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Pressure Systems Stored-Energy Threshold Risk Analysis

SS Paulsen

August 2009



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Pacific Northwest National Laboratory
Richland, Washington 99352

Summary

Federal Regulation 10 CFR 851, which became effective February 2007, brought to light potential weaknesses regarding the Pressure Safety Program at the Pacific Northwest National Laboratory (PNNL). The definition of a pressure system in 10 CFR 851 does not contain a limit based upon pressure or any other criteria. Therefore, the need for a method to determine an appropriate risk-based hazard level for pressure safety was identified. The Laboratory has historically used a stored energy of 1000 lbf-ft to define a pressure hazard; however, an analytical basis for this value had not been documented. This document establishes the technical basis by evaluating the use of stored energy as an appropriate criterion to establish a pressure hazard, exploring a suitable risk threshold for pressure hazards, and reviewing the methods used to determine stored energy. The literature review and technical analysis concludes the use of stored energy as a method for determining a potential risk, the 1000 lbf-ft threshold, and the methods used by PNNL to calculate stored energy are all appropriate. Recommendations for further program improvements are also discussed.

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1.0 Introduction

1.1 Background

Title 10, Part 851, Code of Federal Regulations (10 CFR 851) establishes worker safety and health requirements to govern contractor activities on U.S. Department of Energy (DOE) sites. This regulation went into effect on February 9, 2007. Pressure Safety is one of the disciplines specifically covered by this regulation, as detailed in Appendix A, Section 4. Section 851.3 defines pressure systems as “all pressure vessels, and pressure sources including cryogenics, pneumatic, hydraulic, and vacuum. Vacuum systems should be considered pressure systems due to their potential for catastrophic failure due to backfill pressurization. Associated hardware (e.g., gauges, and regulators), fittings, piping, pumps, and pressure relief devices are also integral parts of the pressure system.”

Appendix A, Section 4 states “contractors must establish safety policies and procedures to ensure that pressure systems are designed, fabricated, tested, inspected, maintained, repaired, and operated by trained and qualified personnel in accordance with applicable and sound engineering principles.” The regulation goes on to state that all pressure systems and components shall conform to the applicable American Society of Mechanical Engineers (ASME) Boiler and Pressure Vessel Code, ASME B31 (Code for Pressure Piping), and the strictest applicable state and local codes. Part (c) further states, “When national consensus codes are not applicable (because of pressure range, vessel geometry, use of special materials, etc.), contractors must implement measures to provide equivalent protection and ensure a level of safety greater than or equal to the level of protection afforded by the ASME or applicable state or local code. Measures must include the following:

- (1) Design drawings, sketches, and calculations must be reviewed and approved by a qualified independent design professional (i.e., professional engineer). Documented organizational peer review is acceptable.
- (2) Qualified personnel must be used to perform examinations and inspections of materials, in-process fabrications, non-destructive tests, and acceptance test.
- (3) Documentation, traceability, and accountability must be maintained for each pressure vessel or system, including descriptions of design, pressure conditions, testing, inspection, operation, repair, and maintenance.”

Pacific Northwest National Laboratory has implemented a graded approach to Pressure System safety based upon the level of risk associated with varying categories of pressure systems to conform to the regulation. There is no pressure limit or other variable defining a pressure system in 10 CFR 851. Therefore, PNNL has established a pressure system level based upon stored energy, which poses minimal risk to PNNL staff during operations.

Stored energy has been used by PNNL as the basis for recognizing a significant pressure risk for over 20 years. Historically, multiple approaches have been implemented throughout the DOE Complex for pressure related risk identification and an inter-laboratory consensus standard has not been developed. The existing threshold limit at PNNL is 1000 lbf-ft of stored energy. Below this limit there are minimal requirements and no formal approvals are required. The stored energy has historically been calculated for gases or vapors above the boiling point by assuming isentropic expansion as shown in equation 1.1 (Lindeburg 2001).

$$W = \frac{P_1 \cdot V_1}{k - 1} \left[1 - \left(\frac{P_2}{P_1} \right)^{\frac{(1-k)}{k}} \right] \quad (1.1)$$

Where:

W = Work Energy
k = Ratio of Specific Heats
P₁ = Initial Pressure
P₂ = 2nd State Pressure
V₁ = Initial Volume

For liquids below their boiling point, the stored energy is calculated using the bulk modulus of the liquid, or a conservative value if one is unknown. Equation 1.2 was implemented at PNNL due to its use in the Lawrence Livermore National Laboratory (LLNL) Pressure Safety Manual.

$$W = \frac{1}{2} \cdot \beta \cdot P^2 \cdot V \quad (1.2)$$

Where:

W = Work Energy
V = Initial Volume
β = Compressibility (1/Bulk Modulus)
P = Pressure

1.2 Purpose

The purpose of this analysis is to show that establishing 1000 lbf-ft store energy as the upper boundary for pre-approved pressure systems is a reasonable, and more importantly, safe approach that limits the hazards associated with pressure systems while not impeding research.

