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Explosion caused by flashing liquid in a process vessel

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Abstract

An explosion occurred at a polyvinyl chloride (PVC) resin manufacturing plant. The explosion originated at an atmospheric storage vessel when it received a slurry discharge from a suspension polymerization reactor. The pressure rise caused by the uncontrolled flashing of superheated liquid vinyl chloride resulted in the complete separation of the roof from the tank shell. A cloud of vinyl chloride vapor was released and ignited resulting in a vapor cloud explosion. The accident caused significant property damage but no serious injuries.

An investigation was conducted to determine the causes of the accident. It was discovered that the facility had experienced numerous overpressure incidents in the atmospheric storage vessels used as slurry tanks. Many of these incidents resulted in modest structural damage to these slurry tanks. It was determined by Exponent that the rapid flashing of residual liquid monomer present in the product slurry stream caused the earlier overpressure incidents. The facility operator did not adequately investigate or document these prior overpressure events nor did it communicate their findings to the operating personnel. Thus, the hazard of flashing liquid vinyl chloride was not recognized.

The overpressure protection for the slurry tanks was based on a combination of a venting system and a safety instrumentation system (SIS). The investigation determined that neither the venting system nor the SIS was adequate to protect the slurry tank from the worst credible overpressure scenario. Fundamentally, this is because the performance objectives of the venting system and SIS were not clearly defined and did not protect against the worst credible overpressure scenario.

The lessons learned from this accident include:

- use prior incident data for recognizing process hazards;
- identify targets vulnerable to these hazards;
- explicitly define performance objectives for safeguards to protect against the worst credible overpressure scenario.

The ultimate lesson learned here is that a liquid trapped under pressure above its normal boiling point represents an overpressure hazard. To avoid exceeding the design pressure of the receiving vessel, the superheated liquid must be discharged slowly so that the vapor production rate caused by flashing does not exceed the venting rate of the receiving vessel.

Keywords: Flashing liquid; Process vessel; Overpressure hazard; Safety instrumented system; Emergency relief system

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1. Introduction

Overpressure is a recognized hazard in process vessels. This hazard can be controlled through a combination of engineering and administrative controls. For overpressure protection to be effective, potential overpressure sources must be recognized and the performance requirements for the overpressure safeguards must be defined. This accident was the result of overpressure developed by the transfer of a liquid that flashed in a process vessel. The overpressure hazard of flashing liquid was not recognized at this facility. The overpressure protection safeguards, an emergency relief system (ERS) and a safety instrumented system (SIS), failed to protect the process vessel from rupture. The ERS and SIS failed in their role because their performance objectives did not define or include the worst credible overpressure scenario.

This case study has been developed from an actual accident investigation. The specific details have been deliberately modified to protect the identity of the parties involved. Also, certain proprietary information has been omitted to protect its confidentiality. Throughout this paper the management organization of this facility is referred to as “the facility operator”. There was more than one owner and operator

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in the history of the subject facility. The emphasis of this paper is on accident investigation and prevention and does not address any legal issues.

The accident site was a facility that manufactured poly vinyl chloride (PVC) by suspension polymerization of vinyl chloride monomer (VCM) in water. The accident occurred when a batch of product was transferred from a reactor to a temporary storage tank. This paper is complimentary to the case study presented in the AIChE/CCPS book entitled *Guidelines for Safe Automation of Chemical Processes* [10]. In that book the case study analyzes overpressure hazards associated with a PVC polymerization reactor. This paper, on the other hand, addresses the overpressure hazards related to discharges from the reactor to the receiving vessel.

2. Background

2.1. Process description

The subject facility manufactured polyvinyl chloride (PVC) using a suspension polymerization process. Pressurized, liquid vinyl chloride monomer (VCM) was dispersed in hot demineralized water by agitation. The polymerization reaction was started with an initiator, and suspension characteristics were controlled with the addition of surfactants.

