Optimal Placement of Relief Devices for Hydrogen Peroxide Pipeline Protection

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Abstract

The causes and effects of hydrogen peroxide decomposition have been widely researched and published. The two most common overpressure phenomena studied are contamination and thermal runaway decomposition. Depending on the cause and concentration, hydrogen peroxide decomposition can generate a large amount of oxygen, resulting in a volume expansion as many as 2,500 times the initial volume. Heat released from the reaction may exceed the rate of heat lost to the surroundings, resulting in temperature increase and further intensifying the rate of decomposition. Relief systems must thus be properly sized in order to protect the equipment from overpressure. While there are various guidelines circulated by leading industry organizations and manufacturers, most have focused on the handling and bulk storage of hydrogen peroxide.

This paper examines an overpressure relief protection for pipeline, specifically designed for hydrogen peroxide transport over an extended distance. Presented as a case study, it includes a series of sensitivity analyses, accounting for all credible overpressure scenarios, to obtain an optimal placement of relief devices along the pipeline. Both contamination and localized abnormal heating are examined for hydrogen peroxide concentrations up to 70 wt%. An assessment on an exposed and insulated pipeline will also be discussed.

1 Introduction

Hydrogen peroxide (HP) is a reactive oxidation chemical. It is known for its environmentally friendly decomposition products. HP is used in various industrial and commercial applications including pulp bleaching, chemical synthesis, and environmental remediation. In addition to the considerable potential energy, the industrial grades of hydrogen peroxide are classified as strong oxidizers and corrosive. Typical industrial products have concentrations with 35%, 50%, and 70 % HP by weight, as aqueous solutions[6]. Table 1 summarizes a general classification based on HP concentrations.

The causes and effects of HP decomposition have been extensively researched and published[1,2,5,6]. It is widely documented that the commercial grades of hydrogen peroxide are basically unstable[1]. HP continuously decomposes and generates heat. Most manufacturer guidelines indicate that HP typically loses less than 1% relative strength per year. At this rate, the heat of decomposition is dissipated readily to the surroundings. When the rate of heat loss to the surroundings is greater than the rate of heat generated, the hydrogen peroxide fluid temperature generally resembles the ambient conditions.

**Table 1: General classification of hydrogen peroxide[3]**

Concentration	Category	Typical Applications
< 8%	Non-hazardous	Toothpaste, general sterilizer, detergent bleach
8-28%	Class 1 Oxidizer	Swimming pool chemical treatment
28-52%	Class 2 Oxidizer; Corrosive and Class 1 Unstable (reactive)	Industrial strength grade
52-91%	Class 3 Oxidizer; Corrosive and Class 2 Unstable (reactive)	Specialty chemical processes
> 91%	Class 4 Oxidizer; Corrosive and Class 3 Unstable (reactive)	Rocket propellent

The two most common HP overpressure phenomena studied are contamination and thermal runaway decomposition. Depending on the cause and concentration, hydrogen peroxide decomposition can generate a large amount of oxygen, resulting in a volume expansion as many as 2,500 times the initial volume[5]. Heat released from the reaction may exceed the rate of heat lost to the surroundings, resulting in temperature increase and further intensifying the rate of decomposition. Relief systems must thus be properly sized in order to protect the equipment from overpressure. While there are various guidelines circulated by leading industry organizations and manufacturers, most have focused on the handling and bulk storage of hydrogen peroxide.

In this paper, we consider pipeline as a means for transporting hydrogen peroxide. We examine the overpressure relief protection for pipeline, specifically designed for hydrogen peroxide transport over an extended distance. Presented as a case study, it includes a series of sensitivity analyses, accounting for all credible overpressure scenarios, to obtain an optimal placement of relief devices along the pipeline. Both contamination and localized abnormal heating are examined for hydrogen peroxide concentration up to 70 wt%. An assessment on an exposed and insulated pipeline will also be discussed.

2 Hydrogen Peroxide Decomposition

Hydrogen peroxide undergoes the following decomposition reaction:

$$H_2O_{2\,(l)} \longrightarrow \frac{1}{2}O_{2\,(g)} + H_2O_{(l)} \quad \Delta H = \text{-98 kJ/mol or -2,882 kJ/kg}$$
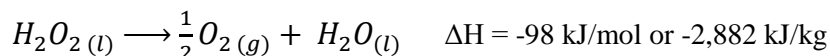
With stabilized, uncontaminated commercial grade HP, the decomposition is very slow[1]. The kinetics of the reaction can be described by the following equation:

$$\frac{d[H_2O_2]}{dt} = -k[H_2O_2]$$

Where:

$$k = 0.81 \cdot 10^7 k_F e^{\frac{-10357}{T}} \quad [\text{min}^{-1}]$$

T is temperature in Kevin and k_F is an acceleration factor [unitless]. For uncontaminated product, $k_F = 1$.

Besides being exposed to an abnormal heat source, contact of hydrogen peroxide with improper materials is one of the primary causes of decomposition. Some common sources of contaminants include transition metals, organic substances, strong acids or bases, groundwater, and dust. The rate of HP decomposition varies, depending on the strength and nature of the impurities exposed.

One way to classify the potential sources of contaminants is to assign each to a level of catalytic activity, represented by the acceleration factor, k_F. For a stabilized and uncontaminated hydrogen peroxide, the product is considered at a normal condition, with the k_F assigned equal to one (1). Table 2 provides some typical k_F values from experimental results for iron content[1].

Table 2: Iron content contamination impact for standard technical grade 70 wt% HP[1]

Iron Content [mg/kg]	k x 10^8 [min^{-1}]$^¥$	Acceleration Factor k_F [unitless]
0.12	0.95	1.46
0.37	3	4.6
7.76	7.56	11.6
15.5	9.42	14.4
31	64.6	98.9
38.8	913	1,398
46.6	6,763	10,366

$^¥$ k values calculated at 25°C

3 Case study

In this paper, we use a practical case study as the basis of our discussions. A major manufacturer has a need to determine how feasible it is to construct a pipeline, transporting hydrogen peroxide product to its customer within a couple of miles away. Since HP is self-reactive, both generating heat and decomposing to form oxygen and water, a major concern is to protect the pipeline from overpressure. The target HP concentrations range from 40 to 70 wt%. The proposed pipeline distance is approximately 10,000 feet, utilizing some existing pipe rack infrastructure. Part of the pipeline may be situated close to public roadway. In addition, certain portions of the pipeline can be in contact with or buried under the ground, a major concern for corrosion/erosion that may cause an increase in metal ions and further HP decomposition.

In this case study, our primary objectives are:

- Determine the critical (maximum) length of a pipe section that can be safely protected with one largest possible relief device

- Present a sound methodology for modeling pipeline relief protection

- Suggest some credible scenarios for pipeline protection considerations

As a result of the maximum pipe length established, we would be able to determine the proper number and placement of relief devices along the entire pipeline.