The remainder of this document will:

- Evaluate the use of stored energy as an appropriate hazard criterion.
- Evaluate the methods used to determine stored energy.
- Establish an acceptable level of risk, or threshold value, with regard to operation of pressure systems.

Note: Formal approval to design and operate pressure equipment that is below the acceptable risk level is not required (i.e., this type of system is considered minimal-action as defined by PNNL).

1.3 Approach

The approach taken within this analysis to accomplish the three purposes was to:

- Review literature regarding compressed gas stored energy and consequences from an over-pressure event.

- Use an alternative method for determining blast wave pressure based upon gas expansion per the Ideal Gas Law as a baseline check of the values obtained by more extravagant methods.
- Evaluate the effects of a resultant blast wave pressure for a given stored energy versus relevant consequence criteria. The stored energies evaluated were 1000 lbf-ft, 1 lbf-ft, 500 lbf-ft, and 10000 lbf-ft.
- Compare stored energy for typical items encountered at home and in a laboratory versus the 1000 lbf-ft threshold to evaluate if this value is reasonable.

2.0 Literature Review

A review of Lees' Loss and Prevention in the Process Industries, the Fire Protection Handbook (FPH), twentieth edition, Los Alamos National Laboratory (LANL) policy P101-34, Pressure, Vacuum, and Cryogenic Systems, ASME PCC-2 - 2008 Repair of Pressure Equipment and Piping, and the LLNL Pressure System and Design Manual reveals stored energy is a widely used method to evaluate pressure risk. Methods for determining the stored energy due to gas expansion, liquid compression, non-ideal gas, vapor, and flashing liquid are discussed in various sections of each document.

Three major hazards are associated with pressure systems—fire, explosion, and toxic release. At PNNL, fire and toxic hazard mitigation are integrated into the Pressure Safety Program through the Chemical Process and Pressure Systems Permit processes, by the proposed integration of compressed gas pipe codes into the PNNL Engineering Standards, and Fire Protection Engineer reviews.

Lees' (2005) states, "Explosions in the process industries cause fewer serious accidents than fire but more than toxic release. When [toxic releases do] occur, however, they often inflict greater loss of life and damage than fire. Explosion is usually regarded as having disaster potential greater than that of fire but less than that of toxic release." This document focuses on the explosive hazard associated with pressure systems.

2.1 Explosion Energy

An explosion is a rapid and violent release of energy that produces potentially damaging pressures. Lees' (2005) breaks down explosions into 3 main types—physical energy, chemical energy, and nuclear energy. Nuclear explosions are not a part of this analysis.

"Physical energy may take such forms as pressure energy in gases, strain energy in metals, or electrical energy. Examples of the violent release of physical energy are the explosion of a vessel due to high gas pressure and the sudden rupture of a vessel due to brittle fracture (Lees' 2005)." Thermal energy is usually linked to failure, but does not contribute to explosion energy. For example, accidental flashing of a superheated liquid due to pressure reduction or introducing a fluid to a surface with a temperature well above its boiling point has explosive potential.

Lees' continues, "Chemical energy derives from a chemical reaction. Examples of the violent release of chemical energy are explosion of a vessel due to combustion of flammable gas, and explosion of a reactor caused by decomposition of reaction products in a runaway chemical reaction. Chemical explosions are either (1) uniform explosions or (2) propagating explosions. An explosion in a vessel tends to be a uniform explosion, while an explosion in a long pipe gives a propagating explosion. (2005)" **Note:** Chemical explosions potential is limited at PNNL by Fire Protection Engineering policies and procedures, such as the Chemical Process Permit.

Lees' Section 17.4 discusses stored energy in great detail. Lees' references the equations PNNL currently uses for gas expansion stored energy and liquid expansion energy. Section 17.4.4 discusses vessel metal strain energy and concludes "the elastic strain energy of the metal is usually small compared with the chemical and fluid expansion energies (Lees' 2005)," and is therefore excluded from this analysis.

The following sections discuss in greater detail calculating stored (explosive) energy for ideal gas expansion, liquid compression, non-ideal gas, vapor, and flashing liquid.