VCM is a colorless gas at room temperature and pressure. Its boiling point is approximately 8 °F. It is a flammable gas and is both toxic and carcinogenic. Its vapor pressure at 70 °F is 35.3 psig with a vapor density approximately twice that of air. The specific gravity of the liquid is 0.91 at 70 °F. It is typically shipped as a pressurized liquid [2].

The polymerization process was conducted as a batch operation at approximately 150 °F and 15 psig with the desired degree of conversion typically achieved in about 3–5 h. The product was a milky-white slurry of PVC resin particles in water. The product slurry was pressurized due to the presence of both unreacted VCM and water vapor. The vapor was vented to the primary gasholder (PGH) to relieve the reactor pressure. VCM was recycled from the PGH for reuse in the process. Residual VCM was removed from the product slurry by steam stripping. The stripped slurry was then centrifuged, dried and stored in silos for eventual loading and shipment. Fig. 1 is a block flow diagram of the process.

Two reactors were connected in parallel to the separation train. The product slurry was transferred from a reactor through a discharge tank to a slurry tank. The discharge tank was essentially a strainer intended to protect downstream pumps and valves from plugging. The volume of the discharge tank was less than 5% of the reactor volume. Thus, slurry simply flowed through the discharge tank and was not stored in it. The discharge tank contained a sloped, perforated plate designed to remove PVC resin chunks from the slurry stream. The discharge tank had a design pressure similar to the reactors.

The slurry tank had a volume capacity equal to approximately two reactor batches. The slurry tank acted as an inventory storage vessel for the downstream processing of the slurry. The reactors and discharge tank were ASME pressure vessels with design pressures of 185 psig. The slurry tank was an atmospheric storage tank with a design pressure of 0.75 psig, a pressure rating 300 times less than the reactors and discharge tank.

Initially all vapor venting (degassing) from the reactors was done directly from the reactor to the PGH. This was the slowest step in the production process. To shorten the production cycle time, the facility operator installed a degas tank, an ASME pressure vessel with a design pressure

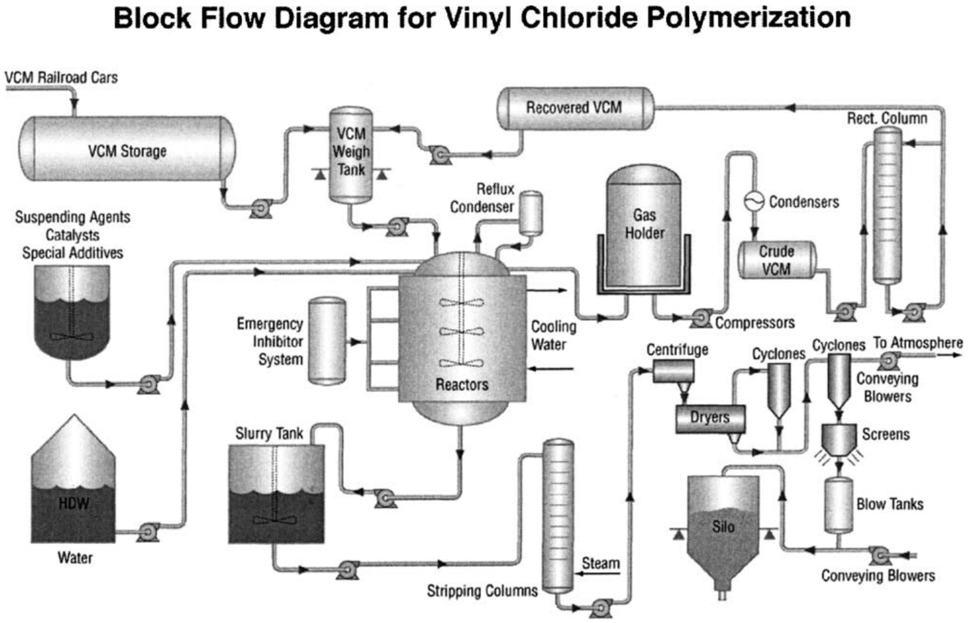

Fig. 1. Block flow diagram.

of 200 psig. The degas tank gave the operators an additional method for degassing a product batch. The degas tank method consisted of transferring the batch of slurry under pressure from the reactor, through the discharge tank and to the degas tank. The slurry was then degassed in the degas tank. After degassing the slurry, it was transferred from the degas tank to the slurry tank. The operation of the degas tank reduced the total cycle time on the reactors.