Table 3 provides a summary of the pipeline considered in this study. The pipeline is designed per ANSI B31. As a result, the pressure rating may be exceeded by 33%. It is assumed that the design scenario does not last more than 10 hours per upset and does not last more than 100 hours per year.

The pressure at the source of the pipeline is approximately 155 psig. All our analyses assume the pipeline to be blocked in at 155 psig and 110°F.

Table 3: Pipeline case study specifications

Parameter	Description
Pipeline size/length	3" schedule 40, 304L stainless steel; 10,000 feet
Pipeline pressure rating	1300 psig at 600°F
Pipe surface roughness	0.00046 m
Design basis	ANSI 31; maximum allowable accumulated pressure, 33%
HP concentrations considered	43 wt% and 70 wt%
Normal/max. operating pressure	150/155 psig
Normal/max. operating temperature	80/110°F
Relief protection device	3L4, set at 170 psig
Surrounding conditions	Stability class D, 5 m/s wind, 105°F ambient temperature

4 Study Approach

The case study was performed using SuperChems™, a detailed dynamic simulator and a component of ioMosaic's Process Safety Office®. The program consists of various models for simulating the fluid dynamics of vessels and pipeline containing multi-phase fluids.

To account for detailed equipment wall and fluid heat transfer dynamics, the simulated equipment is segmented into multiple zones, as shown in Figure 1[4,7]. Detailed heat transfer to/from the surroundings and between the zones are dynamically accounted for. There is no limit on the number of zones a user can specify. The ability to distribute an equipment into multiple segments allows users to closely examine the dynamics of the fluids and equipment wall thermal effects. Other valuable applications of the segmentation approach include the modeling of detailed insulation, external fire, localized heating, and flame jet impingement.
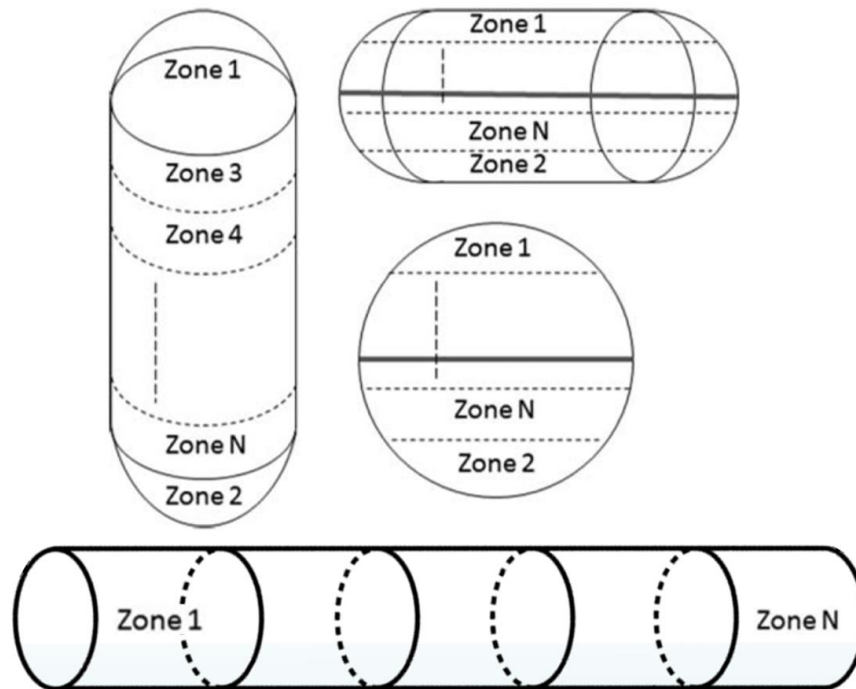
Figure 1. Samples of Equipment Segmentation Scheme

Figure 2 illustrates a simple representation of the pipeline. It illustrates the pipeline being divided into ten segments. As shown, various options are exposed allowing users to specify what to be considered. In our case study, we enable all piping to be visible to solar heating. For external fire, we want to examine what happens if a certain segment is engulfed and visible to fire. To consider insulation, its thickness and relevant properties must be specified (not shown in the figure).

Table 4 summarizes some calcium silicate insulation properties used in this study.

Heat Transfer Segment	Visible to Fire	Engulfed by Fire	Protected by Water Spray	Visible to Solar Heating
Bottom Segment 0 -> 1	☐ Yes	☐ Yes	☐ Yes	☑ Yes
Segment 1 -> 2	☐ Yes	☐ Yes	☐ Yes	☑ Yes
Segment 2 -> 3	☐ Yes	☐ Yes	☐ Yes	☑ Yes
Segment 3 -> 4	☐ Yes	☐ Yes	☐ Yes	☑ Yes
Segment 4 -> 5	☑ Yes	☑ Yes	☐ Yes	☑ Yes
Segment 5 -> 6	☐ Yes	☐ Yes	☐ Yes	☑ Yes
Segment 6 -> 7	☐ Yes	☐ Yes	☐ Yes	☑ Yes
Segment 7 -> 8	☐ Yes	☐ Yes	☐ Yes	☑ Yes
Segment 8 -> 9	☐ Yes	☐ Yes	☐ Yes	☑ Yes
Top Segment 9 -> 10	☐ Yes	☐ Yes	☐ Yes	☑ Yes

Figure 2. Sample of pipeline segmentation specifications

Table 3: Calcium Silicate Insulation Properties

Temperature [ºC]	Density $^\gamma$ [kg·m^{-3}]	Specific heat capacity $^\gamma$ [J·kg^{-1}·C^{-1}]	Thermal Conductivity [W·m^{-1}·ºC^{-1}]
93	288	710	0.078
149	288	710	0.084
204	288	710	0.088
260	288	710	0.092
315	288	710	0.097
370	288	710	0.101
427	288	710	0.105
482	288	710	0.108
538	288	710	0.111

$^\gamma$ *Both insulation density and specific heat capacity are considered constant*

Pipeline has a rather unique configuration. For emergency venting design, its geometry is not generally favorable for a complete vapor-liquid disengagement. On the other hand, its high surface area to volume ratio has a major advantage, providing ample medium for detailed heat transfer considerations. Given its uniqueness, we consider the following assumptions as part of the relief sizing modeling:

- A hydrogen peroxide runaway reaction in a designated pipe section will create a vapor bubble within that section

- The pressure accumulation in the designated section will push the liquid out on both sides of the pipe to accommodate the rapid volume increase caused by the gas generation

- Pressure loss due to friction and the presence of fittings influences the pressure accumulation in the pipe (volume created by driving the liquid out versus volume generated by the reaction)

- Given unfavorable geometry, two-phase flow is assumed, representing a more stringent design

- Since pipeline size is 3", the largest PSV can be installed is equivalent to an 3L4 API orifice

The primary cases considered in this study are summarized in Table 4. All cases assume that a designated pipe section is protected by a single relief device. Each designated pipe section has uniform decomposition and contamination. In the first case, we want to establish a baseline, worst-case scenario by assuming that the designated pipe section is under adiabatic conditions. It implies that there is no heat transfer considered

between the pipeline fluid and the surroundings. Given the proposed relief device and its set point, we want to understand the overpressure impacts at different pipe section lengths and various contamination levels for HP concentrations of 43 wt% and 70 wt%. Ultimately, we want to find the maximum (critical) pipe section that can safely be protected by one 3L4 relief device.

