

## Investigation Report

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### KEY ISSUES:

- Ineffective management of reactive chemical hazards
- Lack of a process safety management system
- Persisting gaps in federal safety regulations for reactive chemical hazards





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## Abbreviations, Acronyms, and Initialisms

ASME	American Society of Mechanical Engineers
CCPS	Center for Chemical Process Safety
CHETAH	Computer Program for Chemical Thermodynamic and Energy Release Evaluation
CSB	U.S. Chemical Safety and Hazard Investigation Board
EPA	U.S. Environmental Protection Agency
ESI	Explosive Service International
MRR	Midland Resource Recovery
NAICS	North American Industry Classification System
NFPA	National Fire Protection Association
OSHA	U.S. Occupational Safety and Health Administration
PHA	Process Hazard Analysis
ppb	parts per billion
psig	pounds per square inch gauge
PSM	Process Safety Management
RMP	Risk Management Plan
SPSI	Specialized Professional Services, Inc
SRS	Specialized Response Solutions
TNT	Trinitrotoluene

## 1 Executive Summary

On May 24, 2017, an explosion occurred at the Midland Resource Recovery (MRR) facility in Philippi, West Virginia, killing two workers<sup>a</sup> and severely injuring another worker. The founder and president of MRR was one of the victims. The CSB initiated an investigation of the incident and deployed an investigative team on May 28, 2017. While the CSB was investigating this incident, the MRR facility experienced a second explosion, on June 20, 2017. This explosion fatally injured a contractor<sup>b</sup> employed by Specialized Professional Services, Inc. (SPSI). MRR had hired SPSI to perform investigation and mitigation work at its Philippi facility following the May 24, 2017, explosion.

The CSB determined that the probable cause of these incidents was reactive, unstable chemicals that exploded when workers tried to drain the uncharacterized, chemically treated liquid from natural gas odorizer equipment. The CSB investigation found that MRR lacked an effective safety management system to identify and control hazards from reactive chemicals. Among other things, MRR had no formal hazard identification process in place to analyze or characterize what chemicals were inside the odorizer vessels—and in what quantity—before decommissioning and chemically treating this equipment with sodium hypochlorite. The company also lacked effective safeguards to prevent unexpected or uncontrolled chemical reactions.

Following these catastrophic incidents, MRR asserts that it has stopped using reactive chemicals, including sodium hypochlorite, and the company now uses a proprietary process to remove the mercaptan smell from decommissioned odorization equipment.

Based on the findings from this incident, the CSB reiterates recommendations to the U.S. Occupational Safety and Health Administration (OSHA) and the U.S. Environmental Protection Agency (EPA).

### Key Lessons

The CSB provides the following key lessons for companies that deal with reactive chemistry:

1. Companies need a robust safety management system in place to prevent reactive chemical incidents. If a process has the potential for uncontrolled chemical reactions to occur, the company should conduct a formal evaluation of the reactive chemistry, perform a hazard analysis, and ensure that sufficient safeguards are in place to prevent reactive chemical incidents.
2. Companies should have a thorough and complete understanding of their reactive chemistry under design conditions and under all foreseeable abnormal conditions. For example, companies should avoid treating uncharacterized waste materials with sodium hypochlorite because of the potential explosive hazards associated with its complex reactive chemistry.

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<sup>a</sup> The May 24, 2017 explosion fatally injured Jan Strmen, 72 and Justin Marsh, 19 [36].

<sup>b</sup> The SPSI employee, Scott Albertini, 53, was also a 35-year member and chief of the McDonald, Pennsylvania volunteer fire department [34], [35].

## 2 Background

### 2.1 About Midland Resource Recovery

In 2006, Midland Resource Recovery (MRR) began operations at its headquarters in Philippi, West Virginia [1]. MRR provides many services related to natural gas odorants, known as mercaptans, to the natural gas and propane industry. For example, MRR delivers various mercaptan products to customers, which are used to add odor to make the gas detectable by smell. Among other services, MRR decommissioned and removed odorizer equipment from sites in the United States and Canada, and transported this equipment to its Philippi, West Virginia, site for chemical treatment to remove the mercaptan odor from the steel before it was scrapped. MRR also treated odorizer equipment at its site in Midland, Texas. At the time of the May 24, 2017, incident, MRR had 14 employees at its Philippi site.

### 2.2 Odorant Information

Natural gas is combustible and odorless. To help avoid unidentified gas leaks that could lead to explosions,<sup>a</sup> federal regulation requires combustible gases that flow through certain distribution pipelines, such as natural gas, to be “odorized” so that at a concentration of one-fifth of the lower explosive limit, the gas can be readily detected by a person with a “normal sense of smell.”<sup>b</sup> Natural gas is odorized by a class of chemicals called mercaptans.<sup>c</sup> It has an odor akin to rotten eggs [2] that can be detected at extremely low concentrations (1 part per billion (ppb)) [3].