The VCM vapor generated by the degas step was recovered and stored for reuse. From the reactors (or degas tanks) the VCM would flow to a gas scrubber to remove PVC resin particles and water aerosol droplets from the vapor stream. The VCM would then proceed through the primary drain pot to remove any remaining water droplets and into the main storage vessel. The main storage vessel for VCM vapor to be recovered was the primary gasholder, PGH. The PGH was a water-sealed vessel with floating bell (roof). The floating bell level rose with VCM inflow and fell with VCM outflow. The VCM was withdrawn on demand by the primary gas purification system. From there the VCM was compressed, condensed and recycled for reuse in the reactors.

VCM vapor that was high in inert gas (nitrogen) concentration was sent to the secondary gasholder, SGH, for storage and eventual processing. The SGH feed streams primarily consisted of purge streams from the reactors, wastewater stripping towers and compressors. Some vessels, including the slurry tanks, had the ability to overflow VCM vapor into the SGH.

The basic configuration of the equipment and piping is shown in Fig. 2.

2.2. Accident summary

On the day of the accident both reactors were in operation. The first batch of the day, Batch 1, had been produced in Reactor 1. Batch 1 was transferred to the degas tank and vented there. It was then transferred to the slurry tank. Batch 2 was produced in Reactor 2. Concerns about potential product quality issues caused a delay in the processing of Batch 2. Meanwhile Batch 3 was prepared and reacted in Reactor 1. Eventually the quality issues with Batch 2 were resolved and Reactor 2 was vented. The next step was to transfer Batch 2 to the slurry tank. Shortly after the operator opened the manual block valve to begin the transfer, the slurry tank ruptured.

The explosion caused the roof of the slurry tank to completely separate from the shell. A cloud of vinyl chloride vapor was released and ignited resulting in a vapor cloud explosion. The accident caused significant property damage but no serious injuries.

3. Investigation

The guidance document, *Guidelines for Investigating Chemical Process Incidents* [3] published by the Center for Chemical Process Safety of the American Institute of Chemical Engineers (CCPS/AIChE), was the primary source used in developing the strategy for this investigation. A wide variety of information sources were reviewed in the course of the investigation including, but not limited to:

- design documents, calculations and drawings,
- operating manuals and procedures,
- process hazard analyses,
- management of change records,
- prior incident reports,
- equipment conditions and interlocks,
- production records,
- process data recorded by the distributed control system,
- operator logs,
- witness interviews.