2.1.1 Compressed Gas Energy

Lees' Section 17.4.5 discusses vessel burst energy for ideal gases. Four separate equations (2.1 - 2.4) from this section and their validity for compressed gas expansion are discussed below.

$$E_{Br} = \frac{(P_1 - P_0) \cdot V}{k - 1} \quad (2.1)$$

Brode

$$E_{Ba} := \frac{P_1 \cdot V_1}{k - 1} \left[1 - \left(\frac{P_0}{P_1} \right)^{\frac{(k-1)}{k}} \right] \quad (2.2)$$

Baker (isentropic; consistent with PNNL Stored Energy Worksheet)

$$E_{Ki} = nRT \cdot \ln \left(\frac{P_1}{P_0} \right) \quad (2.3)$$

Kinney

$$E_{AG} = \frac{P_1 \cdot V_1 - P_0 \cdot V_2}{k_1 - 1} + \frac{P_0 \cdot (V_2 - V_1)}{k_0 - 1} \quad (2.4)$$

Aslanov-Golinsky

Where:

- E_x = Work Energy
- k_1 or k = Ratio of Specific Heats (elevated pressure condition)
- k_0 = Ratio of Specific Heats (ambient conditions)
- P_1 = Initial Pressure
- P_0 = Ambient Pressure
- V = Volume
- n = Number of Moles
- R = Gas Constant
- T = Temperature

Comparisons of the expressions for the energy of explosions given by Strehlow and Ricker (1976) and the Center of Chemical Process Safety (1994/15) both recommend the use of the Brode equation (2.1). The main alternative equation is that of Baker (2.2), which is used by PNNL, Idaho National Laboratory, LLNL, and historically by LANL. Furthermore, ASME PCC-2, Article 5.1, Appendix II (2008) uses a form of Baker to calculate the stored energy for pneumatic pressure testing. Lees' Figure 17.6 and the associated discussion states "...the values yielded by the other expressions (Author's Note: Equations 2.3 and 2.4 above) tend to those of the Brode equation at higher pressures... (Lees' 2005)."

The findings in Lees' that indicate stored energy is an appropriate method to determine the consequences of a compressed gas overpressure event are supported in the FPH. Section 2, Chapter 8,

“Explosions,” states, “A burst pressure vessel releases its energy of compression in the time it takes for a crack to propagate sufficiently far to allow the metal shell to split open. This is typically on the order of 10 microseconds. The peak pressure is approximately equal to the vessel pressure at the time of bursting, P_b (FPH 2008).” Similarly, the FPH uses the Brode equation (2.1) to generate a theoretical stored energy.

2.1.2 Energy in Liquids Below Boiling Point

Liquids are much less compressible than gases when exposed to pressure, and therefore a different method for calculation of stored energy is required. Calculation of the stored energy for liquids below the boiling point is discussed in Lees’ Section 17.4.3. Lees’ uses the same equation recommended by LLNL and that is currently used at PNNL (equation 1.2). This calculation of stored energy for liquids below their boiling point is based upon an experimentally established compressibility of the liquid. The compressibility is equal to $1/\text{Bulk Modulus}$ of the liquid, which is similar to the Modulus of Elasticity for a solid.

2.1.3 Energy for Non-Ideal Gas, Vapor, and Flashing Liquid

Because non-ideal gases, vapors, and flashing liquids are more complex substances, a single equation cannot be derived to establish a theoretical stored energy based upon pressure, volume, and temperature alone. Lees’ Section 17.4.6 describes vessel burst energy for non-ideal gas, vapor, and flashing liquid. In this case, the energy of the explosion is obtained from the difference in the internal energy between the initial and final states assuming an isentropic expansion using suitable thermodynamic diagrams or tables.

3.0 Design Principles

3.1 Basic Overpressure Design Principles

The basic instances that induce an overpressure event are exceeding the design failure pressure or a material imperfection failure at the operating pressure. At PNNL, standard practice is to design to the maximum allowable working pressure (MAWP) of the minimum rated component in any given section of a pressure system. Pressure relief is generally installed whenever there is a potential to exceed the MAWP when the stored energy is above 1000 lbf-ft unless there are extenuating circumstances (e.g., addition of a relief valve could add too much volume space for extremely sensitive experiments with low volume requirements and other protections have been put in place). The pressures used for determining the stored energy in a system are defined, at PNNL, as follows:

Maximum possible pressure should be the lowest of the following:

- Maximum Supply Pressure (Bottle Pressure, Pump Dead Head, Thermal Expansion)
- 1.2 x Relief Device Set Point (valves cannot be between protected device and relief device)
- 1.2 x Component Burst Pressure (for worst case stored energy component).

Another area that merits mention is the effect of temperature on stored energy due to the direct affect it has on the stored energy in a system. The potential to add heat is considered as another source of pressurizing a system due to thermal expansion when determining the maximum possible supply pressure. Heating of closed containers is prohibited unless explicit approvals are granted and appropriate administrative controls are put in place.

