

Are liquid thermal-relief valves needed?

Thermal stresses, or pressures from hydrogen evolution due to corrosion, can rupture a pipe or tube. Here is how to find such forces to see whether a relief valve is needed.

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□ In protecting process pipelines, engineers seldom perform calculations to see whether thermal stresses or pressure buildups (as a result of H₂ evolution from corrosion) exist. Such neglect could lead to rupture, especially if relief valves have not been employed.

Here, we present a calculation method that will determine whether or not a relief valve is required. An example illustrates the method.

Thermal expansion and corrosion

In the case of thermal expansion, when pipes, tubes or process equipment are full of liquid and are blocked in, rupture can result from heat from several sources:

- Solar radiation.
- Heat-tracing coils.
- Heat transfer by radiation and conduction from nearby process equipment.

A typical example would be a heat exchanger blocked-in on the cold side, with flow continuing on the hot side. Such a situation could occur during normal operation, e.g., when a hot product-stream was being pumped through an exchanger to a flash drum and the stream was being used to preheat the feed to a reactor. If a level controller that operated a control valve between the exchanger and flash drum were to close the control valve, the feed would be blocked in.

Then, of course, the system can be subject to thermal expansion. Stresses result from the difference in coefficients of thermal expansion between the liquid and the metal.

On the other hand, corrosion, which generates hydrogen, can also give rise to severe stresses caused by gas pressure. Such a case may occur when, for example, the flow of sulfuric acid is stopped in a steel pipeline and it remains full. After some time, enough hydrogen may be generated to create pressures that will burst the pipe.

To see whether a relief valve is needed, the stresses due to thermal expansion and corrosion must first be found. Here is a method to do this:

Determining thermal stresses

The net volume of liquid that expands is found by subtracting the pipe expansion due to both temperature

rise and pressure rise from the liquid volume expansion due to temperature rise:

$$\Delta V = (V_t - V_{t0}) - \Delta V_p - \Delta V_{Pr} \quad (1)$$

The volumetric expansion of the liquid at temperature t above a reference temperature is given by:

$$V_t = V_{tr}(1 + at + bt^2 + ct^3) \quad (2)$$

The reference temperature tr is 0°C. Values of a , b , and c are given for some liquids in Table I.

When a liquid expands from temperature t_0 to temperature t , its volume at t is:

$$V_t = V_{t0} + V_{tr}[a(t - t_0) + b(t^2 - t_0^2) + c(t^3 - t_0^3)] \quad (3)$$

The pipe expansion due to temperature is given by:

$$\Delta V_p = \pi/4[(D + CD)^2(L + CL) - D^2L] \quad (4)$$

In Eq. (4), L is the total pipe length including fittings, i.e., it must account for the total restricted fluid volume. Typical values of C appear in Table II.

The increase in pressure of the liquid—due either to heat or to gas buildup—will expand the pipe further [1]. Such an increase is usually minimal when compared with the effects of heat alone, and can be ignored in making calculations. However, an equation for this effect (pipe expansion due to pressure) is presented:

$$\begin{aligned} \Delta V_{Pr} &= [\pi (\Delta R)^2] L + \pi R^2 [\Delta L] \\ &= \pi L \left[\frac{R}{E} \left(\frac{PR}{T_h} - \gamma \frac{PR}{2T_h} \right) \right]^2 + \pi R^2 \left[\frac{P L A_{ID}}{E A_{metal}} \right] \end{aligned} \quad (5)$$

Poisson's ratio, γ , is 0.3 for steel and Alloy 20, as given in the American Natl. Standards Institute (ANSI), New York, ANSI Standard 31.3. Liquid compressibility is defined as:

$$\beta = - \left(\frac{\text{Final volume} - \text{Initial volume}}{\text{Final pressure} - \text{Initial pressure}} \right) \times \left(\frac{1}{\text{Initial volume}} \right) \quad (6)$$

For a liquid of volume V_t in a pipe of fixed volume V_{t0} , β is expressed as:

$$\beta = - \left(\frac{V_{t0} - V_t}{\Delta P} \frac{1}{V_t} \right) \quad (7)$$

Coefficients of cubical expansion for some typical liquids

Table I

Liquid	Range, °C	a^* , 10^{-3}	b , 10^{-6}	c , 10^{-8}
Benzene	11- 81	1.17626	1.27755	0.80646
Toluene	0-100	1.028	1.779	—
Methyl alcohol	-38-+70	1.18557	1.56493	0.91113
<i>n</i> -Butyl alcohol	6-108	0.83751	2.8634	-0.12415
<i>iso</i> -Propyl alcohol	0- 83	1.04345	0.44303	2.7274
Chloroform	0- 63	1.10715	4.66473	-1.74328
Carbon tetrachloride	0- 76	1.18384	0.89881	1.35135
Ethyl acetate	-36-+72	1.2585	2.95688	0.14922
Hydrochloric acid, 33.2%	0- 33	0.4460	0.215	—
Sulfuric acid, conc.	0- 60	0.5758	-0.864	—
<i>n</i> -Pentane	-190-+30	1.50697	3.435	0.975

The coefficients are for $tr=0^\circ\text{C}$

*For example, for benzene: $V=V_{tr} [1+1.17626 \times 10^{-3} t + 1.2775 \times 10^{-6} t^2 + 0.80646 \times 10^{-8} t^3]$

From Ref. [2].