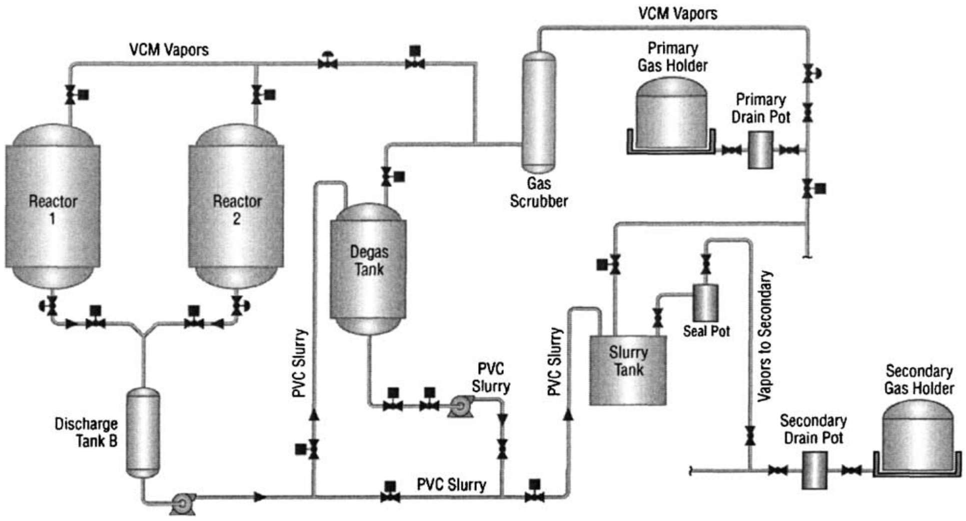

Fig. 2. Piping and equipment diagram for Reactor Discharge Operation.

An analysis of this information revealed a history of overpressure events in the slurry tanks caused by flashing liquid VCM.

4. Accident analysis

4.1. Explosion analysis: what was the source of overpressure?

There were several potential sources of overpressure for the slurry tank. These hypotheses were evaluated by comparing the predicted pressure and energy of these sources with the observed damage.

The first step was to evaluate the failure pressure of the slurry tank. A structural analysis based on the slurry tank design documents, failure analysis reports and the design standard API 650 resulted in a predicted failure pressure of at most 40 psig. Therefore, a potential source of overpressure must be capable of generating a final pressure on the order of the failure pressure of the vessel.

Another important characteristic of the explosion was the energy released [4]. The maximum available energy of the explosion can be calculated from thermodynamics. This can be compared with the observed explosion damage. If the proposed explosion mechanism does not have sufficient energy to create the observed damage, that proposed mechanism can be ruled out. One measure of work performed by the explosion was the work required to lift the roof of the slurry tank to a sufficient elevation (equal to the radius of the roof) so that it could tip over onto the adjacent pipe rack. This work was calculated to be approximately 300 kJ.

Three hypothetical sources of overpressure were identified for further evaluation:

- internal deflagration of VCM vapor,
- high pressure VCM vapor trapped in the discharge tank,
- superheated VCM liquid trapped under pressure in the discharge tank.

The expansion behavior of the VCM vapor depends on whether any liquid VCM is present. If no liquid is present, the pressure of VCM vapor can be treated as a nearly ideal gas over the pressure and temperature range of interest. If liquid VCM is present, the pressure of the system is determined by the VCM vapor pressure curve, a graph of which is shown below (Fig. 3) [5].

The following evidence and analysis refuted the hypothesis that the explosion was caused by an internal deflagration of VCM. The entry of fugitive air into the vapor space of the slurry tank was extremely unlikely since the entire vapor recovery process was carefully inerted with nitrogen gas. Also, the slurry tank had been recently filled with slurry to a level of approximately 50%. This would tend to prevent fugitive air from entering the tank. Finally, there was an absence of ignition sources in the vapor space region of the slurry tank.

The following evidence and analysis refuted the hypothesis that the explosion was caused by high-pressure VCM vapor trapped in the discharge tank. This calculation was based on the adiabatic, irreversible expansion of an ideal gas into a larger volume. The final pressure attained by establishing mechanical equilibrium between the discharge tank and the slurry tank would have been 1.5–1.7 psig. This is significantly less than the failure pressure of the slurry tank, and in fact would not have been capable of lifting the roof from the tank.

The only plausible hypothesis that explains the explosion is that VCM liquid was trapped in the discharge tank. This calculation was based on the isothermal flashing of liquid VCM at the temperature of the hot slurry. The final pressure attained by establishing mechanical equilibrium between the discharge tank and the slurry tank would have been 15–33 psig. This would have been sufficient to cause the failure of the slurry tank. The thermodynamic availability released by the failure of slurry tank was on the order of 10 megajoules, a quantity more than sufficient to lift and tip the slurry tank roof (neglecting venting losses).