Based on the insights obtained from the adiabatic analyses, we would pick a pipe length as the primary pipe section for the subsequent evaluations. Accounting for potential contact with soil and groundwater, we use 1,500 as the acceleration factor (k_F), forming the basis for product contamination. Though it is slightly conservative, k_F equaling 1,500 is reasonably consistent with the CEFIC's suggestion (1,000) for the design of a safety vent[1].

The subsequent cases consider detailed heat transfer to and from surroundings. Although we can consider partially buried or shaded segments, our primary focus in this case study is to examine a bared, fully exposed pipeline. We then want to compare with situations where a full insulation is considered.

While there are no flammable liquids neighboring the pipeline infrastructure, the pipeline exposed to an abnormal heat source is a possibility. Notice the case study states that the pipeline may be situated close to a public roadway. It is known that truck carrying flammable materials using the nearby public road is a common occurrence. A concern is that there might be incidents involved truck rollover or spills of flammable liquids along the pipeline. As a result, a localized fire or flame impingement is credible.

By evaluating all these sensitivity cases, our ultimate objective is to find an optimal replacement of relief devices along the pipeline proposed.

Table 4: Summary of Sensitivity Analysis Cases

Case	k_F	Description
Adiabatic Pipeline	Varied	Both 43 wt% and 70 wt% HP, assuming adiabatic conditions for various contamination levels and pipe sections
Bared Pipeline	1,500	70 wt% HP, exposed pipeline and accounted for immediate surroundings
Insulated Pipeline	1,500	70 wt% HP, assuming 1" calcium silicate insulation, accounted for immediate surroundings
Fire Exposed Pipeline	1	70 wt% HP, uncontaminated, with localized fire exposure, accounted for immediate surroundings

5   Results Analysis

The sensitivity analyses of different pipe section lengths and contamination levels are shown in Figures 3 through 5. All cases assume adiabatic conditions. Each pipe section is equipped with one relief device equivalent to an 3L4 API orifice. Figure 3 illustrates the results for a 4,000-feet pipe section with 43 wt% HP. At acceleration factor (k_F) equal to 1,500 or higher, the simulations show that accumulated pressures exceed the maximum allowable accumulated pressure (MAAP), which is 1729 psig. On the other hands, the pipe section can safely be protected with k_F equal to 150 or lower.