3.2 Criteria of Damage/Injury

The causes of explosion injury to a person include the blast wave, missiles, thermal effects, and toxic effects. This analysis is concerned with physical explosions; therefore, thermal effects (fire) and toxic effects are not discussed in great detail because PNNL implements other policies and procedures to mitigate the possibility of fire and toxic releases. Typically research processes take place in ventilated enclosures or are separated from staff when flammable or toxic hazards are present.

The modes of physical explosion injury of interest are eardrum rupture, lung hemorrhage, and missile injury. These types of injury are evaluated based upon the probability of injury. For each type of injury, a threshold value has been established at which there is approximately a 1% chance of injury. Multiple studies have been conducted for each type of injury and are discussed in Lees' Section 17.38 and 17.39 and Section 2, Chapter 8 of the FPH. Lees' data indicates a minimum threshold for ear drum rupture at 2.4 psig and lung hemorrhage at 14.5 psig whereas the FPH lists 5.1 psig and 29 psig respectively.

3.3 Determining the Blast Wave Pressure

Pressure propagating away from an explosion is usually referred to as a blast wave. As the blast wave moves away from the release point, the shock amplitude decreases due to atmospheric resistance, and the time duration of the pressure disturbance increases. Both Lees' and FPH discuss the calculation of a blast

wave by utilizing an equivalent energy in terms of TNT (trinitrotoluene). Various correlations and theoretical models of ideal blasts waves show that the shock pressure can be correlated with an energy-scaled distance consistent with:

$$\frac{Z}{E^{.333}} = \frac{Z}{W_{\text{TNT}}^{.333}} \quad (5.1)$$

Where:

Z = Distance from explosion site

E = Blast wave energy

W_{TNT} = TNT equivalent weight for the same blast wave energy

Table 2.8.1 in the FPH shows the consequences of representative values for overpressure and the associated TNT equivalent scaled distance.

Note: The TNT equivalence method for determining blast wave consequences was discussed with PNNL Fire Protection Engineering staff. This method is considered conservative per Fire Protection Engineering with relation to compressed gas expansion during an overpressure event.

4.0 Calculations

This section explores blast waves in relation to various stored energy situations. Calculations are performed using equation 2.2 (Baker) to determine the pressure wave propagation. The ultimate purpose of the calculation is to validate 1000 lbf-ft as a reasonable limit when determining a pressure hazard.

4.1 Ideal Gas Expansion

An attempt to determine the pressure at a distance from an over-pressurized vessel (Table 4.1) was calculated using a form of the Ideal Gas Law, where $P_1 \cdot V_1 = P_2 \cdot V_2$ (aka, Boyle's Law). This method acts as a baseline check of other methods used to calculate the blast wave of an over-pressure event. First, the required pressure to generate 1000 lbf-ft in a sphere with a given diameter was calculated. The diameters evaluated are below 6" because diameters greater than this are governed by the ASME Boiler and Pressure Vessel Code. These starting pressures and volumes resulting in 1000 lbf-ft of stored energy were used to determine the pressure at a given distance assuming consistent expansion.

Table 4.1. Pressure Wave using Ideal Gas Law

The pressure wave is determined based upon the ideal gas law, where $P_1 V_1 = P_2 V_2$

V1 and V2 are assumed to be spherical, due to pressure wave of an explosion point.

Brittle Materials are not allowed for use with compressed gas, and therefore only a point explosion is reasonable.

(Based upon a beginning sphere of air pressure, $k = 1.4$ that results in 1000 lbf-ft)

	Volume 1	Volume, in ³ at	Distance (inch)							
Diameter	cu-in									
0.0625	1.28E-04	5	35	117	274	533	919	2170	4228	7295
0.125	1.02E-03	5	37	120	281	543	933	2195	4268	7352
0.25	8.18E-03	6	40	128	294	564	963	2247	4348	7467
0.5	6.54E-02	8	48	144	322	606	1023	2352	4511	7700
1	0.52	14	65	180	382	697	1150	2572	4849	8181
1.5	1.77	22	87	221	449	796	1288	2806	5204	8682
2	4.19	34	113	268	524	905	1437	3054	5575	9203
3	14.14	65	180	382	697	1150	1767	3591	6371	10306
4	33.51	113	268	524	905	1437	2145	4189	7238	11494
5	65.45	180	382	697	1150	1767	2572	4849	8181	12770
6	113.10	268	524	905	1437	2145	3054	5575	9203	14137

