Lessons Learned on Surviving Worst-Case Reactivity Hazards

Special considerations for designing a facility for operating pressure vessels and equipment for processing highly reactive chemicals.

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Agenda

Introduction:

- **Location and history of where I work.**
- **Describe the type of work I do.**

Discussion: Two events that changed the way we do work.

- **Event #1: Reactor Exploding in 1961.**
- **Event #2: Chemical Re-entrainment Event in 1998.**

Lessons Learned: A listing of key learnings from these and other experiences.

Disclaimer

This is just an overview of things that can go wrong.

- **There is no detailed chemistry discussion.**
- **The approach to this presentation is that something will eventually fail.**
  - **The technical safety assumption is that a failure will occur between 1 to 3 times during a lifetime of a facility (~30 years).**
  - **For similar examples see discussions on "Black Swan" events.**
- **Warning: Always get expert help from those specializing in managing reactivity hazards.**

References and Resources

- Various Engineering Studies and Consultations by Chet Grelecki and Frank Bender.
  - Hazards Research Corporation, Fire and Explosion Hazards Evaluation.
- RWDI, Exhaust Dispersion Study, Ray Sinclair, Mike Ratcliff, et al.
  - (RWDI = Rowan, Williams, Davies, and Irwin Inc.)
- “Explosion Problems in the Chemical Industry”
  - Robert W. Van Dolah, David S. Burgess, American Chemical Society.
- "Structures to Resist the Effects of Accidental Explosions“
  - U.S. Army Publication AD/A716 673, Vol. II, "Blast, Fragment, and Shock Loads", Dec. 1986.
- Perry's Chemical Engineers' Handbook; October 2007.
- NFPA 45, Standard on Fire Protection for Laboratories Using Chemicals.
- NFPA 68, Standard on Explosion Protection by Deflagration Venting.
- NFPA 69, Standard on Explosion Prevention Systems.

High Pressure Chemistry Facility

- Designed for high hazard chemical reactions and procedures.
- Primary barricade wall rated to ~4 # TNT.
- High air flow and tall exhaust stacks for dilution of flammable and toxic materials.
- Explosion-Proof Electrical Systems.
- Heavily Computerized Reactor Systems.

Areas Supported

- Process Research
- Organic Synthesis
- Physical Property Studies

Typical Applications

- **Any Reactive Gas**
- **Reactions that generate pressure or require added pressure to suppress the boiling points of reagents or solvents.**
- **Most reactions are completed in one step.**