For a smaller pipe section with 2,000 feet, Figure 4 shows that it is still impractical to protect the pipeline with k_F at 15,000 or higher. At k_F equal to 1,500, the simulations show that the accumulated pressure is 1,300 psig, which is below the MAAP. Since we apply 1,500 as the k_F level for vent sizing, the results indicate that a 2,000-feet pipe section is acceptable for 43 wt% HP.
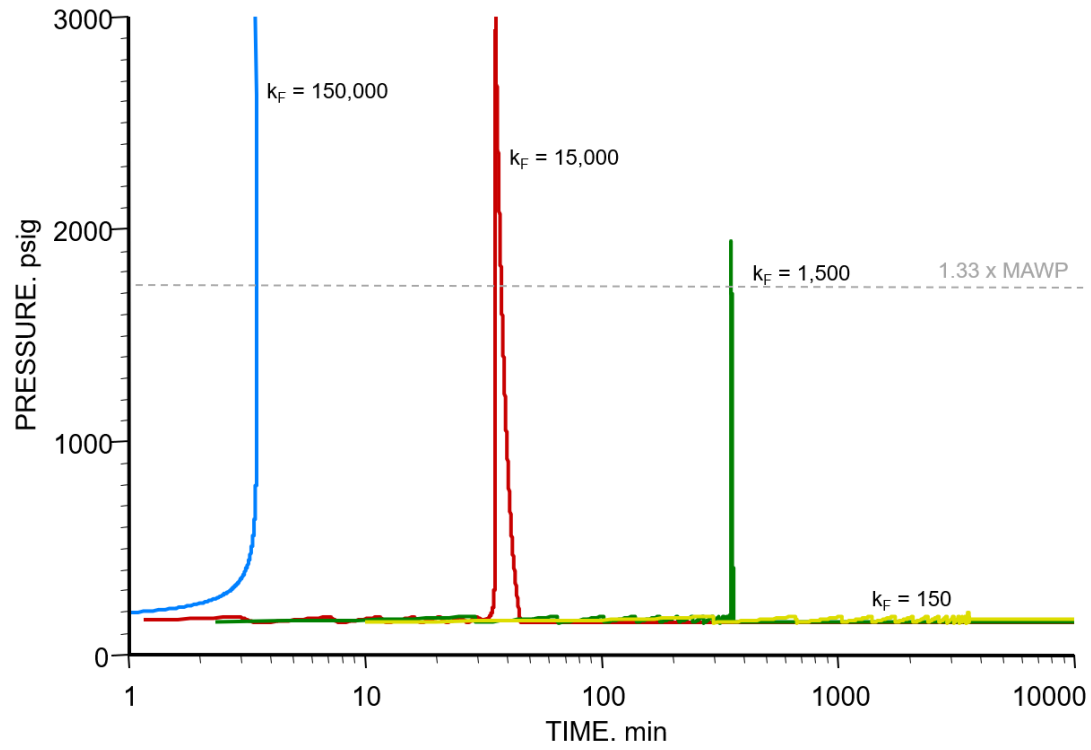
Figure 3. 4,000-feet, 43 wt% HP Pipeline at Different Levels of Contaminations (Adiabatic)
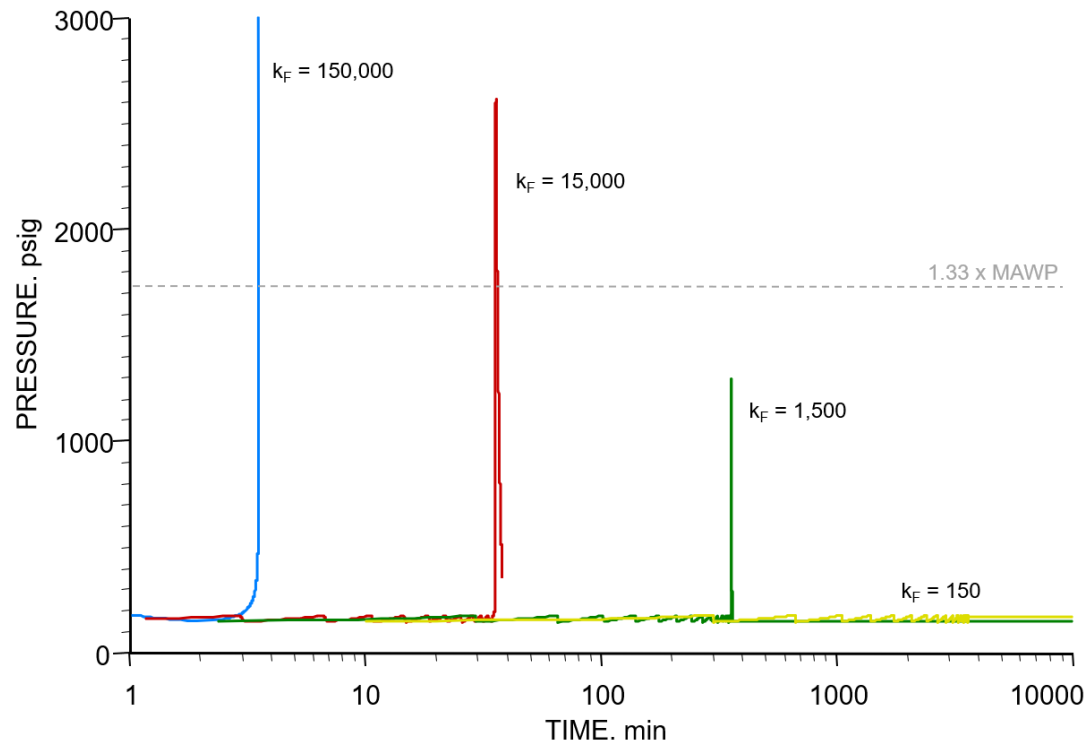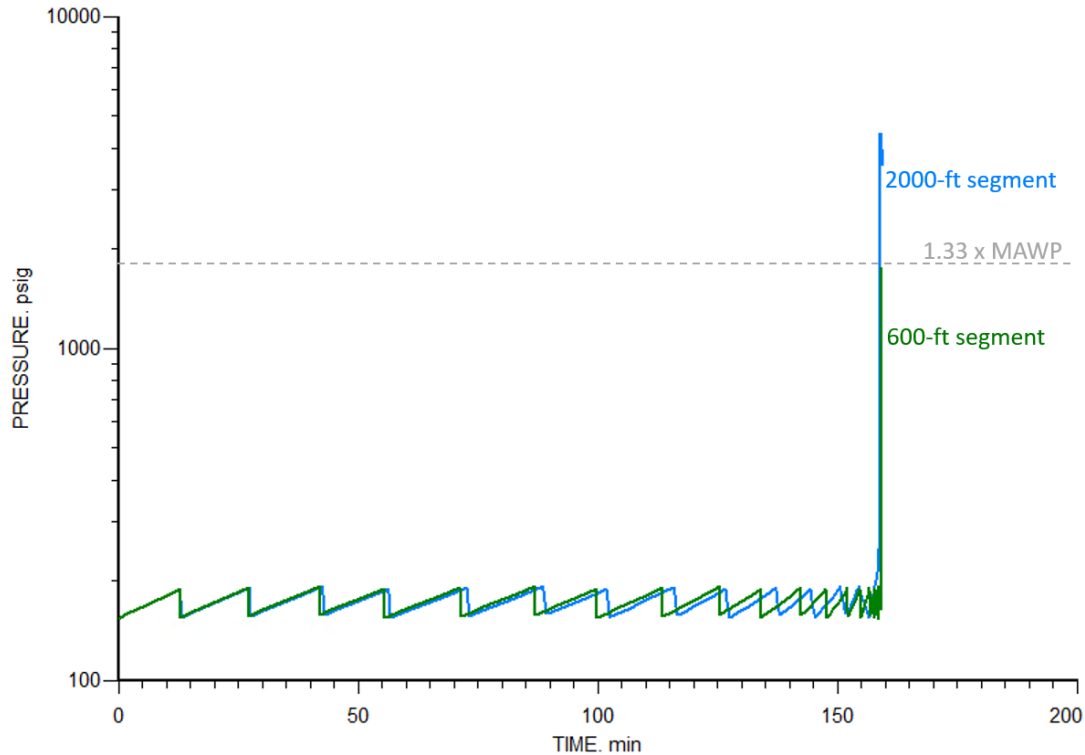

Figure 4. 2,000-feet, 43 wt% HP Pipeline at Different Levels of Contaminations (Adiabatic)

Figure 5. Comparison of different adiabatic pipeline segment lengths with 70 wt% HP (k_F = 1,500)

Figure 5 shows the simulations for 70 wt% HP concentration. As expected, higher HP concentrations would generate greater overpressure impacts. Based on the 2,000-feet pipe section, the simulation shows that the accumulated pressure reaches 4,500 psig, which far exceeds the MAAP. The overpressure is far worse than the longer 4,000-feet pipe section (43 %wt HP) at the highest considered acceleration factor (see Figure 3). In order to stay within the MAAP for 70 wt% HP, the pipe section must be shortened to 600 feet.

Although the adiabatic assumptions result in rather conservative accumulated pressure consequences, the simulations give us some insights. First, these cases confirm that it is almost impractical to protect the pipeline with high contamination level, where k_F is at or above 1,500. They illustrate the sensitivity and correlations among different concentrations and pipe sections considered. Second, these simulations help set the boundaries for the lower and upper worst-case scenarios. At 43 wt% HP, the critical (maximum) length that can be safely protected by a 3L4 relief device is 2,000 feet. As a lower worst-case limit, the 2,000-feet pipe section is a logical option selected as the basis for further evaluation, as described below.