Absolute Pressure for 1000 lbf-ft		Pressure Resultant (psi)								
0.0625	4000000	1113	146	44	19	10	5.56	2.36	1.21	0.70
0.125	4900000	997	136	42	18	9	5.37	2.28	1.17	0.68
0.25	620000	850	126	40	17	9	5.27	2.26	1.17	0.68
0.5	80000	640	110	36	16	9	5.12	2.23	1.16	0.68
1	11000	407	88	32	15	8	5.01	2.24	1.19	0.70
1.5	3450	272	70	28	14	8	4.73	2.17	1.17	0.70
2	1560	195	58	24	12	7	4.55	2.14	1.17	0.71
3	535	116	42	20	11	7	4.28	2.11	1.19	0.73
4	258	76	32	17	10	6	4.03	2.06	1.19	0.75
5	152	55	26	14	9	6	3.87	2.05	1.22	0.78
6	101	43	22	13	8	5	3.74	2.05	1.24	0.81

Distances from the edge of the vessel that are of interest based upon this approach are 1) at 3 inches the maximum pressure is 44 psig (~ pressure for lung hemorrhage), 2) at 6 inches the maximum pressure is 5.56 psig (~ pressure for ear drum rupture), and 3) at 12 inches the maximum pressure is 0.81 psig (less than the pressure required for missile debris).

4.2 Blast Wave Calculations

The approach presented by Lees' and in FPH is used to determine the blast wave propagation and potential consequence as outlined in Chapter 8, Section 2 of the FPH.

4.2.1 1000 lbf-ft Blast Wave

The blast wave for an over-pressure event in a system with 1000 lbf-ft is calculated using a 4 inch sphere as an example pressure vessel:

$$r := 2 \cdot \text{in}$$

Radius of Sphere

$$V_1 := \frac{4 \cdot \pi \cdot r^3}{3} = 33.51 \text{ in}^3$$

Volume

$$P_0 := 15 \cdot \text{psi}$$

Atmospheric Pressure

$$P_1 := 260 \cdot \text{psi}$$

Vessel Pressure (245 psig)

$$k := 1.4$$

Ratio of Specific Heats for Air

$$E_{Ba} := \frac{P_1 \cdot V_1}{k - 1} \left[1 - \left(\frac{P_0}{P_1} \right)^{\frac{k}{k-1}} \right]$$

Equation 4.2 (Baker)

$$E_{Ba} = 1372 \text{ J} \quad \text{converts to} \quad E_{Ba} = 1012 \cdot \text{lbf} \cdot \text{ft}$$

Energy

$$E_{TNT} := 4850 \cdot \frac{\text{J}}{\text{gm}}$$

TNT equivalent Energy of Explosion (Lee's Section 17.4, page 17/22)

$$z_1 := 200 \cdot \text{ft}$$

Worst Case - scaled distance for "Minimum overpressure for debris and missile damage" with overpressure of .2 psi - .4 psi. (See FPH, Table 2.8.1.)

$$z_2 := 15 \cdot \text{ft}$$

Worst Case - scaled distance for "eardrum rupture" with overpressure of 5.1 psi - 14.5 psi. (See FPH, Table 2.8.1.)

$$z_3 := 6.7 \cdot \text{ft}$$

Worst Case - scaled distance for "lung damage" with overpressure of 29.0 psi - 72.5 psi. (See FPH, Table 2.8.1.)

$$D = z \cdot \sqrt[3]{W_{TNT}}$$

Distance from blast point for related consequence. (See FPH, example calculation pages 2-95 and 2-96.)

$$W_{tnt} := \frac{E_{Ba}}{E_{TNT}} = 2.828 \times 10^{-4} \text{ kg}$$

Energy Equivalent in TNT, kg

$$W_{TNT} := \frac{W_{tnt}}{\text{kg}} = 2.828 \times 10^{-4}$$

Energy Equivalent in TNT, Unitless Conversion

$$D_1 := z_1 \cdot \sqrt[3]{W_{TNT}} = 13 \cdot \text{ft}$$

Maximum distance for debris and missile damage.

$$D_2 := z_2 \cdot \sqrt[3]{W_{TNT}} = 12 \cdot \text{in}$$

Maximum distance for eardrum rupture.

$$D_3 := z_3 \cdot \sqrt[3]{W_{TNT}} = 5 \cdot \text{in}$$

Maximum distance for lung damage.