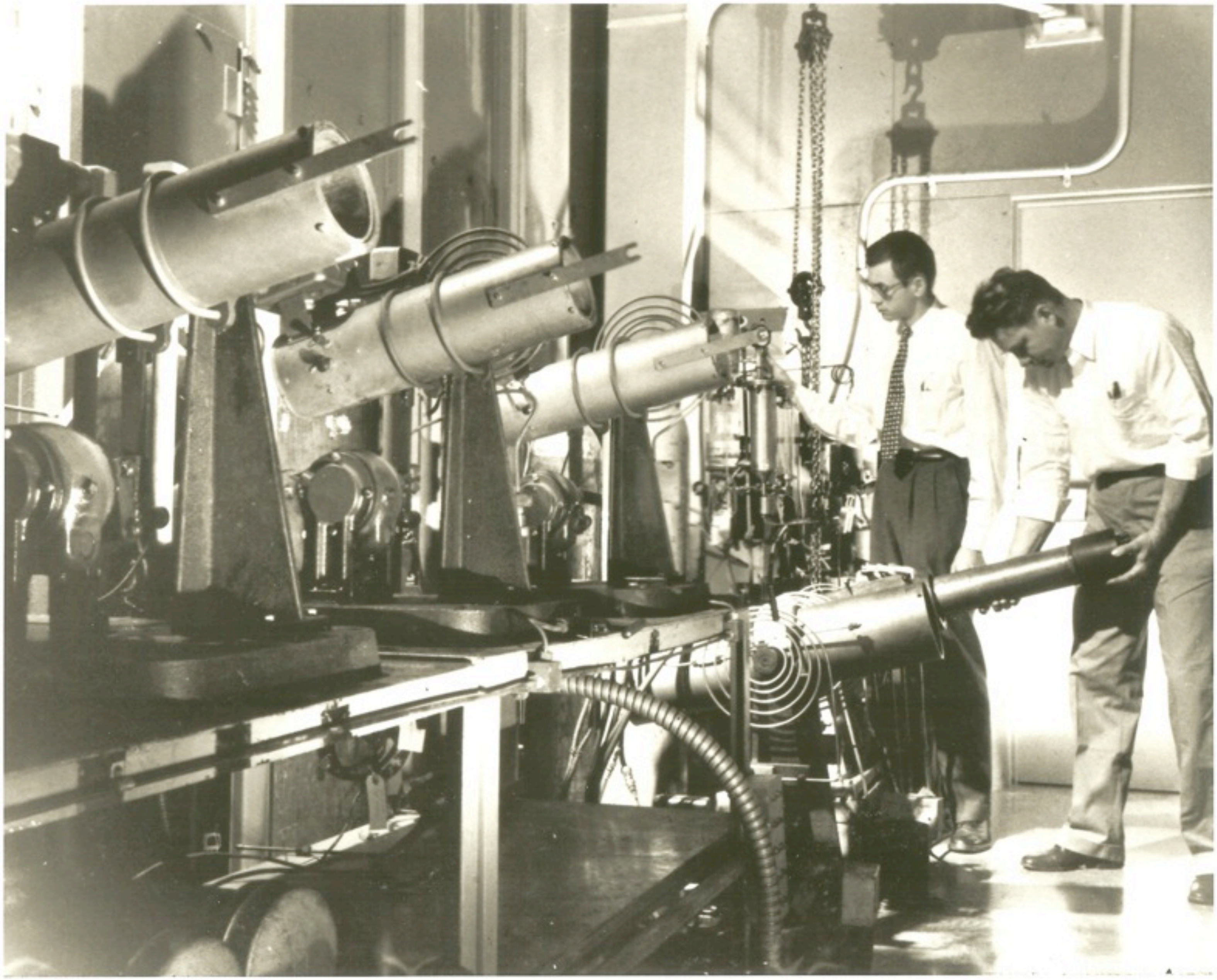
High pressures, reactivity, and toxicity create significant safety issues.

Reactivity Event #1

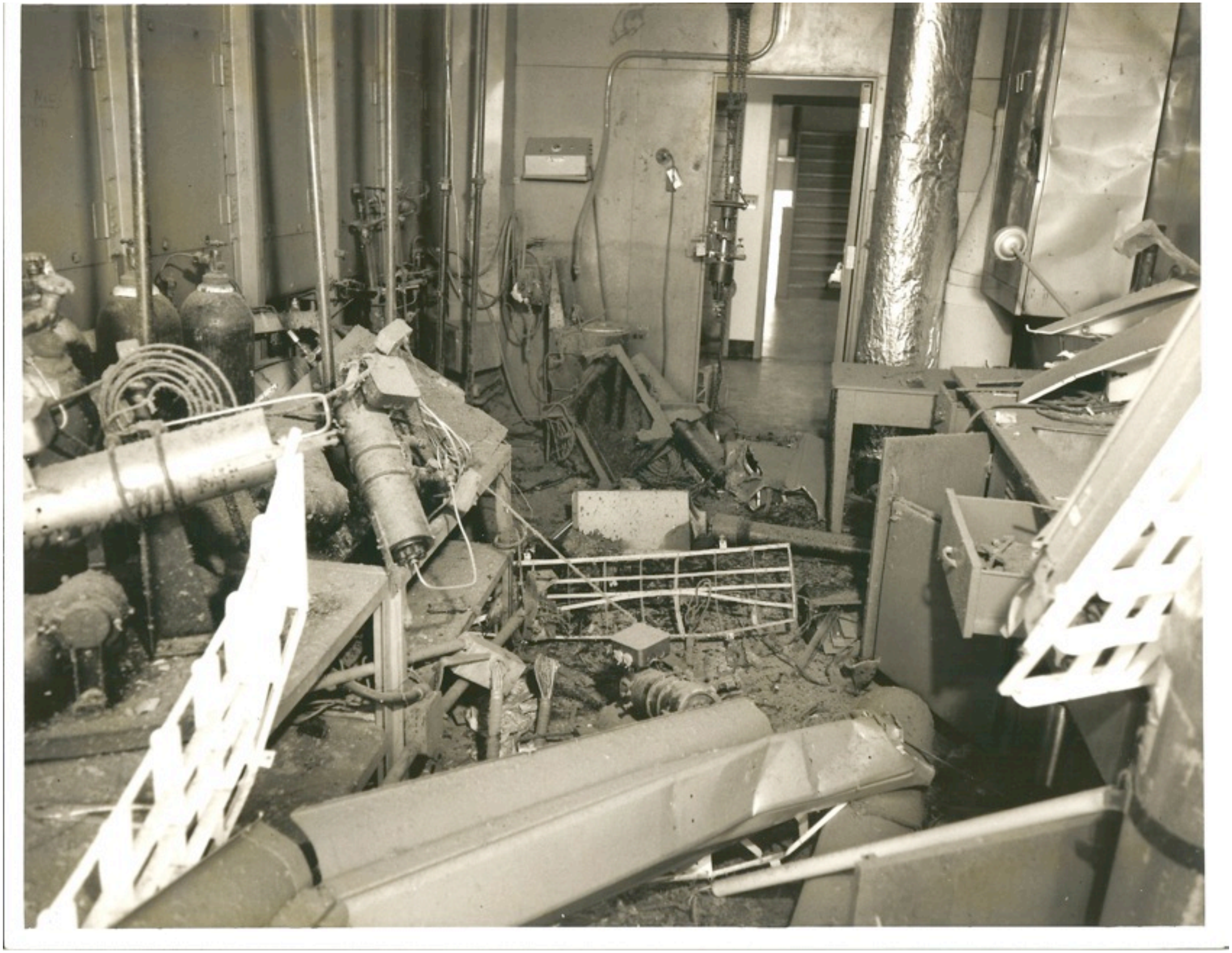
A 3-Liter reactor exploded in 1961 significantly damaging the lightly barricaded facility housing it and other equipment.