In the late 1930s, Peerless Manufacturing Company developed odorizer equipment to introduce mercaptan odorant to natural gas pipelines [4]. In recognition as a dependable safety device, the American Society of Mechanical Engineers (ASME) designated the Peerless metering-type odorizer as a national historic mechanical engineering landmark [5], [6]. The technology used in that equipment was applied to a later model of the equipment, called Peerless “MP” odorizers, which were sold and installed in the 1960s (Figure 1).

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<sup>a</sup> In 1937, unodorized natural gas leaked into a school in New London, Texas and ignited, causing a catastrophic explosion that fatally injured about 300 people—mostly students in grades 5 through 11. That incident spurred Texas and the nation to pass laws requiring natural gas to be odorized so leaks could be detected [31].

<sup>b</sup> 49 C.F.R. § 192.625. The American Gas Association website includes a [page](#) that describes how the natural gas delivery system works and which pipelines are odorized [41].

<sup>c</sup> Natural gas is odorized with various chemicals including tertiary butyl mercaptan, tetrahydrothiophene, isopropyl mercaptan, dimethyl sulfide, and methyl ethyl sulfide [42].

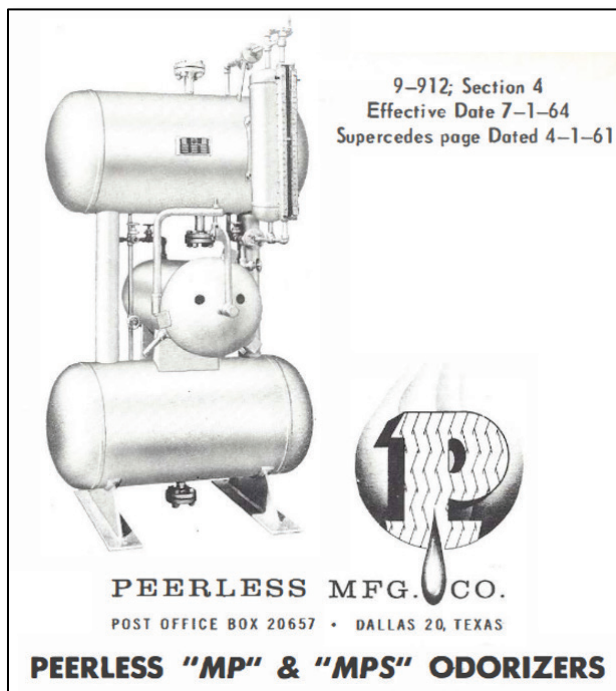


Figure 1. Peerless MP Odorizer. This figure, adapted from a 1964 Peerless Manufacturing Company parts price list, shows a Peerless MP Odorizer. (Credit: MRR).

Peerless metering-type gas odorizers as Peerless MP Odorizers are constructed of three tanks with interconnected piping (Figure 2). The top tank is the storage tank that contains mercaptan to be introduced to the pipeline. The middle tank is the odorizer compartment, where unodorized natural gas enters the tank, is odorized, and exits the tank to be routed back to the pipeline. The bottom tank is a safety tank, providing overflow protection for both the top and middle tanks. The odorizers involved in both the May 24, 2017 and June 20, 2017, incidents were MP 85 units, with a nominal odorant capacity of 85 gallons.<sup>a</sup> MRR stated to the CSB that before the May 24, 2017, incident the company had successfully removed the mercaptan smell from more than 150 MP style vessels.

<sup>a</sup> The top and bottom chambers of an MP 85 odorizer have the same physical dimensions. The vessels have a diameter of two feet and a seam-to-seam length of three feet.