Coefficients of linear thermal expansion for a few typical alloys

Table II

Temperature, °F	Carbon steel	18-8 stainless steel	25-Cr 20-Ni	Wrought iron
50	-0.14	-0.21	-0.16	-0.16
70	0	0	0	0
100	0.23	0.34	0.28	0.26
125	0.42	0.62	0.51	0.48
200	0.99	1.46	1.21	1.14
250	1.40	2.03	1.70	1.60
300	1.82	2.61	2.18	2.06
400	2.70	3.80	3.20	3.01
500	3.62	5.01	4.24	3.99
700	5.63	7.50	6.44	6.06
900	7.81	10.12	8.78	8.26

From Ref. [5].

Compressibilities of some selected liquids

Table III

Liquid	Temperature, °C	Pressure, atm	β , 10^{-6} , atm
Ethyl alcohol	20	1-50	112
	20	200-300	86
Methyl alcohol	0	1-500	79.4
<i>n</i> -Butyl alcohol	17.4	8	90
<i>iso</i> -Butyl alcohol	17.95	8	98
<i>n</i> -Propyl alcohol	0	1-500	69
<i>iso</i> -Propyl alcohol	5.65	8	95
	17.85	8	103
Chloroform	20	0-98.7	94.9
	100	8-9	211
Ethyl acetate	13.3	8.1-37.4	104
	99.6	8.13-37.15	250
Benzene	20	1-2	95.3
	20	98.7-197.4	58.4
Toluene	10	1-5.25	79
	100	1-5.25	150
Sulfuric acid, 70%, wt.	60.3	(wide range)	50-100
Water	0	1-25	52.5
	100	100-200	46.8

From Ref. [2, 4].

Nomenclature

a, b, c	Coefficients for Eq. (2)
A	Surface area of pipe in contact with liquid, ft^2
A_{ID}	Pipe cross-sectional area, ft^2
A_{metal}	Cross-sectional area of pipe metal (of the "ring" of a section of pipe), ft^2
C	Coefficient of linear thermal expansion of pipe material, ft/ft
C_R	Corrosion rate, mils/yr
D	Pipe inside dia., ft
E	Modulus of elasticity, lb/in^2
H	Henry's law constant, atm
L	Pipe length between block valves, ft
L_m	Gas evolved, moles H_2/wk
M_p	Hydrogen equivalent weight of pipe material, moles
P	Pressure, psi or atm
ΔP	Pressure change due to thermal stresses, psi or atm
ΔP_c	Pressure change due to corrosion, psi or atm
R	Pipe radius, ft
T_h	Pipe thickness, ft
t	Temperature, $^\circ\text{F}$ or $^\circ\text{C}$
t_{avg}	Average temperature, $^\circ\text{F}$ or $^\circ\text{C}$
t_r	Reference temperature, here 0°C
V_t	Volume of liquid at t , ft^3
V_{t_0}	Volume of liquid at t_0 , ft^3
V_{t_r}	Volume of liquid at t_r , ft^3
ΔV	Net volume change, ft^3
ΔV_p	Pipe volume change due to temperature rise, ft^3
ΔV_{pr}	Pipe volume change due to pressure rise, ft^3
$\Delta V_{thermal}$	Liquid volume expansion due to temperature rise, ft^3
X_L	Amount of liquid in pipe, moles
Greek letters	
β	Liquid compressibility, atm^{-1}
γ	Poisson's ratio
ρ_p	Pipe material density, lb/ft^3

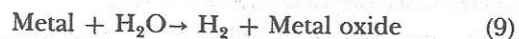
Eq. (7) can be rearranged and expressed in terms of the coefficients of liquid volume expansion to yield the following expression:

$$\Delta P = \left(\frac{1}{\beta} \right) \left(\frac{a(t-t_0) + b(t^2-t_0^2) + c(t^3-t_0^3)}{1 + at + bt^2 + ct^3} \right) \quad (8)$$

Usually, $(V_t - V_{t_0})$ is much greater than ΔV_p and ΔV_{pr} . Thus, Eq. (7) is generally sufficient for calculating the pressure rise due to thermal stresses.

Determining stresses due to corrosion

In an aqueous medium, the corrosion reaction of a metal may be represented by:



One mole of hydrogen is released for every mole of

bivalent metal that reacts. If L_m is the moles of hydrogen evolved/wk, then:

$$L_m = \left(C_R, \frac{\text{mils}}{\text{yr}} \right) \left(\frac{\text{in.}}{1,000 \text{ mils}} \right) \left(\frac{\text{ft}}{12 \text{ in.}} \right) (A) (\rho_p) \times \left(\frac{\text{mole}}{M_p} \right) \left(\frac{\text{yr}}{52 \text{ wk}} \right) = \left(\frac{1}{624 \times 10^3} \right) \left(\frac{C_R A \rho_p}{M_p} \right), \text{ moles/wk} \quad (10)$$

The number of moles of H_2 evolved will vary if the valence of the metal is different. Such an effect must be accounted for in calculations.