- No one was hurt but it was a wake-up call that a better facility was needed.
- It also showed us how small reactors can result in huge and unexpected explosions.

High Pressure Chemistry Facility - Late 50's



Former High Pressure Chemistry Facility – May 1961



Failed Pressure Vessel Parts

- **3 Liter reactor failed due to detonation reaction between N_2O_4 and DMSO.**
- **Explosion estimated to be ~1# TNT equivalents in scale.**

Reactivity Event #2

- A runaway reaction in 1998 resulted in the external venting of a chemical cloud that significantly engulfed the several buildings on the site from just 10 kilograms of total mixture.
- It was completely unanticipated since the reaction included a chemical that had a NFPA Reactivity Hazard of 1 mixed with a chemical that had a Reactivity Hazard of 0.
- Significant precautions had been taken including testing at small scale and gradually increasing to 10 kilograms of total chemical mixture.
    - The reaction was also performed several times at the 10 kilogram scale without incident.
- Changing one minor detail probably caused the incident.

More Info on Event #2

- This was one of the worst chemical incidents in recent P&G history resulting in the site being evacuated with 33 people reporting to health services with various health complaints.

- This experience taught us we needed to significantly improve the way our exhaust systems were designed to reduce the risk of chemical exposure and re-entrainment.

Lesson Learned #1

Small Reactions can make big explosions.

- **The size of the explosion depends on the size and strength of the reactor.**

Bigger stronger reactors make bigger explosions.

- **It is possible to have a reactor that is too strong.**
  - **The reactor may be less likely to fail but when it does fail the damage can be more than the barricade and facility can manage.**

Lesson Learned #2

The barricade has to be engineered to protect you from the reactor if it explodes.

- **Example: a ¼" polycarbonate lab shield is not adequate protection.**
- **Barricades are usually significantly strong structures.**
  - **Our facility uses 12 inch and 18 inch reinforced concrete walls that are covered with 1/4" steel plating.**
  - **Stronger reactors require thicker, stronger walls.**
- **You can calculate the amount of energy that a reactor will generate when it fails.**
- **These calculations can be used by experts to specify the barricade needed to survive an explosion.**

Examples of Calculated Reactor Energies

(based on an ultimate strength or burst pressure that is 4 times the MAWP)

Reactor	MAWP (psig)	Vessel Volume (Liters)	Equivalents of TNT (pounds)	Equivalents of TNT (grams)
10 Gallon Pfaudler	300	38.0	0.67	304
5 Gallon Parr	2000	19.0	3.15	1432
2 Gallon AE	5325	7.6	3.87	1760
3 Liter Rocker	5000	3.0	1.42	647
1.8 Liter Parr (EO)	5000	1.8	0.85	388
0.5 Liter Rocker	5000	0.5	0.24	108

Lesson Learned #3

Adding a pressure safety factor is not enough to prevent a reactor from failure.