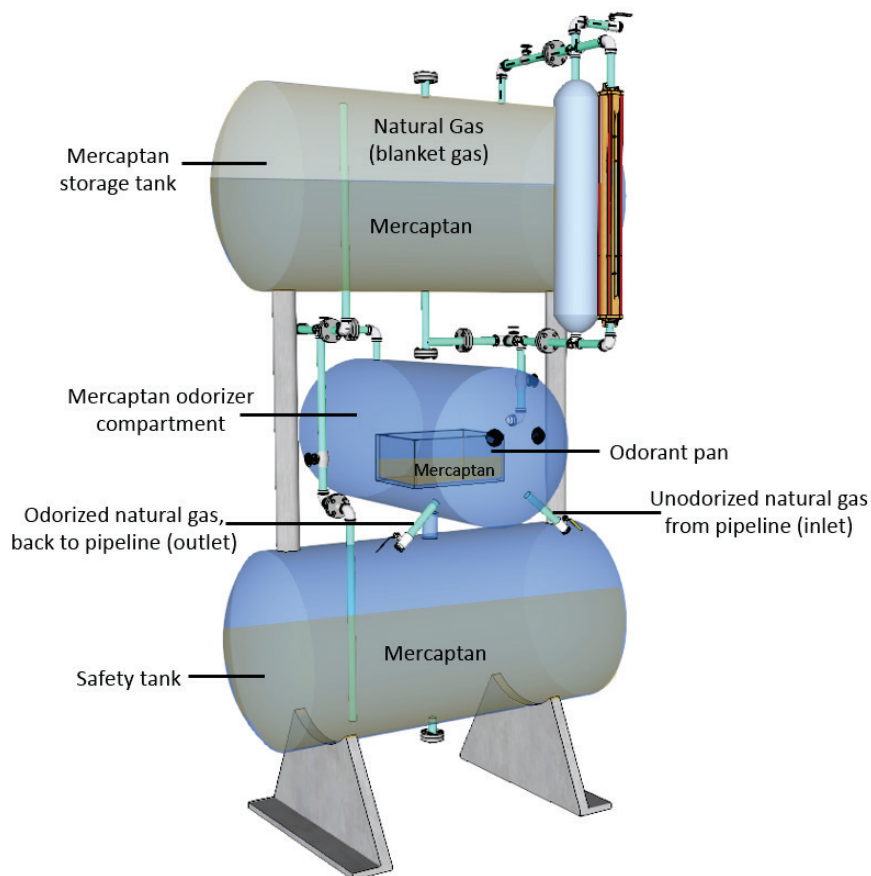


Figure 2. Peerless MP Odorizer. This graphic shows some of the piping and internal equipment associated with a Peerless MP Odorizer. (Credit: CSB).

The MP odorizer involved in the May 24, 2017, explosion came from Kansas, where it was used to odorize natural gas in an intrastate pipeline. The company that owned the pipeline told the CSB that the vessel used Spotleak® 1007 odorant [7], which is composed of about 80 percent tert-butyl mercaptan, and 20 percent ethyl methyl sulfide [8].<sup>a</sup> The tank was taken out of odorant service in 1997 and sat in a lay down yard in Kansas for 18 years. It was brought to the MRR Philippi site in December 2015.<sup>b</sup> A specification plate found at the scene of the explosion that appears to have been installed on the vessel indicates that the MP unit was manufactured in 1960 and had a design pressure of 550 pounds per square inch gauge (psig) and a test pressure of 825 psig.

Though such odorizers successfully odorized natural gas pipelines for decades, gas odorization technology has evolved since their development, and Peerless MP Odorizers are no longer manufactured. Many of the operating Peerless MP Odorizers are being phased out and decommissioned in favor of modern odorizers. Decommissioning and disposing of odorizer equipment such as Peerless MP Odorizers, however, presents unique challenges for two reasons:

<sup>a</sup> The safety data sheet for Spotleak® 1007 specifies a composition of about 80 percent 2-propanethiol, 2-methyl- (CAS No. 75-66-1). A synonym for this chemical is tertiary butyl mercaptan [8]. Spotleak® 1007 also contains about 20 percent Ethane, (methylthio)- (CAS No. 624-89-5) [8]. A synonym for this chemical is ethyl methyl sulfide. The flash point of Spotleak® 1007 is less than negative 15 degrees Fahrenheit [8].

<sup>b</sup> MRR technicians chemically treated this MP odorizer on April 18, 2017.

1. The vessels often still contain mercaptan, which, if exposed to the atmosphere during the decommissioning process can cause the nearby area to smell of mercaptan and as one MRR employee explained, “it can cause a horrible public disturbance,” as the odor is widely associated with gas leaks.
2. The steel walls of the vessel are permeated with mercaptan, causing the metal itself to smell strongly of mercaptan. As an MRR manager explained to the CSB, the vessels therefore cannot be simply cut apart and taken to a scrap yard because “you would end up with gas leak calls for 20 miles [from the scrap yard] probably.”

MRR positioned itself as a company to fill the niche of decommissioning and disposing of obsolete odorizer equipment and developing systems to address these challenges.<sup>a</sup>

## 2.3 Method to Decommission and Drain Peerless MP Odorizers

When MRR arrives at a site to remove odorizer equipment, about half of the time the odorizer tank is still in service, and half of the time the tank is disconnected from the process. From MRR employee interviews, the CSB learned that the tanks often contain some type of gas or liquid, such as mercaptan, but some companies do not have a written record or safety data sheet (SDS) for the full range of possible materials inside the tank. MRR typically must rely solely on verbal communication from the client company of the likely material present in the odorizer equipment. An MRR employee told the CSB:

We don't really get involved in how the people are really operating [their odorizer equipment]. I think those people are retired already. ... [I]t's more of a, really an obsolete tank that's there, and how it was operated in, in the '80s is not really, we [are not] privy to that information.

To decommission and drain Peerless MP Odorizers, MRR technicians perform the steps described below and illustrated in Figure 3:

1. Open a valve to vent any natural gas from the top chamber through a carbon filter;
2. Insert a wooden dowel into the top chamber to check the liquid level;
3. Add nitrogen to pressure liquid from the top chamber through the dip tube and into a drum;
4. Add nitrogen to the middle chamber to transfer liquid from the bottom chamber up and into the top chamber;
5. Repeat steps one through three to transfer liquid from the top chamber into a drum; and
6. Seal vessel connections and transport the MP odorizer for chemical treatment.