4.2.2 1 lbf-ft Blast Wave

The blast wave for an over-pressure event in a system with 1 lbf-ft is:

$E_{Ba1} := 1 \cdot \text{lbf} \cdot \text{ft}$	Energy
$W_{tnt1} := \frac{E_{Ba1}}{E_{TNT}} = 2.796 \times 10^{-7} \text{ kg}$	Energy Equivalent in TNT, kg
$W_{TNT1} := \frac{W_{tnt1}}{\text{kg}} = 2.796 \times 10^{-7}$	Energy Equivalent in TNT, Unitless Conversion
$D_{1a} := z_1 \cdot \sqrt[3]{W_{TNT1}} = 16 \cdot \text{in}$	Maximum distance for debris and missile damage.
$D_{2a} := z_2 \cdot \sqrt[3]{W_{TNT1}} = 1.2 \cdot \text{in}$	Maximum distance for eardrum rupture.
$D_{3a} := z_3 \cdot \sqrt[3]{W_{TNT1}} = 0.5 \cdot \text{in}$	Maximum distance for lung damage.

4.2.3 500 lbf-ft Blast Wave

The blast wave for an over-pressure event in a system with 500 lbf-ft is:

$E_{Ba2} := 500 \cdot \text{lbf} \cdot \text{ft}$	Energy
$W_{tnt2} := \frac{E_{Ba2}}{E_{TNT}} = 1.398 \times 10^{-4} \text{ kg}$	Energy Equivalent in TNT, kg
$W_{TNT2} := \frac{W_{tnt2}}{\text{kg}} = 1.398 \times 10^{-4}$	Energy Equivalent in TNT, Unitless Conversion
$D_{1b} := z_1 \cdot \sqrt[3]{W_{TNT2}} = 10.4 \cdot \text{ft}$	Maximum distance for debris and missile damage.
$D_{2b} := z_2 \cdot \sqrt[3]{W_{TNT2}} = 9 \cdot \text{in}$	Maximum distance for eardrum rupture.
$D_{3b} := z_3 \cdot \sqrt[3]{W_{TNT2}} = 4 \cdot \text{in}$	Maximum distance for lung damage.

4.2.4 10000 lbf-ft Blast Wave

The blast wave for an over-pressure event in a system with 10000 lbf-ft is:

$E_{Ba3} := 10000 \cdot \text{lbf} \cdot \text{ft}$	Energy
$W_{tnt3} := \frac{E_{Ba3}}{E_{TNT}} = 2.796 \times 10^{-3} \text{ kg}$	Energy Equivalent in TNT, kg
$W_{TNT3} := \frac{W_{tnt3}}{\text{kg}} = 2.796 \times 10^{-3}$	Energy Equivalent in TNT, Unitless Conversion
$D_{1c} := z_1 \cdot \sqrt[3]{W_{TNT3}} = 28 \cdot \text{ft}$	Maximum distance for debris and missile damage.
$D_{2c} := z_2 \cdot \sqrt[3]{W_{TNT3}} = 25 \cdot \text{in}$	Maximum distance for eardrum rupture.
$D_{3c} := z_3 \cdot \sqrt[3]{W_{TNT3}} = 11 \cdot \text{in}$	Maximum distance for lung damage.

4.3 Comparative Stored Energy

To get an understanding of stored energy in real world applications, a variety of items encountered in daily life and laboratory operations are evaluated in Table 4.2.

Table 4.2. Stored Energy of Everyday Items

Item	Volume (ft ³)	Gas	Pressure (psig)	Stored Energy (lbf-ft)	Method
Compressed Gas Cylinder	1.42	Air	2500	982,500	Stored Energy Spreadsheet
Standard Air Compressor, 50 gal	6.68	Air	125	159,000	Stored Energy Spreadsheet
Standard Air Compressor, 20 gal	2.67	Air	125	64,000	Stored Energy Spreadsheet
Propane Tank (grill, compressed gas expansion only)	0.63	Propane	200	35,000	Stored Energy Spreadsheet
Paint Ball Tank (20 oz)	0.02	Air	3000	21,300	Stored Energy Spreadsheet
M-80 (2.5 grams of powder)	N/A	N/A	N/A	17,000	See Appendix A
State Limit for Third Party Inspection of ASME Coded Vessel	5	Air	15	9,700	Stored Energy Spreadsheet
Car Tire	0.97	Air	35	5100	Stored Energy Spreadsheet
Mountain Bike Tire	0.2	Air	65	2,230	Stored Energy Spreadsheet
CO2 2L Pop Bottle Bomb	0.05	CO2	150	1,750	Stored Energy Spreadsheet and Appendix A
Typical CO2 Cartridge (16 gram)	0.0047	CO2	900	1,263	Stored Energy Spreadsheet
STORED ENERGY LIMIT				1000	
BMX Bike Tire	0.11	Air	50	915	Stored Energy Spreadsheet
Road Bike Tire	0.04	Air	110	820	Stored Energy Spreadsheet
Typical CO2 Cartridge (12 gram)	0.0058	CO2	420	650	Stored Energy Spreadsheet
Typical Firecracker (50 mg powder)	N/A	N/A	N/A	340	See Appendix A
Dust Spray Can	0.02	Mix	85	335	Stored Energy Spreadsheet
Soccer Ball	0.215	Air	12	320	Stored Energy Spreadsheet
Party Balloon	2.42	Air	1	255	Stored Energy Spreadsheet
Basketball	0.26	Air	8	250	Stored Energy Spreadsheet

4.4 Tabulated Results

The following results are tabulated from the calculations performed above.

