxygen and water according to the following stoichiometry:

$$H_2O_2 \rightarrow \frac{1}{2}O_2 + H_2O \tag{7}$$
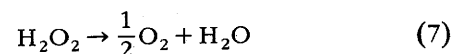
The reaction is first order and has a temperature dependent rate described by the following expression:

$$K = 1.5 \times 10^{12} \exp\left(-\frac{12,832}{T}\right) \tag{8}$$

where K is in s^{-1} and T is in Kelvins.

The pressure history is shown in Figure 27. Homogeneous-equilibrium two-phase flow is used to estimate the flow from the rupture disk upon actuation. At an external heat flux value of five kW/m² (simulating a process upset) the 3 inch rupture disk is properly sized. As shown in Figure 27, higher external heat flux values (simulating a fire)
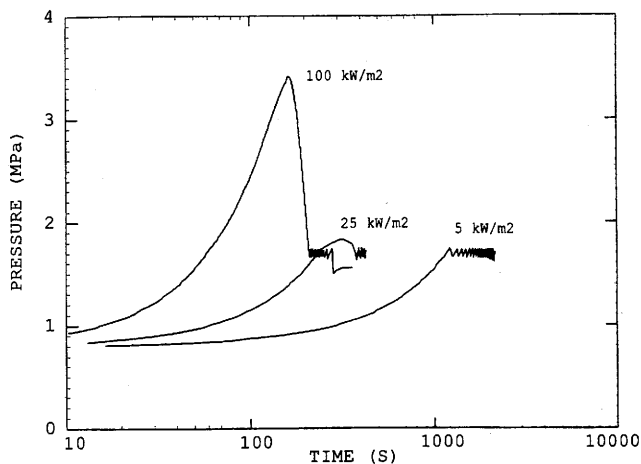
TABLE 9. Calculated Maximum Flow Capacity of Inclined (Downflow) Water Pipe

Pipe Length (m)	Pipe Diameter (mm)	Pipe Angle (degrees)	Flow Rate (kg/s)
5	50.8	−45	17.76
48.9	50.8	−45	13.09
487.8	50.8	−45	12.064
5	50.8	−90	18.6
48.9	50.8	−90	15.11
487.8	50.8	−90	14.336
5	203.2	−90	410
48.9	203.2	−90	492
487.8	203.2	−90	≥ 528

FIGURE 26 Sensitivity of pressure to external fire loading for the non-reactive propane system.
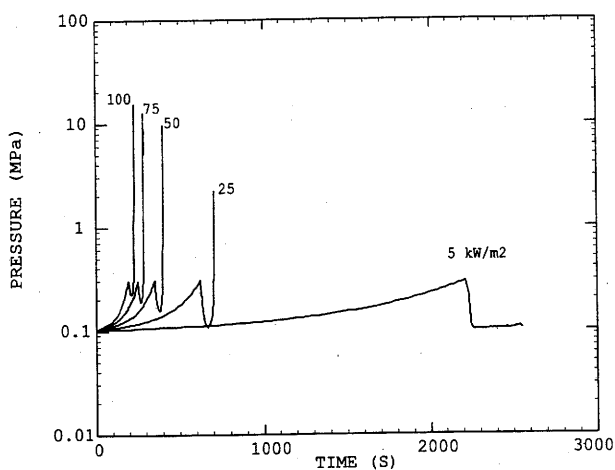

FIGURE 27 Sensitivity of pressure to external fire loading for the reactive hydrogen peroxide-water system.
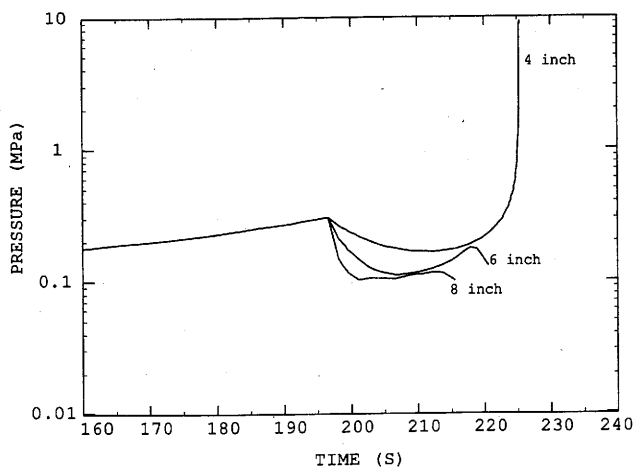

FIGURE 28 Sensitivity of maximum pressure level reached in vessel with various rupture disk sizes at an external heat flux of 100 kW/m² for the reactive hydrogen peroxide-water system.

lead to much faster reaction rates and higher peak pressures in the vessel. With the existing rupture disk the vessel pressure reaches three times the MAWP with an external heat flux of 25 kW/m².

Figure 28 illustrates the maximum pressure level reached in the vessel during runaway reaction conditions caused by a fire exposure with a heat flux of 100 kW/m². Rupture disk sizes of 4, 6, and 8 inches are shown. The effect of rupture disk size on the peak pressure reached in the vessel can be more pronounced with piping attached to the rupture disk. This is attributed to mass flow reduction effects resulting from continuing reaction in the piping [2].

CONCLUSION

This paper presents an advanced modeling approach and introduces computer software which significantly improves predictions of reaction rates and critical data that engineers need to design effective emergency relief systems.

The comprehensive approach and user friendly program discussed in this paper provide a reliable design basis for difficult systems, including highly energetic and nonideal reactions, systems with continuing reactions in piping and containment vessels, etc.

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