- **Example:**
  - **Reactor has a pressure rating of 3000 psig.**
  - **Running at 500 psia does not necessarily protect you from reactor failure.**
- **Reason:**
  - **Reactors are more likely to fail from the condensed phases (solids and liquids) than from the gas phase.**
  - **There’s significantly more material in the condensed phase than in the gas phase.**

Lesson Learned #3

Example:

- Using a 2-gallon reactor rated at 5325 psig (MAWP).
- Reaction conditions:
  - Pressure = 4000 psig hydrogen
  - Reactor is half full (3.8 liters or ~7 pounds of liquid)
  - Temp = 300°C
- Reactor contains ~24 grams of hydrogen (~0.05 pounds)

0.05 pounds of hydrogen cannot fail a reactor

that is rated at ~ 4 pounds of TNT

(assumption is that reactor is well maintained and system is properly designed)

Lesson Learned #4

A rupture disk alone is not enough to protect you.

- **It helps and is very important, but**
- **Rupture disc sizes delivered with many pressure vessels will not protect you against all potential reaction failures.**
- **Reactions that detonate can fail a reactor regardless of the size of the rupture disk.**
- **Reactions that deflagrate can fail a reactor if pressure is generated faster than the rupture disk can vent the pressure.**

Calculations: Maximum Pressure Generated from 1 Kilogram of Ethylene Oxide

1.8-Liter Reactor		5-Gallon Reactor	
RUPTURE DISC SIZE (inches)	Maximum Reactor Pressure (psig)	RUPTURE DISC SIZE (inches)	Maximum Reactor Pressure (psig)
1.0	1,350	2.0	2,430
0.5	5,350	1.75	3,180
0.375	9,500	1.5	4,325
0.25	119,000	1.0	9,750

Ethylene Oxide does not detonate in the liquid phase but can detonate in the vapor phase. The amount of material in the vapor phase is generally not high enough to fail the reactor from a detonation.

Partial Listing of Rupture Disk Watch-Outs

Key Point: Don't trade one problem for another problem.

These are complicated systems. Get expert help on designing the venting system.

- **Vent the rupture disc to a safe area.**
- **The outlet of the pipe can be venting fire when the rupture disk fails.**
- **What happens to the vapor once it exits the vent pipe?**
  - **Consider the impact of a deflagration of a venting gas.**
  - **Can it be sucked into an air intake?**
- **Consider using a cyclone separator to separate liquids from gasses so only gas exits the end of the vent pipe.**
- **Make sure the venting system can take the pressure.**
- **Can materials solidify in the lines and keep the rupture disk from venting?**
- **Keep the venting system valve free.**
- **Make sure it is properly sized for the length of the pipe.**
- **What else is connected to the vent pipe? Can it back-feed into other areas?**
- **Inspect it at least annually.**
  - **Birds, bugs, and freezing water (ice) can clog the venting system.**

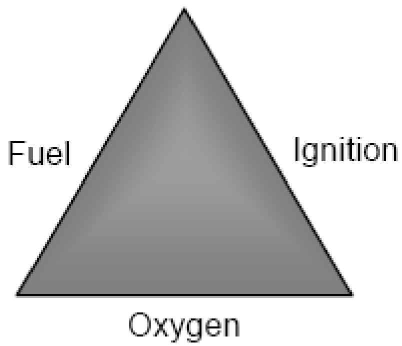
Lesson Learned #5

Explosions don't just come from the reactor bursting.

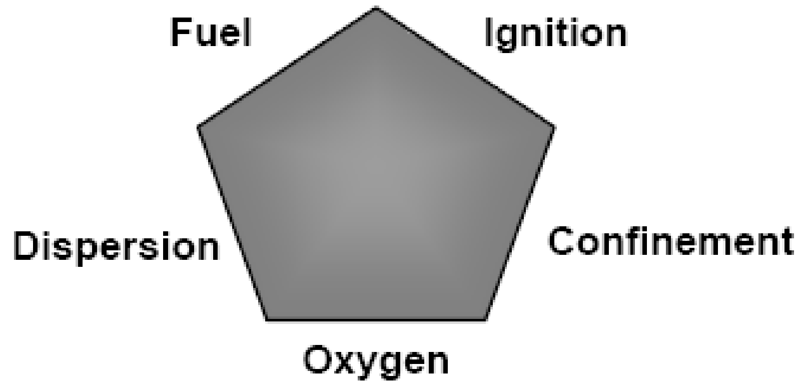
- **Significant hazards exist from vapors or gasses leaking from process equipment and igniting to create a deflagration.**
- **Liquids are especially hazardous.**
  - **A pound of acetone can generate the power of 10 pounds of TNT.**
- **The size of the explosion is largely determined by the size of the room**
  - **Bigger rooms make bigger explosions.**
- **Most solvents with vapor volume concentrations of ~4% can result in significant explosions .**
  - **More material generally doesn't make it significantly worse.**
- **The size of the fireball is generally ~6 times the vapor volume.**
- **Amount needed for 1100 cubic foot blast cell**
  - **~2 Liters Acetone (boiling liquid)**
  - **~90 grams of Hydrogen (2-Gal reactor only has 24 grams in above example)**