Table 4.3. Tabulated Stored Energy Analysis Results

Description	Worst Case Distance for Possible		
	Missile/Debris Damage	Ear Drum Rupture	Lung Hemorrhage*
Ideal Gas Expansion; $P_1V_1 = P_2V_2$ @ 1000 lbf-ft	> 1 ft	~ 6 in	~ 3 in
1000 lbf-ft Blast Wave	13 ft	12 in	5 in
1 lbf-ft Blast Wave	16 in	1.2 in	0.5 in
500 lbf-ft Blast Wave	10.4 ft	9 in	4 in
10000 lbf-ft Blast Wave	28 ft	25 in	11 in

*These values are not considered realistic at such short distances.

Description of Item*	Stored Energy
Compressed Gas Cylinder	982,500lbf-ft
WA State Limit for 3 rd Party Inspection of ASME Coded Vessel	9,700 lbf-ft
PNNL Stored Energy Limit	1,000 lbf-ft
Typical CO2 Cartridge (12 gram)	650 lbf-ft
Party Balloon	255 lbf-ft

*See Table 4.2 for the stored energy of additional items.

5.0 Conclusions

Based upon a review of applicable literature and the supporting calculations performed, the following conclusions were derived:

1. Stored energy is an appropriate method to determine the potential hazards of an overpressure event.
2. Calculating Stored Energy:
 - a. The Baker equation is an acceptable method to determine the stored energy of compressed gases. Although Brode is identified by Lees' and the Fire Protection Handbook as the preferred method for determining compressed gas stored energy, PNNL will continue to use Baker. Baker is considered the best alternative, and is being used by PNNL, INL, and historically by LANL and LLNL. A switch from Baker to Brode would highly impact operations, confuse the pressure safety stored-energy relation, and add little value. Furthermore, the use of stored energy is inherently conservative because the Baker model is a reversible (isentropic expansion) process.
 - b. The stored energy in liquid systems shall continue being calculated using fluid compressibility.
 - c. For non-ideal gases, cryogenes, and flashing liquids the use of enthalpy and internal energy tables shall be utilized.
3. The use of a 1000 lbf-ft energy limit is consistent with an acceptable level of risk. The conservative blast wave equation shows that a possible personnel injury could occur ~ 1 foot away from a pressure release; however, this stored energy is no greater than the energy encountered by items used every day in our homes. 1000 lbf-ft is also nearly 10 times less than the stored energy at which the State of Washington requires inspections for ASME Coded Vessels. Furthermore, the culture of safety glass use, wearing proper attire in laboratories, and minimizing the use of brittle materials all mitigate the probability of missile debris causing injury during an overpressure event. Lastly, the 1000 lbf-ft limit is consistent with perceived hazards based upon everyday experience with common household and laboratory items. During pressure systems reviews, engineering judgment is consistent with the 1000 lbf-ft limit as a practical measure of risk.

6.0 Recommendations

During the development of this analysis, certain aspects regarding PNNL Pressures Safety Program were deemed to have a potential weakness. Recommendations to remedy these possible deficiencies are listed below. Each recommendation will be assigned as an Action Tracking System (ATS) Item to the Pressure Systems Engineer, and tracked through closure.

1. Implement the use of enthalpy differentials for non-ideal gas, vapor, and flashing liquid. This should be clearly identified in the Pressure Systems subject area and the Engineering Standard: Pressure/Vacuum Systems.
2. Use of fluids that do not fall into the “non-hazardous” category should require an added stage of rigor beyond a pressure safety review. The use of a Chemical Process Permit should be evaluated to ensure hazardous fluid systems below the risk limit are being safely designed.
3. Ensure that brittle materials are not used for compressed gas service. Guidance should be added to the Pressure Systems subject area and the Engineering Standard: Pressure/Vacuum Systems.
Note: Glass systems already have a category in the Pressure Systems subject area, and other items, such as PVC and cast fittings, are not allowed for compressed gas service.

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Appendix A

Internet Articles Regarding Flash Powder Energy

Appendix A: Internet Articles Regarding Flash Powder Energy

What is an "M-80," anyway?