Impact of detailed heat transfer considerations

Based on the 2,000-feet pipe section selected, Figures 6 through 8 show the pressure, temperature, and venting dynamics for the 70 %wt HP. The simulations consider the entire pipe section exposed to the given surrounding conditions. Detailed heat transfer from and to the surroundings are accounted for, including the impact of site location and full cycles of solar fluctuations. As shown in Figure 6, the pipeline fluid temperature rises and falls following the solar patterns. It should be noted that the pipeline fluid is heating up due to both self-heating and heat absorption from solar radiation. During the day, the heat generated and absorbed from solar radiation are greater than that dissipated to the surroundings. Consequently, both temperature and pressure rise.
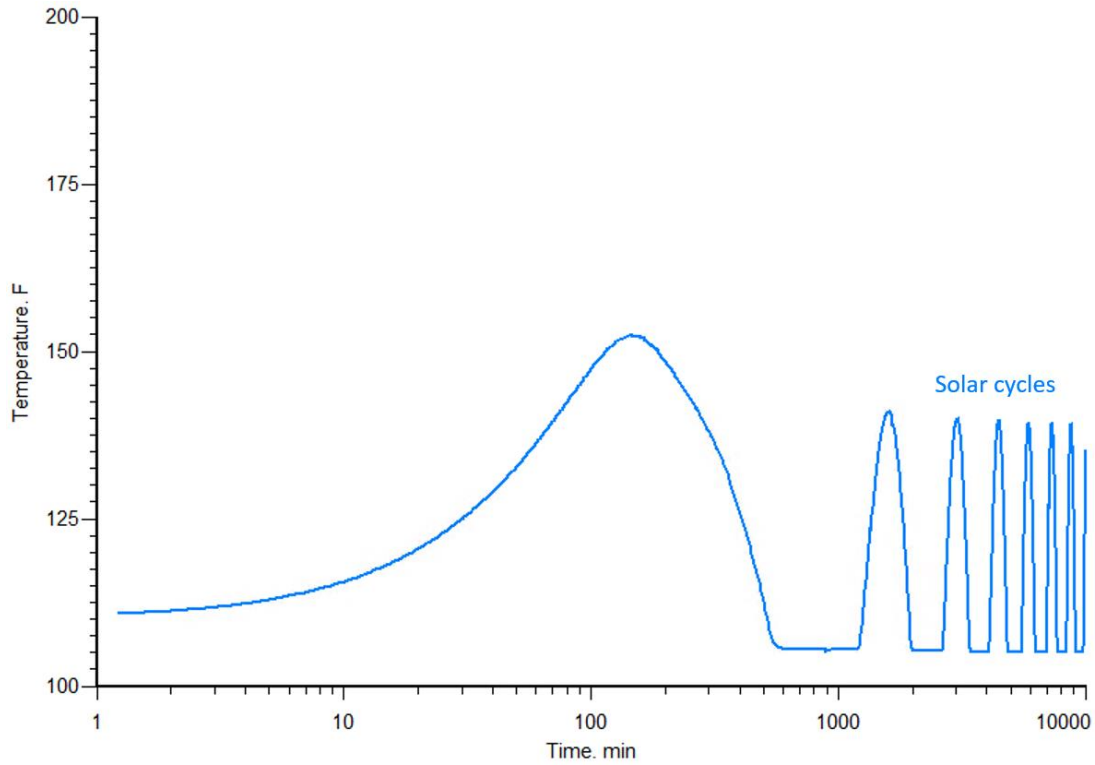
Figure 6. Exposed 2,000-feet pipeline with 70 wt% HP (k_F = 1,500) shows fluid temperature follow solar cycles
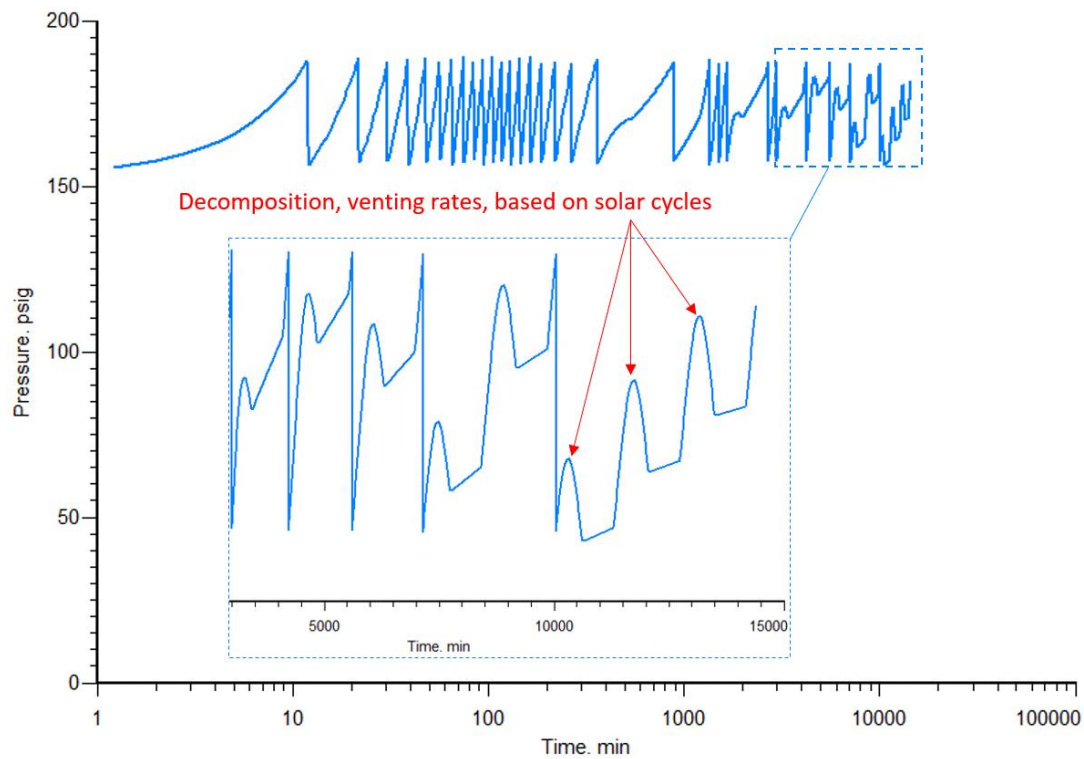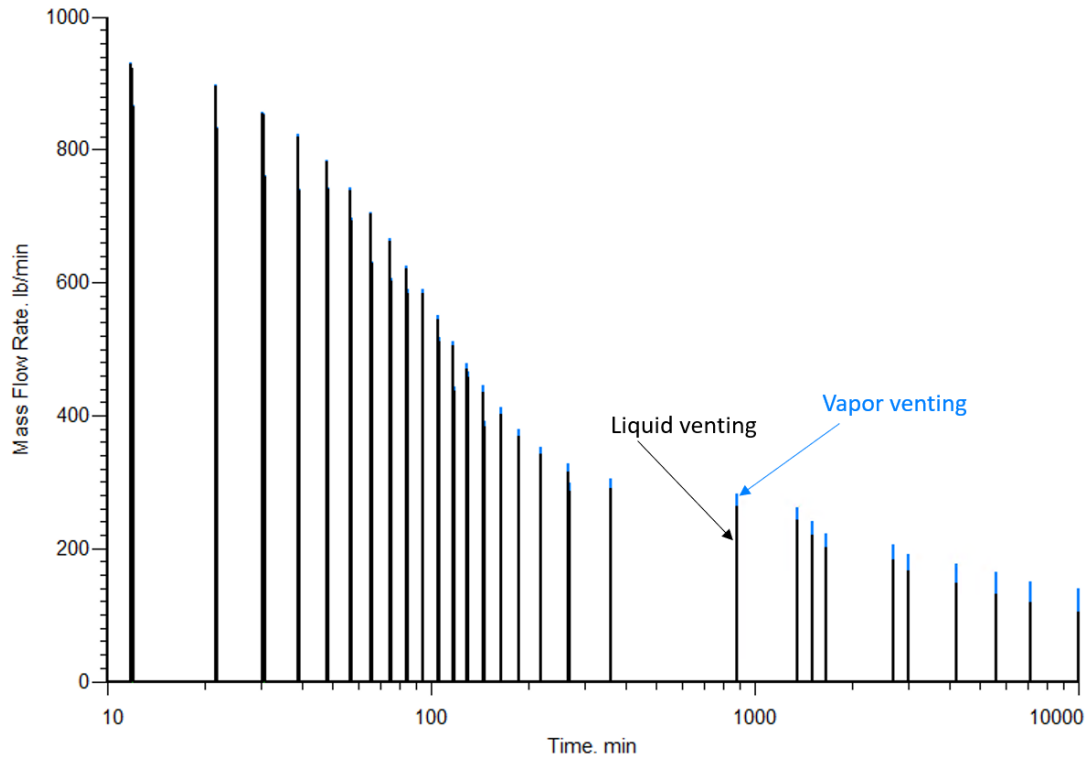