Using Henry's law (i.e., the solubility of a gas in a liquid—its mole fraction—is directly proportional to the pressure of the gas above the liquid), the pressure rise is:

$$\Delta P_c = H \left(\frac{L_M}{X_L + L_M} \right) \quad (11)$$

H , Henry's law constant, is available in the literature. Eq. (11) is based on the following assumptions: (1) H is not a function of pressure; (2) the hydrogen gas-phase is ideal; (3) the pipe is full of liquid and the liquid is incompressible; and (4) the pipe is rigid.

Eq. (11) gives an approximate pressure rise for one week with no flow in the pipe.

Example

A 4-in. Alloy 20, Sch. 10 pipeline is used to transport 70% H_2SO_4 . The pipe's pressure rating is 500 psi and its I.D. is 4.26 in. The temperature is expected to rise occasionally to 130°F (54.8°C) from its normal value of 100°F (38.1°C). The pipeline could be out of service for up to one week. The distance between block valves is 9,900 ft. Is a thermal-relief valve needed?

Consider the worst case—130°F and 1 wk. From Table I, for 70% H_2SO_4 , use the volume for concentrated sulfuric acid, which is expressed as:

$$V_t = V_{t_0} + V_{tr} [0.5758 \times 10^{-3} (t - t_0) - 0.864 \times 10^{-6} (t^2 - t_0^2)] \quad (12)$$

Eq. (12) is written in °C. The coefficient of linear thermal expansion for Alloy 20 (25Cr, 20Ni) is, from Table II, 0.556 in./100 ft, or 46.3×10^{-3} ft/100 ft.

Calculate the liquid volume expansion due to the temperature rise. In Eq. (12), substituting the following:

$$t - t_0 = 16.7 \text{ }^\circ\text{C}, \text{ and } t_0 = 38.1 \text{ }^\circ\text{C}$$

and rearranging, yields:

$$\left(\frac{V_t - V_{t_0}}{V_{t_0}} \right) = \frac{(0.5758 \times 10^{-3} (16.7) - 0.864 \times 10^{-6} (54.8^2 - 38.1^2))}{1 + 0.5758 \times 10^{-3} (38.1) - 0.864 \times 10^{-6} (38.1)^2} = \frac{0.008275}{1.020684} = 0.008107 \quad (13)$$

The initial volume of acid in the pipe is:

$$V_{t_0} = (\pi/4) D^2 L = (\pi/4) (4.26/12)^2 (9,900) = 979.9 \text{ ft}^3 \quad (14)$$

And the change in volume is:

$$\Delta V_t = 979.9 \times 0.008107 = 7.94 \text{ ft}^3 \quad (15)$$

Calculate the pressure rise due to the liquid volume

expansion. Rewriting Eq. (7) and substituting values from Eq. (13) into it:

$$\Delta P = - \left(\frac{V_{t_0} - V_t}{\beta} \right) \left(\frac{1}{V_t} \right) = - \left(\frac{V_{t_0} - (V_{t_0} + 0.008107 V_{t_0})}{V_{t_0} (1.008107)} \right) \left(\frac{1}{\beta} \right) = \left(\frac{0.008042}{\beta} \right) \quad (16)$$

From Table III, β for 70% H_2SO_4 is: $50 \times 10^{-6} < \beta < 100 \times 10^{-6}$. Thus, substituting into Eq. (16) yields: 80 atm $< \Delta P < 160$ atm. Calculations for ΔV_{Pr} and ΔV_p are omitted, since they are assumed to be much smaller than the above-calculated pressure rise. Now, the pressure rise due to corrosion is calculated.

The corrosion rate for Alloy 20 in H_2SO_4 at 54.8°C is about 5 mils/yr. Assume that this value is accurate enough. The density of Alloy 20 is 499 lb/ft³, and M_p is 50.8. M_p is calculated by multiplying the moles \times valence/2 for each element in an alloy and adding up the total of such terms. Substituting into Eq. (10):

$$L_m = \left(\frac{1}{624 \times 10^3} \right) \left(\frac{5\pi (4.26/12) 9,900 \times 499}{50.8} \right) = 0.87 \text{ moles of } H_2 \text{ generated/wk} \quad (17)$$

The moles of H_2SO_4 in the pipe are:

$$979.9 \text{ ft}^3 \times 115.19 \text{ lb/ft}^3 \times (1/98) \text{ mole/lb} = 1,152 \text{ moles; where } 115.19 \text{ lb/ft}^3 \text{ is the density of sulfuric acid and } 98 \text{ is its molecular weight.}$$

Henry's law constant for H_2 in water at 20°C is 6.83×10^4 atm. Thus:

$$\Delta P_c = (6.83 \times 10^4) [0.87 / (1,152 + 0.87)] = 51.5 \text{ atm, or about } 760 \text{ psi in one week.}$$

A relief valve is needed, since the pressure calculated due to either heat or corrosion (or certainly from both) exceeds the design pressure of the piping.

Richard Greene, Editor

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