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<sup>a</sup> MRR asserted to CSB investigators that it was not the only company that was chemically treating obsolete odorization equipment with sodium hypochlorite to remove the mercaptan smell.

MRR technicians do not perform any testing to analyze or characterize what chemicals are present in the MP odorizer. Also, due to the design of the odorizer itself and the decommissioning process MRR established, MRR technicians do not have a way to remove all the uncharacterized liquid from the bottom chamber or the middle chamber.<sup>a</sup>

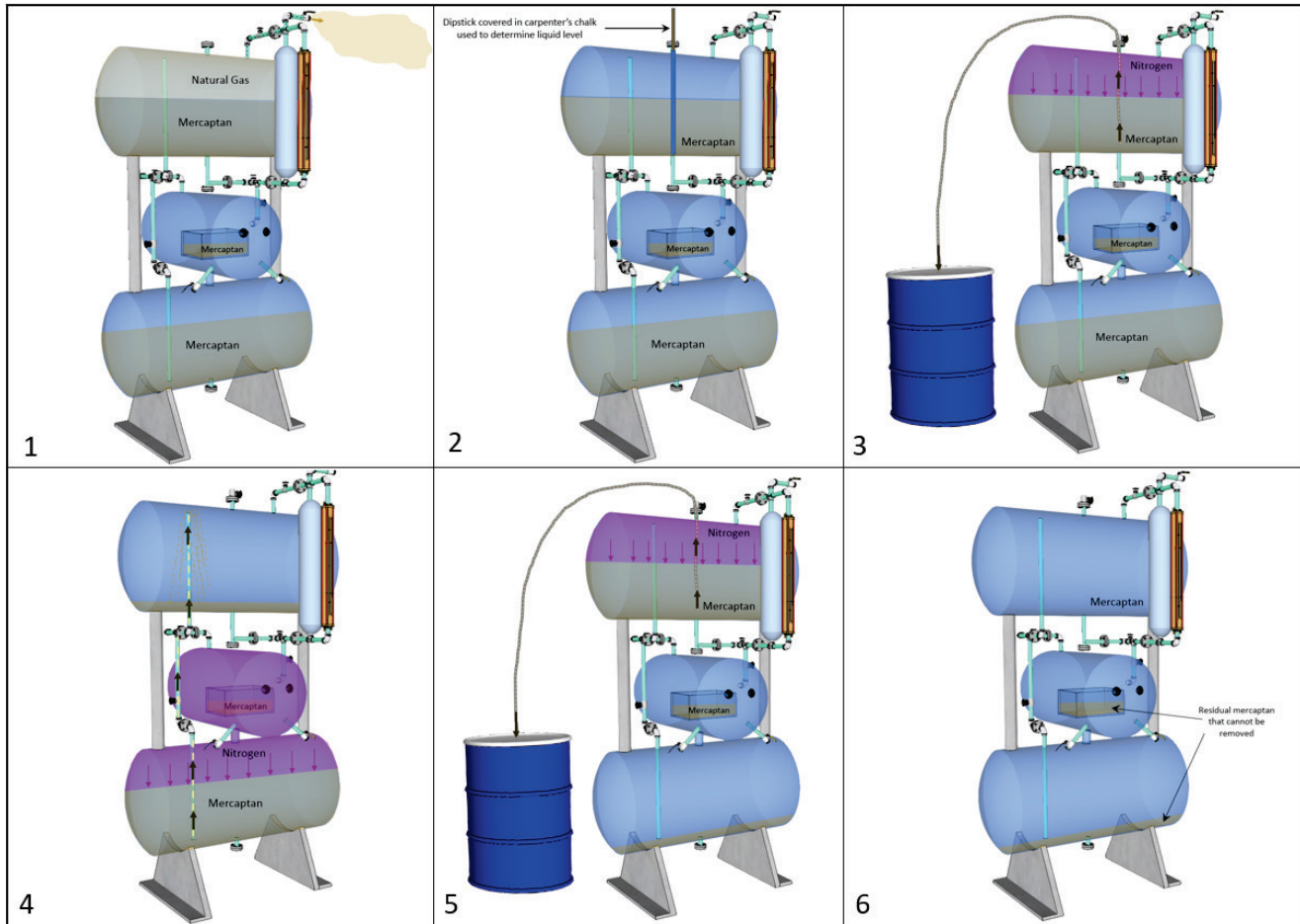


Figure 3. Odorizer Decommissioning and Draining. These graphics outline the steps MRR technicians typically performed to drain liquid from MP odorizers tanks in preparation for transport and chemical treatment. (Credit: CSB).

## 2.4 Chemical Treatment of MP Odorizers to Remove Mercaptan Smell

The primary purpose of chemically treating odorizing equipment is to remove the mercaptan smell before disassembling and scrapping the steel components. Equipment that once contained mercaptan is frequently recycled in a scrapyard, but during the scrap process mercaptan residue can enter the surrounding air. Even small quantities of released mercaptan can raise false concerns of gas leaks and cause odor complaints among community residents.