Figure 7. Exposed 2,000-feet pipeline with 70 wt% HP (k_F = 1,500) shows adequate protection

Figure 8. Venting profiles with the exposed 2,000-feet pipeline with 70 wt% HP (k_F = 1,500)

As the day turns into night, the solar impact is gradually diminished, resulting in reduced HP decomposition activities and self-heating. Ultimately, the pipeline fluid temperature equalizes with the surrounding temperature.

Figures 7 and 8 show that the relief valve opens as needed, dispelling the fluid to make room for the gas generated. Initially, there are mostly liquid being forced out. As the pipeline inventory depletes, there are more room for gas, resulting in higher vapor quality and lower mass venting. Note that while the fluid pressure may to follow the patterns of solar cycles, the valve lifting may not.

In this simulation, the results show that the 2,000-feet pipe section is adequately protected for up to at least 70 wt% HP. The analysis confirms the pipeline's unique advantage. Its high surface area to volume ratio indeed enhances heat transfer mechanisms and pipeline protection.

Impact of pipeline insulation

Although there are many practical applications and remedies for insulation, insulating pipeline with self-heating fluid such as hydrogen peroxide is generally not advisable. Figures 9 and 10 show what happen when insulation is considered. In this case, a 1-inch of calcium silicate insulation (see Table 3) is applied to the same 2,000-feet pipe section. As shown in both figures, the heat dissipated to the surroundings is considerably less than the heat self-generated, resulting in significant temperature rise. Note that comparing with the adiabatic assumptions, the insulated pipeline shows some heat shedding. First, the accumulated pressure does not reach the MAAP. Second, it is further evident by the delay in the temperature and pressure rise. One thing worth pointed out is that the bare (exposed) pipeline has a higher initial temperature rise. This is because the bare pipeline is initially heated by solar radiation, which accelerates HP self-heating decomposition resulting in temperature increase. On the other hands, the adiabatic and insulated cases, while not fully heated by solar, have no or limited means to dissipate the heat to the surroundings.
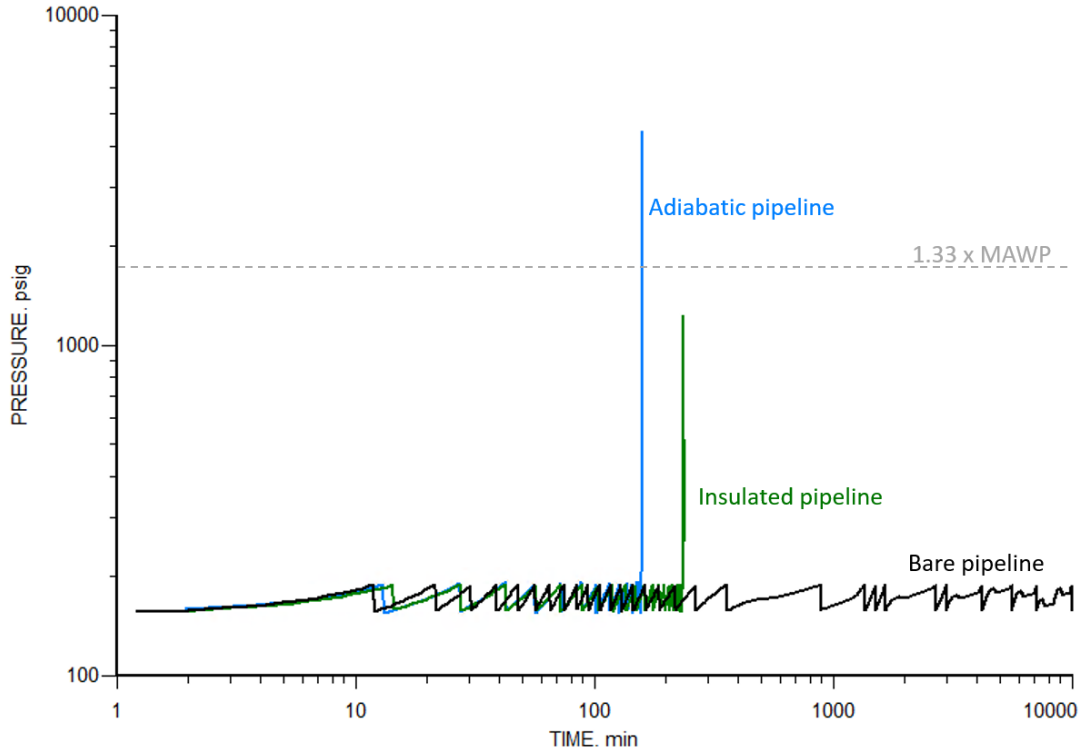
Figure 9. Pressure impact comparison for the 2,000-feet 70 wt% HP pipeline (k_F = 1,500)
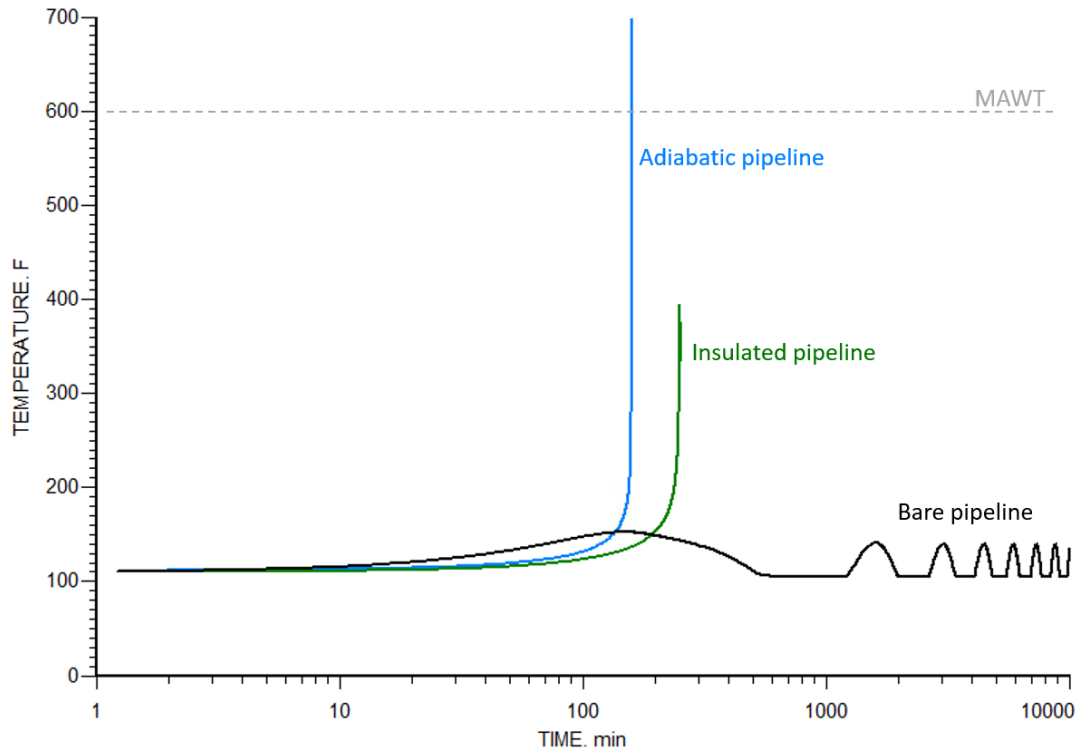