Lesson Learned #5

Fuel – Air Explosions



Classic Fire Triangle



Fuel – Air Pentagon

- **A fuel can be anything that can be dispersed into a cloud and ignited.**
- **Includes hydrogen gas, paint fumes, sugar, flour, or sawdust.**
- **All can generate significant energy upon ignition.**
- **Many large explosions are dust based.**
- **Explosions can come in pairs: the first explosion disperses more material that can generate a second explosion.**

Lesson Learned #6

A barricade alone is not enough to protect you.

- Make sure the facility is designed to handle the pressure that is generated from a failing reactor or a fuel-air explosion.
  - Again, the right size venting is critical to not blowing the building up.
- Explosions can generate fireballs and pressure waves that can be significant.
  - Where does the fireball go?
  - Pressure waves can travel hundreds of feet.
    - Pay attention to where the pressure is vented to.

Effects of Pressure Waves

Expected impact from overpressure and damage generated by a 2-Gallon reactor failing at it's ultimate strength of ~4 pounds of TNT.

Distance (feet)	Overpressure (psig)	Damage
23	5.0	Can collapse a cinder block wall or small buildings.
31	3.0	Steel frame buildings shifted from foundation.
68	1	Partial demolition of houses. Knock people over.
110	0.5	Shatter most windows.
188	0.25	Many larger standard strength windows may break.

Key Point: Pressure is very difficult to protect against.

Lesson Learned #7

Mixing and cooling is critical to safety.

- **The vessel in Event #2 was not pressurized or closed.**
- **Changing one minor detail probably caused the incident.**
  - **No mixing!**
  - **The exact cause of the event is not well understood but thought to be due to phase separation and something occurring at the interface of the two phases.**
  - **Frank Baker (HRC) said that nearly every incident investigation that he has been involved with <u>was caused by loss of agitation or cooling.</u>**

Lesson Learned #8

Record Keeping:

- If you build a high pressure lab, keep track of all the engineering studies.
- The original engineering studies for the MVIC and SWIC HP Labs have been lost resulting in expensive re-studies.
    - >$100,000 total.
- We had to do x-rays of the existing structures to understand how strong they were.
- These studies were essential to determine what reactors could safely be used based on the reactor ultimate strengths.

Record Keeping

After doing the engineering studies make sure you can find the information.

- **Have an effective sustainability program that includes record keeping.**
- **Store records in more than one place.**
- **Make sure you can locate the records.**
- **If you are subcontracting out record keeping, what happens when you get a new contractor?**
- **Remember we are talking about keeping access to these records for decades into the future.**

Lesson Learned #9

Re-entrainment Hazards:

- After Event #2, P&G enlisted the help of RWDI to help design chemical ventilation exhaust systems that significantly prevented exhausted chemicals from being sucked back into the building through air intakes.
- RWDI built a scale model of several P&G facilities and placed them in wind tunnels.
- They then used tracer gases and sensors on the scale model structures to determine the effects of the terrain, other buildings, and wind direction to create data that helped to determine the best location for air intakes and to determine the height and location of exhaust stacks.

Conclusion

- Working with pressure vessels or reactive chemicals has a range of hazards that are not obvious to many of us working in R&D.
- Consequently, it's best to get help from the right experts to make sure you understand the risks and correctly employ the countermeasures needed for protection.
- Kelly Thomas of Baker Engineering and Risk Consultants (BakerRisk) will now discuss methods for evaluating blast loads and fragments resulting from pressure vessel failure.
  - BakerRisk did the analysis on the upgraded HP Lab at SWIC.