4.2. Process data analysis: what was the source of liquid VCM?

The subject facility had operated for over 20 years and had produced on the order of 100,000 batches of product. Why did this particular batch cause an explosion? The answer, documented in the process data, was a series of small changes from the normal operating conditions. The sequence of events and causal factors are summarized in Fig. 4.

The original design for the reactor discharge operation involved venting and depressurizing the reactor to essentially atmospheric pressure. This was necessary due to the design of the slurry tank, which was designed to operate at atmospheric pressure, and was consequently much weaker than the reactor. With the introduction of the degas tank, it was no longer necessary to thoroughly vent the reactor. In fact, the facility operator revised the reactor charging procedure and loaded liquid VCM into the reactor while it was still pressurized. This revision of the procedure reduced the reactor cycle time. During normal operation this change in charging procedure had little impact on the reactor. If the reactor idle period was too long, however, the unreacted VCM vapor in the reactor could condense as the reactor cooled. Condensation depended on a number of factors including the reactor jacket temperature, the ambient temperature and the timing of the reactor cleaning cycle (performed with cold water).

On the day of the accident, after Batch 1 had been depressurized and transferred to the slurry tank, Reactor 1 remained pressurized with VCM and left idle for an unusually long time. The recorded reactor temperature and pressure values decreased during this time, tracking the VCM vapor

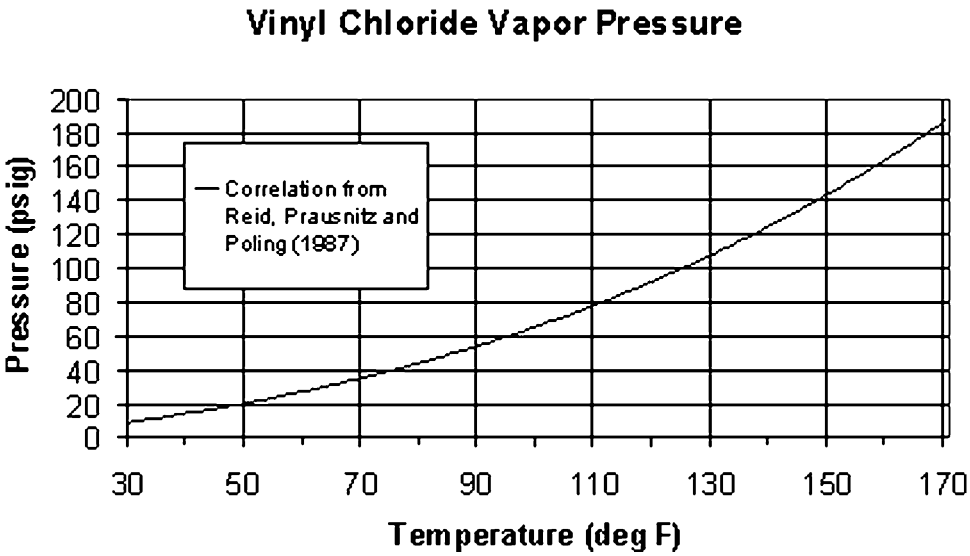

Fig. 3. Vapour pressure curve.

pressure curve. This implies condensation of the VCM. Thermodynamic calculations indicate that approximately 15 wt.% of the vapor condensed. Within a period of approximately 2 h the reactor fluid temperature equilibrated with the jacket temperature (the cooling water temperature was approximately equal to the ambient temperature of 60 °F).

At the end of this cooling period, the reactor cleaning cycle was initiated. This rinse water accumulated at the bottom of the reactor; the liquid VCM would float on top. Since the rinse water would contaminate the reactants charge to the reactor for the next batch, it was drained from the reactor by briefly opening the bottom valve on the reactor. The rinse water, followed by the liquid VCM, filled the discharge tank and associated piping. The liquid VCM would have been the fluid closest to the reactor drain valves.