<sup>a</sup> Although MRR does not evaluate the mechanical integrity of the dip tube in the bottom chamber, remove the bottom flange or otherwise ensure the bottom chamber does not contain liquid, the company asserted to the CSB that the MP odorizer vessels are “RCRA” empty as otherwise defined by 47 C.F.R. 1250. Guidance provided by the EPA in 1982 states that, “A tank will be considered “empty” when its contents have been drained to the fullest extent possible. Since many tank designs do not allow for complete drainage due to flanges, screens, or syphons, it not expected that 100% of the wastes will always be removed. There may be cases where a tank is never “completely empty” (47 FR 1250; January 11, 1982)” [52].

When Peerless MP Odorizers arrived at the Philippi, West Virginia site, they sat in the yard containing odorizer equipment until MRR had the personnel and resources needed to treat them. Philippi had a few years' worth of accumulated MP odorizer inventory on site at the time of the May 24, 2017, incident.

When MRR technicians begin the process of treating an MP odorizer, they first check the equipment to verify that liquid was drained from the MP odorizer. Although most liquid should be removed during the decommissioning process, MRR has received tanks at its Philippi site that still contained excessive amounts of liquid. If excess liquid is present, MRR technicians repeat the draining process outlined in Section 2.3.

MRR technicians then chemically treat the MP odorizers by filling them with diluted sodium hypochlorite<sup>a</sup> (Figure 4) to remove the mercaptan odor from the steel. MRR refers to the liquid remaining in the treated MP as “process water.” After chemical treatment, MRR transfers the process water to a tote (Figure 5). To chemically treat the odorizers at the Philippi facility, MRR performs the steps outlined in Figure 6 below.<sup>b</sup>



Figure 4. Sodium Hypochlorite Tote. This picture shows one of the totes at MRR that contained sodium hypochlorite. (Credit: CSB).

<sup>a</sup> Diluted sodium hypochlorite is the product referred to commercially as liquid bleach. Household bleach is a solution of sodium hypochlorite, generally containing seven percent or less (by weight) sodium hypochlorite [19, pp. 2-3]. According to The Chlorine Institute's *Pamphlet 96, Sodium Hypochlorite Manual*, sodium hypochlorite is made by reacting chlorine with sodium hydroxide solutions. The manual notes that “[a] slight excess of sodium hydroxide is needed for stability [19, p. 6].”

<sup>b</sup> At times, MRR technicians may have deviated from the typical chemical treatment steps outlined in this report because of problems such as inoperable valves, plugged or otherwise damaged dip tubes, or from sludge or other process buildup within the MP odorizer.



Figure 5. Process Water Totes. This picture shows totes at MRR containing “process water” that MRR technicians have pumped out of treated odorizer equipment. (Credit: CSB).