<http://www.fireworksland.com/html/m80.html>

“...Up until 1966, large firecrackers such as M-80s and cherry bombs **were** legal in the United States, and anyone could buy them and shoot them off. If you look through old fireworks catalogs from the 1930s, '40s and '50s, you will see these and even larger firecrackers advertised, all of them perfectly legal **at that time**. But it all ended in 1966. The Child Protection Act, passed by the U.S. Congress in 1966, specifically banned these devices. In 1976, the federal regulations were rewritten specifying a limit of 50 milligrams of pyrotechnic composition for any firecracker sold to the public in the United States, and that limit is still in effect today. It doesn't matter what they look like or what they are shaped like - **ground firecrackers can only contain 50 milligrams of pyrotechnic content per cracker** (Emphasis added). (Aerial "reports," which are contained within aerial devices such as rockets and shells, can contain up to 129.6 milligrams of composition per report.)...”

The Relative Explosive Power of an M-80 vs. a Dry Ice Bomb

http://dryicebomb.info/m-80_explosive_power.html

Conclusion

An M-80 is 33 times more powerful than a dry ice bomb.

Explosives

An explosion is the sudden release of energy, and an explosive is a device that stores energy and allows its sudden release. The power of an explosive is directly proportional to the amount of stored energy that it releases. The stored energy of explosive devices is straightforward to estimate. This page compares the stored energy of a bottle bomb with that of an M-80, a common firecracker.

Calculations show that a bottle bomb releases a tiny fraction of the energy of an M80, and that it is therefore far less dangerous.

Dry Ice Bombs

A dry ice bomb, also called a bottle bomb, usually consists of a 2-liter plastic soda bottle filled partially with dry ice and water. The water heats the dry ice and causes it to sublime into gaseous CO₂. When the pressure from the CO₂ reaches the bursting pressure of the bottle, the bottle explodes, releasing the available energy of the pressurized gas (there is no combustion, no heat, and no fire). The energy stored in the bottle before it ruptures is the product of the pressure of the CO₂ gas in the bottle and the volume of the bottle. The energy in that same CO₂ after the rupture is product of its pressure and the volume of the same molecules of CO₂ that were in the bottle before it ruptured. The difference between these two energies is the energy available to make a boom or to cause damage. The gas volume before rupture is the volume of the bottle less the volume of the water and dry ice placed inside the bottle.

For purposes of these estimates, the volume used is 75% the volume of the bottle, leaving 25% of the volume for water and dry ice. Since the burst pressure depends only on the strength of the plastic bottle, the released energy does not depend on the amount of dry ice in the bottle (other than that due to the loss of volume in the bottle taken up by the dry ice and water). The Coca Cola web site states that the bursting pressure of a 2-liter bottle is 150 PSI. After converting to the appropriate units, the volume of CO₂ is 0.0015 m³, the pressure is about 1.1 MPa (converting 150 PSI into metric), giving an energy in the compressed CO₂ the instant before rupture as 1672 Joules.

After the bottle ruptures, the gas expands adiabatically (this means that it does not have time to exchange heat with its surroundings), so the volume increases by the following factor

$$(\text{Pressure before rupture/pressure after rupture})^{1/\gamma}.$$

(see <http://hyperphysics.phy-astr.gsu.edu/hbase/thermo/adiab.htm> and <http://encyclopedia.airliquide.com/encyclopedia.asp?GasID=26>)

With a pressure ratio of about 11, and using γ for CO₂, 1.29, the volume increases by a factor of 6.4. The volume of the CO₂ is now 0.0096 m³, the pressure is 0.101 MPa, giving an energy in the CO₂ of 975 Joules.

Thus the energy released at rupture is 1672-975 = 697 Joules.

Note that there is no heat generated or combustion or chemical change with a bottle bomb. There is no opportunity for fire and no opportunity for burns. The water in the bottle would, if anything, contribute toward the extinguishing of any fire that happened to be present. There may be a fog produced that looks like smoke (dry ice is commonly used in fog makers).

M-80 firecracker

M-80 firecrackers were popular during the 50's and 60's and are now illegal under federal law (<http://www.cdc.gov/NCIPC/factsheets/fworks.htm>). They were intended to make sound like a gun being fired. They are paper tubes about 1½ inches long and 9/16 inch in diameter filled with 2.5 to 3 grams (38 to 46 grains) of flash powder with a fuse at the side of the tube (<http://www.pyrowiki.com/>). The stored energy of an M-80 is estimated from the energy density of the flash powder and its mass. The energy density of flash powder is 2200 cal/g = 9196 Joules/g (<http://www.powerlabs.org/chemlabs/deflagrants.htm>).

Using the 2.5 g mass of the flash powder gives the energy in an M-80 of 22,990 Joules, some 33 times that of an exploding bottle.

Note that the energy release of M-80's involves combustion. Thus an M-80 could cause burns and fire and all the dangers associated with fire.

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