Figure 10. Temperature impact comparison for the 2,000-feet 70 wt% HP pipeline (k_F = 1,500)

Impact of localized fire exposure

Fire or abnormal heating input on pressure equipment is generally undesirable. It is particularly so when the system contains material with potential for exothermic runaway. In this case study, we want to examine what happens when a certain portion of the HP pipeline is exposed to fire. Note we consider hydrogen peroxide at its normal, uncontaminated condition (k_F=1) in all fire exposure cases. Using the same 2,000-feet pipe section, we want to further evaluate how much of the pipe section can be exposed to fire without overpressurizing the pipeline. As shown in Figure 2, a designated pipe section can be further divided into multiple segments. For example, dividing the 2,000-feet pipe section into ten (10) would result in ten 200-feet segments. Each segment has its own attributes. For instance, each segment can be designated as exposed to fire, visible to solar, being buried, or insulated. Likewise, if evaluating a 100-feet segment is required, the 2,000-feet pipe section should be divided into 20 segments.

Figure 11 shows a series of simulations, considering fire exposed on segments up to 10% (200-feet) of the 2,000-feet pipe section. All cases contain 70 wt% HP. The simulations indicate that 10% of the 2,000-feet pipe section exposed to fire would generate pressure up to 1,900 psig, which exceeds the MAAP. At 165-feet or shorter lengths exposed to fire, the accumulated pressures are well below the MAAP. It can thus be concluded that the given 2,000-feet pipe section is adequately protected for up to 8% (165-feet) of the pipe exposed to fire. Note that although detailed heat transfer is accounted in this situation, its impact is insignificant. This is because the heat rate dissipated the surroundings is diminutive compared to the intense heat from the fire and the self-heating generated from the accelerating reactions.

Figure 12 shows the pipeline wall temperatures as a function of time for the 200-feet fire exposure. Note that (a middle) segment 4 is picked as the portion of the pipeline exposed to fire. As shown, wall temperature for segment 4 is heated up rather quickly. It ultimately approaches the flame temperature while the other segments are hovering around the design temperature of the pipeline.
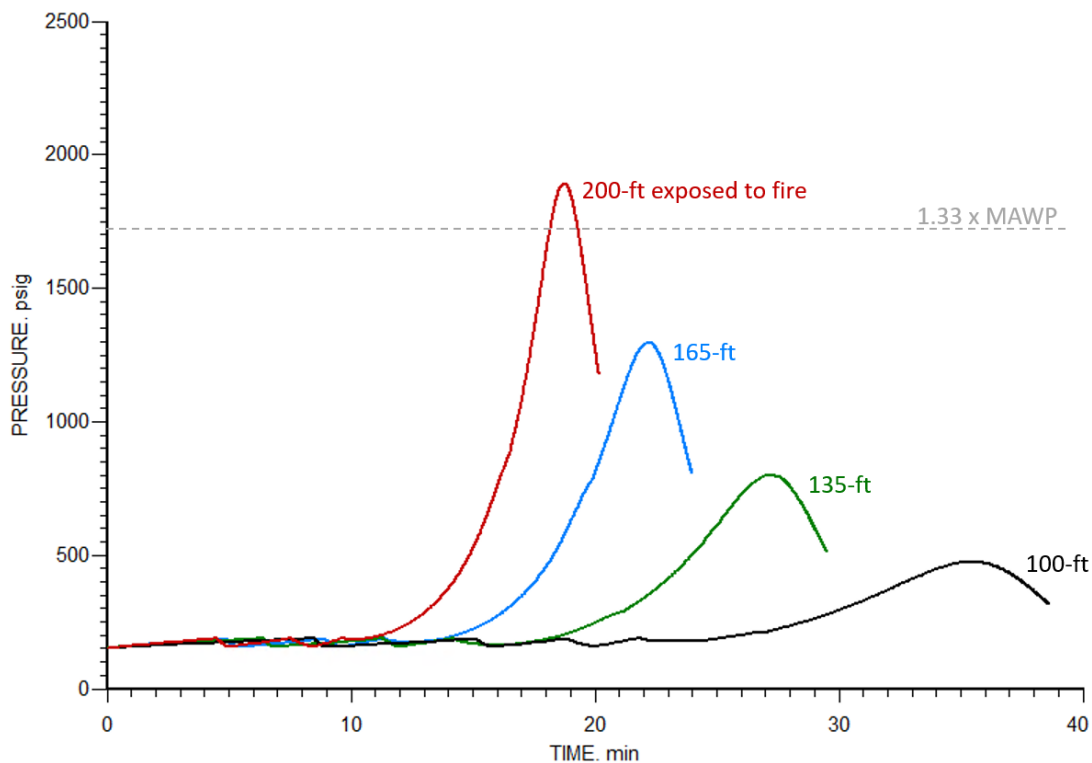