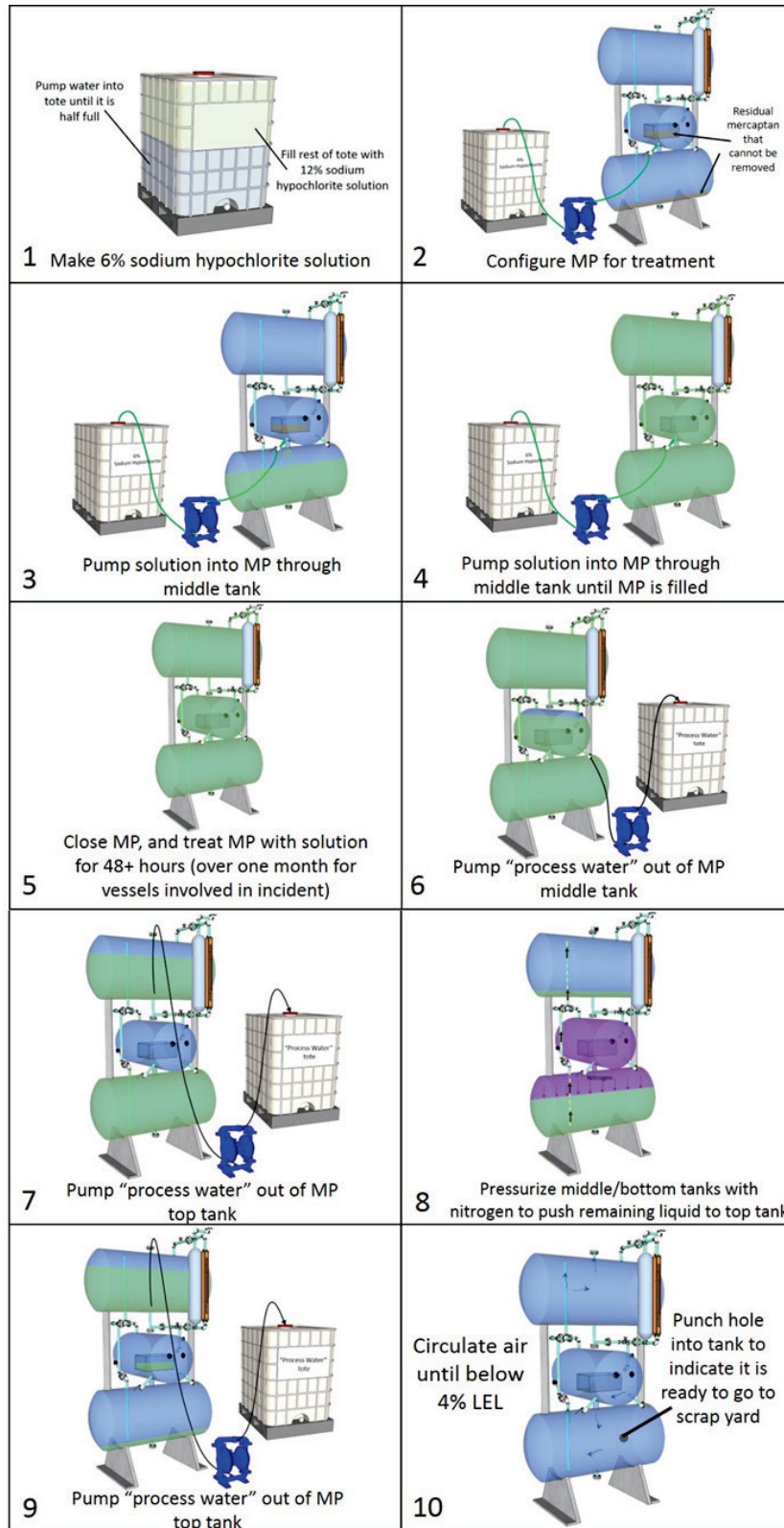


Figure 6. Chemical Treatment. This graphic depicts the typical steps MRR technicians perform to chemically treat MP odorizers to remove the smell of mercaptan from the steel. (Credit: CSB); LEL refers to the Lower Explosive Limit.

MRR technicians typically observed an operating pressure of -0.25 to 5 psig during the chemical treatment process. The tanks are rated at 125 to 1,000 psig. MRR therefore did not install pressure relief on the tanks because the company thought it was not needed.

### 3 May 24, 2017 Explosion

MRR decommissions up to 20 Peerless MP Odorizers per year. In early 2017, MRR had accumulated 16 MP odorizers at its Philippi site that needed chemical treatment. MRR had treated those MP odorizers by May 2017 with a solution of diluted sodium hypochlorite. The chemical treatment was done by completely filling the three vessels of each MP with the diluted sodium hypochlorite solution. Some of the MP odorizers were spray painted with the date they were treated (Figure 7). MRR generally tracked what stage of the decommissioning process a tank was in by spray painting a symbol, such as “T” for *treated* and “D” for *drained*, on the vessel.<sup>a</sup>



Figure 7. Treatment Status. This photo shows how MRR technicians used red spray paint to record the date the MP was chemically treated, April 19, 2017. (Credit: CSB).

In May 2017, after roughly one month of chemical treatment with the sodium hypochlorite, MRR personnel began draining the treated MP odorizers. Spray paint markings (Figure 8) and equipment connections indicated that three of the 16 treated MP odorizers had been drained.

<sup>a</sup> MRR asserted that the company “also used a tag system for MP style vessels, including written logs showing when they were treated, drained, purged and scrapped.” The CSB investigation revealed, however, that for half of these 16 MP odorizers (8 of 16), MRR lacks records showing when the company chemically treated the equipment or which MRR technicians performed the chemical treatment.



Figure 8. Drained Status. This photo shows how MRR technicians spray painted odorizer equipment with a “D” or a “DR” for *drained* (in yellow) after they drained the sodium hypochlorite treatment solution from the odorization equipment. (Credit: CSB).

On May 24, 2017, two workers were assigned to drain some of the chemically treated MP odorizers. While working, they were accompanied by the company owner, who was at the Philippi site on a routine visit. The company owner developed MRR’s reactive chemical treatment process and at times, he trained MRR technicians and took part in chemical treatment operations. The MRR site manager told the CSB that during the late morning, the two workers and the company owner were preparing to drain one of the MP odorizers. MRR surveillance video shows that at 11:08 a.m., while the personnel were working on the odorizer, the top tank of the MP odorizer violently exploded, killing one worker and the company owner, and severely injuring the other worker.

MRR personnel on site told the CSB that the explosion was one sharp and quick noise, and it “sounded like dynamite.” One witness felt the ground shake, and another felt the trailer he was in rock. One witness estimated that explosion debris launched 300 to 500 feet in the air. Several witnesses saw a brown mist in the air, consistent with the appearance of the solution that was generally within the tanks after chemical treatment (the “process water”). None of the witnesses the CSB interviewed saw any smoke or flame. One witness said the area smelled like process water after the explosion, and another said the area smelled like a match—the typical smell when mercaptan vapors are being flared.