During this time Reactor 2 was charged, reacted and degassed. The appropriate valves were selected for a transfer from Reactor 2 of hot slurry (at approximately 190 °F) to the slurry tank. When the drain valve for Reactor 2 was opened, the hot slurry contacted the cold VCM liquid in the discharge tank/piping and caused it to flash abruptly. This flashing two-phase flow caused a rapid generation of vapor that exceeded the venting capacity of the slurry tank. The

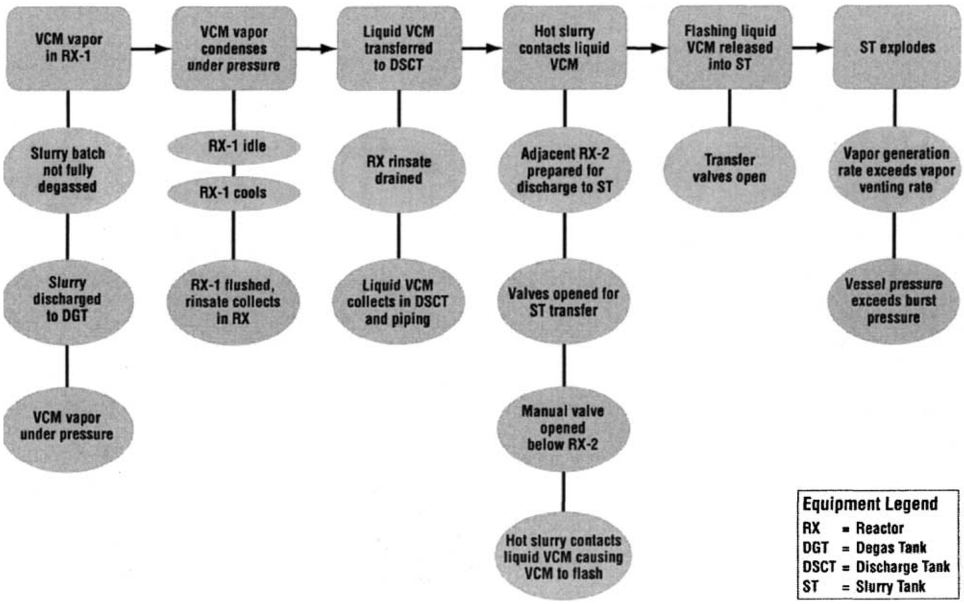

Fig. 4. Event and causal factors chart for Process Vessel Explosion.

internal pressure of the slurry tank exceeded its burst pressure and the tank ruptured.

5. Root cause analysis

The ultimate purpose of an accident investigation is to prevent the recurrence of the accident. To this end, the accident investigation should determine the root causes. A root cause is defined as the “the most basic cause(s) that can be reasonably identified and that management has the control to fix” [6]. Typically, an accident in a complex setting like a chemical plant is the result of many root causes. A root cause analysis does not seek to place blame, but rather seeks to identify opportunities for improvement in the safety management system. The progenitor of structured root cause analysis is the management oversight and risk tree (MORT) system [7]. There are many variations of the basic MORT system [6,8–10]. Root cause analysis was applied to this investigation to identify the deficiencies of the safety management system.

5.1. Investigation of prior overpressure events

The first root cause of this accident was the facility operator’s inadequate investigation, documentation and communication of prior overpressure events. The facility operator’s investigation of prior incidents identified flashing liquid VCM as source of overpressure. However, investigations consistently focused on only one consequence (VCM release to the environment) while failing to recognize signs of a potentially more serious consequence, overpressurization of the slurry tank.

5.2. Process hazard analyses

The facility operator conducted five process hazard analyses (PHAs) on the reactor discharge operations. These PHAs were deficient for two reasons: they failed to recognize flashing liquid VCM as a recurring problem and they failed to identify the slurry tanks as being particularly vulnerable to overpressure. These two factors taken together should have triggered a reassessment of the strategy for overpressure protection for the slurry tanks.