Figure 11. Fire exposure impact for the 2,000-feet 70 wt% HP pipeline (k_F = 1)
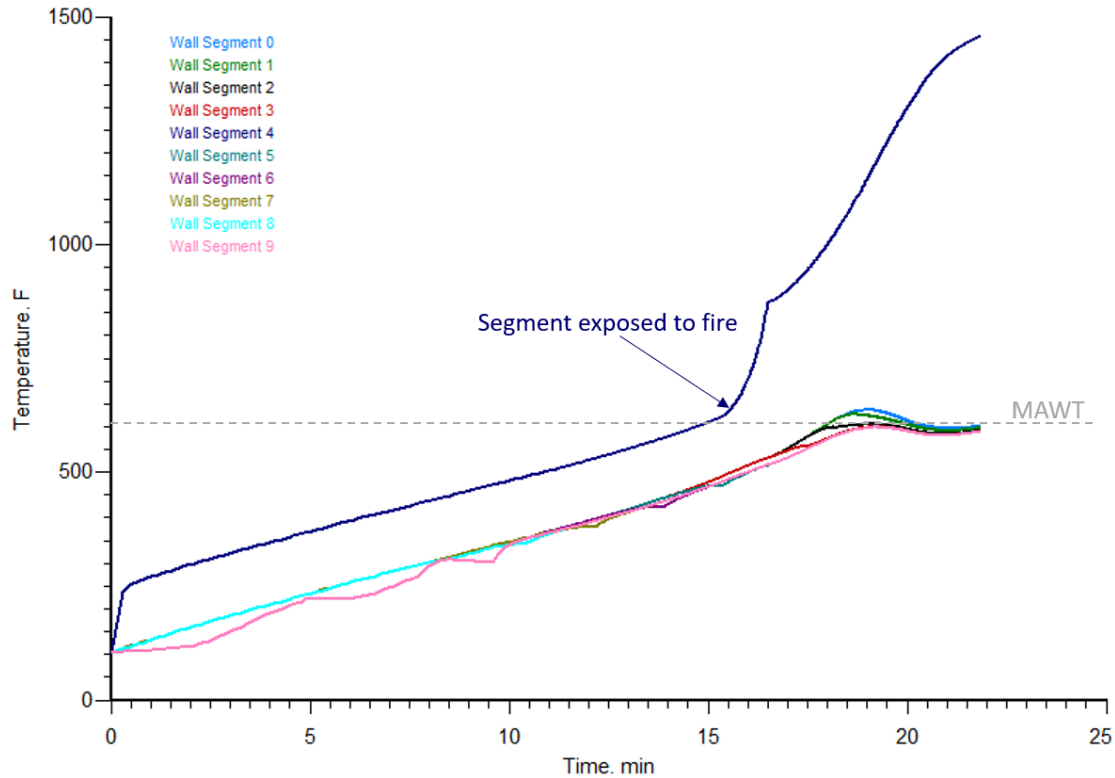
Figure 12. Segment temperature profiles of the 2,000-feet 70 wt% HP pipeline ($k_F = 1$)

In summary, all credible overpressure scenarios should be considered as part of pipeline relief protection. Based on the approach and assumptions stated, each relief device 3L4 is found adequate to protect a maximum length of 2,000 feet from its location. Accounting for both directions from its placement, one relief device is thus equipped to protect up to 4,000-feet section. The design basis in this case study is fire exposure for up to 165 feet per 2,000-feet pipe section.

Given the 10,000-feet pipeline, a total of three 3L4 relief devices are thus required. Figure 13 shows a proposed placement of relief devices along the pipeline. Starting from the left end (0 feet), the first device PSV-1 should be situated at 1,000 feet mark. It is designed to protect the pipeline from the left end up to mark point 3,000 feet. The second device (PSV-2 placed at 5,000 feet mark), is designed to protect the pipe sections from point 3,000 to 7,000 feet. Lastly, PSV-3 is placed at 9,000 feet mark, which is designed to protect the pipe sections from 7,000 feet to the end of the pipeline.
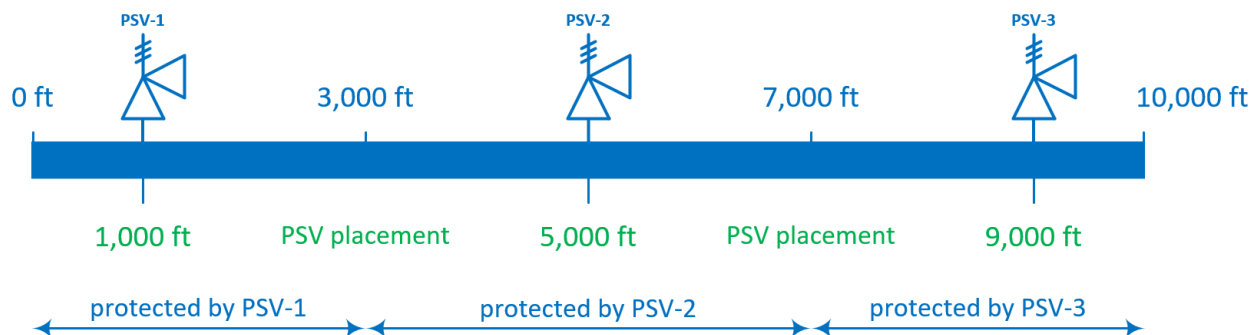

Figure 13. Proposed placement of relief devices along the 10,000-feet pipeline

6 Conclusions

Pipeline has a rather unique configuration. Its high surface area to volume ratio has a major advantage, providing ample medium for detailed heat transfer considerations. Given that hydrogen peroxide is self-reactive and self-heating, detailed heat transfer mechanisms from and to the surroundings should be accounted for, including the impact of site location and full cycles of solar thermal radiation.

The pipeline segmentation used in this paper demonstrates a reliable approach for modeling detailed pipe segments and wall dynamics. It provides engineers with sound tools to properly evaluate the causes and effectively address the consequences.

In order to protect the entire pipeline, all credible overpressure scenarios must be considered. In accordance with the basis and assumptions outlined, each relief device 3L4 is found adequate to protect a maximum length of 2,000 feet from within its location. Accounting for both directions from its placement, one relief device is thus equipped to protect up to 4,000-feet pipe section. Given the 10,000-feet pipeline, a total of three 3L4 relief devices are required.

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