The CSB could not determine the exact actions of the three personnel leading up to the explosion because there were no immediate witnesses, and surveillance footage could not be used to determine their actions definitively. Figure 9 shows still frames of the explosion from the surveillance footage. Figure 10 and Figure 11 show the MP odorizer after the incident. Figure 12 shows the variation in appearance of process water within MRR’s chemical treatment process. Figure 13 shows aluminum components that were likely inside the middle chamber of the MP odorizer. MRR



provided the CSB documents from 1964, showing that Peerless used aluminum components in the middle chamber as part of the gas metering and odorant delivery system.



Figure 9. Surveillance Video Capturing May 24, 2017, Explosion. These still frames from an MRR surveillance camera capture the May 24, 2017, explosion. (Credit: MRR).



Figure 10. MP Odorizer That Exploded on May 24, 2017. This photo shows the failed MP odorizer from the May 24, 2017, explosion. (Credit: MRR).



Figure 11. MP Odorizer Fragment from May 24, 2017, Explosion. This photo shows a portion of the top chamber of the MP odorizer after the May 24, 2017, explosion. (Credit: CSB).



Figure 12. Process Water. The light-yellow samples (top row) were taken from the bottom chamber of the MP odorizer that exploded on May 24, 2017. The brown samples (bottom row) were taken from a “process water” tote not involved in the May 24, 2017, incident. Note the color differences showing the drastic color variation of the process water, indicating that different vessels likely had different types and quantities of materials in them before chemical treatment. (Credit: CSB).



Figure 13. Aluminum Parts. This photo shows aluminum internal components that were likely in the middle chamber of the MP odorizer, found after the May 24, 2017, incident. The explosion destroyed the aluminum pan and components that were inside the middle chamber of the MP odorizer. (Credit: SPSI).

## 4 June 20, 2017 Explosion

### 4.1 CSB Research Leading Up to Second Incident

Following the May 24, 2017, explosion, CSB investigators began reviewing literature on explosive chemistry that might help with understanding incident. The CSB located a paper that described alkyl hypochlorite hazards from treating sulfur-containing waste materials with sodium hypochlorite “to get rid of the smell” [9, p. 80] (a process like MRR’s). The authors noted that alkyl hypochlorites have been identified in such waste streams and “have also been cited as the reason for explosions” [9, p. 80]. The paper described alkyl hypochlorites as being “heat, light, and shock sensitive,” “thermally unstable,” and “highly explosive” [9, p. 80]. The authors of this paper also highlighted the potential explosive hazard of methyl hypochlorite (an alkyl hypochlorite) and stated, “methyl hypochlorites in particular being classified as a high explosive having a similar explosive potential to TNT [trinitrotoluene]”<sup>a</sup> [9, p. 80]. Further, the authors noted that:

Bretherick’s *Handbook of Reactive Chemical Hazards* cites a number of incidents which have been attributed to the presence of alkyl hypochlorites generated during waste treatment operations. All led to explosions, but thankfully [with] no reported

<sup>a</sup> Trinitrotoluene “is commonly known as TNT and is an explosive used in military shells, bombs, and grenades, in industrial uses, and in underwater blasting” [39].

fatalities, however it should be noted that there is only circumstantial evidence relating to the presence of alkyl hypochlorites [9, p. 80].

The paper also explained that explosive alkyl hypochlorites “can be formed relatively easily by the action of sodium hypochlorite on an alcohol under laboratory conditions” [9, p. 87]. This information suggests that methyl hypochlorite could be formed by the reaction of methanol with sodium hypochlorite. MRR has methanol on site that its technicians use to wash customers’ odorization tanks if, for example, water gets into them. Lacking any analysis of what was in a given odorization tank that MRR transported to its Philippi site for decommissioning, it seems plausible that methanol could have been present, making it possible that methyl hypochlorite could have formed when MRR added sodium hypochlorite.

In addition, during the MRR investigation, the CSB was conducting an ongoing investigation of the November 15, 2014 incident at the DuPont La Porte, Texas, facility. Documentation DuPont provided the CSB as part of its investigation of the La Porte incident included potential hazards of methyl hypochlorite. These records showed that in 1976, a DuPont facility had an explosion that the company attributed to methyl hypochlorite. The DuPont La Porte documentation had only high-level summary information from DuPont’s 1976 explosion learnings, but one document said, “... the reaction of the **hypochlorite with mercaptan** (from another vessel) had brought the pH into the range for methyl hypochlorite formation.” (emphasis added). The DuPont La Porte documents referenced other DuPont reports and studies that CSB investigators thought might be important to understanding the chemistry taking place in the MP odorizers at MRR. The CSB asked DuPont to voluntarily provide this information to the CSB, but DuPont declined, as the company did not want to get involved in the MRR incident.

Given that the MP vessels were filled with unknown liquid chemicals and sealed tight, along with the potential for reactive alkyl hypochlorite chemistry that appeared to fit the scenario of the May 24, 2017, incident, the CSB investigation team’s hypothesis was that MRR’s equipment deodorizing process had created the possibility that each of the chemically treated MP odorizers was essentially a bomb.