5.3. Design objectives for the overpressure protection system

The facility operator relied on four safeguards for overpressure protection: administrative controls, interlocks (safety instrumented system), venting (emergency relief system) and a weak-seam roof. The design objectives for these safeguards were not clearly defined. Specifically, it was never clear what specific overpressure scenarios the safeguards were intended to manage.

These four safeguards constituted independent layers of protection [1]. At a minimum the design objective for each safeguard should have been defined as a specific performance requirement. Here is an example of design objectives for overpressure protection:

- *Administrative controls*: Reactor operator to monitor and control transfers to the slurry tank to prevent the occurrence of overpressure.
- *Interlocks*: Interlocks to isolate the slurry tank if a high-pressure condition is detected in a reactor or in any slurry or vapor piping connection.
- *Venting*: Relieve pressure in the slurry tank by venting VCM vapor. Vent size based on worst credible overpressure scenario.
- *Weak-seam roof*: In the event of fire exposure, relieve pressure in the slurry tank by allowing the roof to separate from the shell.

The facility operator failed to define the performance requirements at this simplest level.

5.4. Administrative controls for overpressure protection

The facility operator used administrative controls for overpressure protection including procedures and training. However, these administrative controls were ineffective because they only considered normal operation. Reactor operators were not given a specific objective to monitor, detect, and correct abnormal process conditions that could lead to overpressure in the slurry tanks. The process instrumentation and control elements necessary for this purpose were available. If the procedures and training had alerted the reactor operators to overpressure hazards in the slurry tanks, the accident could have been prevented.

5.5. Design basis for the safety instrumented system (interlocks)

There were a number of process interlocks on the slurry tank. Most of these were intended to prevent overfilling the tank. There was no interlock linked to a measurement of the slurry tank pressure. Furthermore, there were no pressure sensors on the slurry tanks. Pressure was monitored only in vessels upstream of the slurry tanks. Finally, there were no interlocks preventing a transfer to the slurry tank if a high pressure condition was detected in the reactor.

The facility operator did install an interlock as a safeguard to prevent further VCM releases. The interlock was installed to isolate the primary vent line from the slurry tank in the event of reverse flow from the PGH, through the slurry tank and to the SGH. The interlock was based on a level measurement in the SGH.

This design decision was inadequate for three reasons. First, the interlock measurement was not based on the hazard of concern: overpressure in the slurry tank. It was based on slurry level in the SGH, a parameter not directly and uniquely related to slurry tank pressure. The second problem with this decision was that the interlock was not based on a process measurement in the slurry tank, the vessel of concern. Instead the process measurement was based on a process measurement in a vessel downstream of the slurry tank. The proper interlock design for this overpressure scenario would have been based on a pressure measurement in the slurry tank or upstream vessels or piping. Finally, interlocks should have been installed to isolate the slurry tank from any source of overpressure (via slurry or vapor piping). Instead, the interlock installed by the facility operator isolated the slurry tank from only one source of overpressure.

5.6. Design basis for venting

Normal venting is defined in API 2000 (1998) [11], as the venting required because of operational requirements (filling or withdrawing liquid from the tank) or thermal (atmospheric) changes.

The appropriate design basis for normal venting of the slurry tanks was vapor displacement by liquid filling or draining of the vessel.

The facility operator knew that the slurry contained liquid VCM. The presence of liquid VCM had the potential to overwhelm the normal venting capacity of the slurry tanks. In fact the facility operator had numerous overpressure events caused by flashing liquid VCM. Hence, they should have followed the guidelines of API 2000 and taken this flashing phenomenon into account in their design for normal venting [12].

The facility operator did not adequately define the worst credible overpressure scenario for the slurry tank. The worst credible scenario was determined to be a volume of liquid VCM equal to twice the volume of the discharge tank. The accident was caused by a fraction of the worst credible scenario (estimated to be less than 5% of a discharge tank volume).

The facility operator had direct evidence that the venting system was inadequate: the occurrence of numerous overpressure events, overpressure damage such as buckling of the slurry tank roof and damage to anchor bolts (stripped threads). If the facility operator had heeded these warning signs, they could have taken corrective action that may have prevented this accident.

5.7. Design of the weak-seam roof for pressure relief

The facility operator incorrectly assumed that the slurry tank was designed and fabricated with a weak-seam roof in accordance with API 650 [13]. It was not. The roof-shell weld design did not match the specifications of API 650 and the weld thickness was two times too large. The most serious deviation from API 650 was the presence of equipment, bracing and a working platform that *tripled* the weight of the roof. Thus, the roof could not fail in a reliable fashion at a predictable pressure.

API 2000 specifies that pressure relief by failure of a weak-seam roof is acceptable for external fire exposure only. There was no fire prior to this accident. Another disadvantage with pressure relief by roof failure is that VCM is a flammable, toxic and carcinogenic chemical. The roof failure in this accident resulted in a vapor cloud explosion and release of a reportable quantity of VCM to the environment.

Finally, pressure relief by roof failure could have occurred while workers were on the tank platform. This could have led to serious injury. Taking these factors into account, it was not appropriate to rely on pressure relief by failure of the roof.

6. Lessons learned

An examination of the root causes of this accident suggests some lessons learned for preventing similar accidents:

1. *Hazards can be managed only if they are recognized*. Incident investigation and process hazard analysis are complimentary activities. Objective investigation of incidents can reveal important information about unexpected hazards at a facility. In this case study the facility operator failed to realize that prior overpressure events were a significant clue regarding the hazard of flashing liquid VCM. This would have been a significant finding to incorporate into their process hazard analyses. Because it was absent, the facility operator never questioned the adequacy of their overpressure protection strategy.
2. *Identify vulnerable targets and protect them with multiple safeguards*. For example, consider a system of two process vessels connected by piping. If the MAWP of the source vessel is much greater man the MAWP of the receiving vessel (on the order of 100 times), the receiving vessel is a vulnerable target because it is susceptible to catastrophic failure. To reduce the probability of catastrophic failure, use multiple safeguards for overpressure protection of the receiver vessel. If the MAWP of the source and receiver vessels is comparable, perhaps a single safeguard is adequate.
3. *When using multiple safeguards, explicitly define the objectives for each safeguard*. Multiple safeguards will be most effective when they are complimentary in their function and offer some degree of redundancy. It is imperative to communicate the purpose and function of these safeguards to operating and maintenance personnel.
4. *Beware of situations where saturated liquids are trapped under pressure*. Saturated liquid will flash and generate vapor as its pressure is reduced. To reduce the potential to over-pressurize downstream vessels, the pressure of the trapped saturated liquid must be reduced slowly. Specifically, the rate of vapor production caused by flashing must not exceed the venting rate of the receiving vessel.

7. Conclusions

An explosion of an atmospheric storage tank occurred at a polyvinyl chloride resin manufacturing facility during a reactor discharge operation. This explosion was ultimately caused by the failure of the facility operator to understand and control the overpressure hazard of a flashing saturated liquid. During the 2-year time period when the facility was modifying its process to reduce environmental releases, a series of at least six overpressure events occurred, some of which resulted in structural damage to the subject atmospheric storage tank. Flashing liquid vinyl chloride monomer caused each of these overpressure events. The facility operator downplayed the significance of these events and did not incorporate these findings into the five process hazard analyses conducted on the reactor discharge operation during a 5-year time period. Failing to see the significance of these overpressure events, the facility operator never questioned the adequacy of the overpressure safeguards on the storage tank. This accident offers four important safety lessons: (1) incident investigations are an opportunity to identify previously unrecognized hazards; (2) identify vulnerable targets and protect them with multiple safeguards; (3) clearly define the performance requirements for the engineering and administrative controls used for overpressure protection; and (4) beware of the overpressure hazard posed by a saturated liquid trapped under pressure.

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