## 4.2 Day of the Second Incident

Among those from other state and federal agencies, CSB representatives were at the MRR Philippi, West Virginia, facility on June 20, 2017, to conduct interviews related to the investigation of the May 24, 2017, incident. After arriving on site, MRR counsel informed CSB investigators that MRR planned to drain the remaining MP odorizers. MRR legal counsel had hired Specialized Professional Services, Inc.<sup>a</sup> (SPSI) to conduct this activity.

Because SPSI was hired directly by MRR legal counsel, MRR asserted attorney work product over what SPSI had learned about the May 24, 2017, incident and over SPSI’s research and theories on the cause of the incident.<sup>b</sup> On this basis, MRR asserted that CSB investigators were not permitted to speak with SPSI employees regarding these specific

<sup>a</sup> SPSI’s company literature highlights the experience its staff gained through their careers as DuPont employees. Among other things, SPSI highlights that they have responded to more than 1,000 incidents without a single injury. In its company literature, SPSI also uses DuPont’s process safety management (PSM) wheel to highlight the company’s experience with planning and managing process safety.

<sup>b</sup> Despite SPSI being hired by and working under the control and direction of MRR legal counsel, MRR asserts that, “MRR did not control the site, or the processes or the protocols employed on June 20, 2017.” In contrast, the CSB investigation team’s experience with MRR up through June 20, 2017, clearly demonstrated that through its legal counsel, MRR maintained complete control of the site and ongoing activities, including delaying the delivery of SPSI’s protocol, for draining process water from remaining MP odorizers, to the CSB until the investigators were in travel status from Denver to Philippi, controlling the sign in log sheet upon entry, and by preventing a frank and open discussion between the CSB (and other agencies) and SPSI about why SPSI believed their planned activities could be performed safely.

topics. One of the CSB investigators explained to MRR legal counsel that the CSB had been researching explosive chemistry and had learned about the potential for methyl hypochlorite formation and its history of being associated with hypochlorite treatment explosions. The MRR attorney relayed his understanding that SPSI's theory on what caused the May 24, 2017, explosion was that it was not related to a hypochlorite reaction. He added that he hoped at some point to be able to share SPSI's theory with the CSB, but it could not happen at that time.

Before starting the MP odorizer draining operation, SPSI's business development and special project manager, a former DuPont employee with 30 years of emergency response experience and at that time a governor-appointed officer on the West Virginia State Fire Commission, conducted a briefing for MRR and agency representatives. When asked by a representative from a state agency why SPSI thought this operation would be safe – given that a similar approach to draining the MP odorizer had resulted in the May 24, 2017, explosion – the SPSI manager asserted, "If our science is right, this will be fine."

Unable to directly engage SPSI about the safety issues regarding its plan and lacking confidence that MRR or SPSI understood either the cause of the May 24, 2017 incident or the full range of possible reactive chemistry involved, CSB investigators took shelter behind a shipping container (conex box) located behind a building more than 150 feet away from the SPSI operation.

SPSI first tried to drain an MP odorizer that SPSI personnel believed, based on not seeing liquid through the sight glass, did not have any liquid in its second chamber (Figure 14). In other MP odorizers where SPSI had concluded liquid was present, SPSI workers could see "liquid there, various shades of yellow liquid."

SPSI had installed an additional (new) valve and pressure gauge into the piping coming off the middle chamber (Figure 14—piping to the left of sight glass). SPSI had also put a rope on the existing valve on the pipe, for use in opening the valve (Figure 14). To start the draining operation, SPSI's field supervisor opened the valve using the rope. The pressure gauge indicated zero pressure in the MP odorizer. SPSI's procedure called for halting the operation if the pressure gauge showed more than 30 psig. Because the pressure gauge showed no pressure, the operation continued.



Figure 14. MP Odorizer Before June 20, 2017 Explosion. This pre-incident photo shows the MP odorizer and equipment connections that SPSI workers were using to drain liquid when the June 20, 2017 explosion occurred.<sup>a</sup> (Credit: CSB).

The field supervisor then opened the secondary valve. A pressure surge went through the hose connected to the valve. One SPSI witness explained, “[I] saw the line kick a little bit, which was sort of a surprise...because the gauge had said zero [pressure].” After the pressure surge, the field supervisor closed the valve. Pressurized liquid flowed through the hose toward the tote. SPSI, however, had not expected liquid to be in the middle chamber because when looking through the sight glass during their planning activities the workers did not see any liquid. The field supervisor then reopened the secondary valve and SPSI workers filled sample jars with the liquid flowing from the hose.

Based on surveillance video, the MP odorizer exploded less than five minutes after the draining operation had begun (Figure 15 and Figure 16). A portion of the MP chamber struck and fatally injured the field supervisor. Figure 15 shows still frames of the explosion from a security video.

<sup>a</sup> MRR records show that the MP odorizer involved in the June 20, 2017 explosion was removed from a site in Wisconsin in November 2016 and it was chemically treated on May 15, 2017.

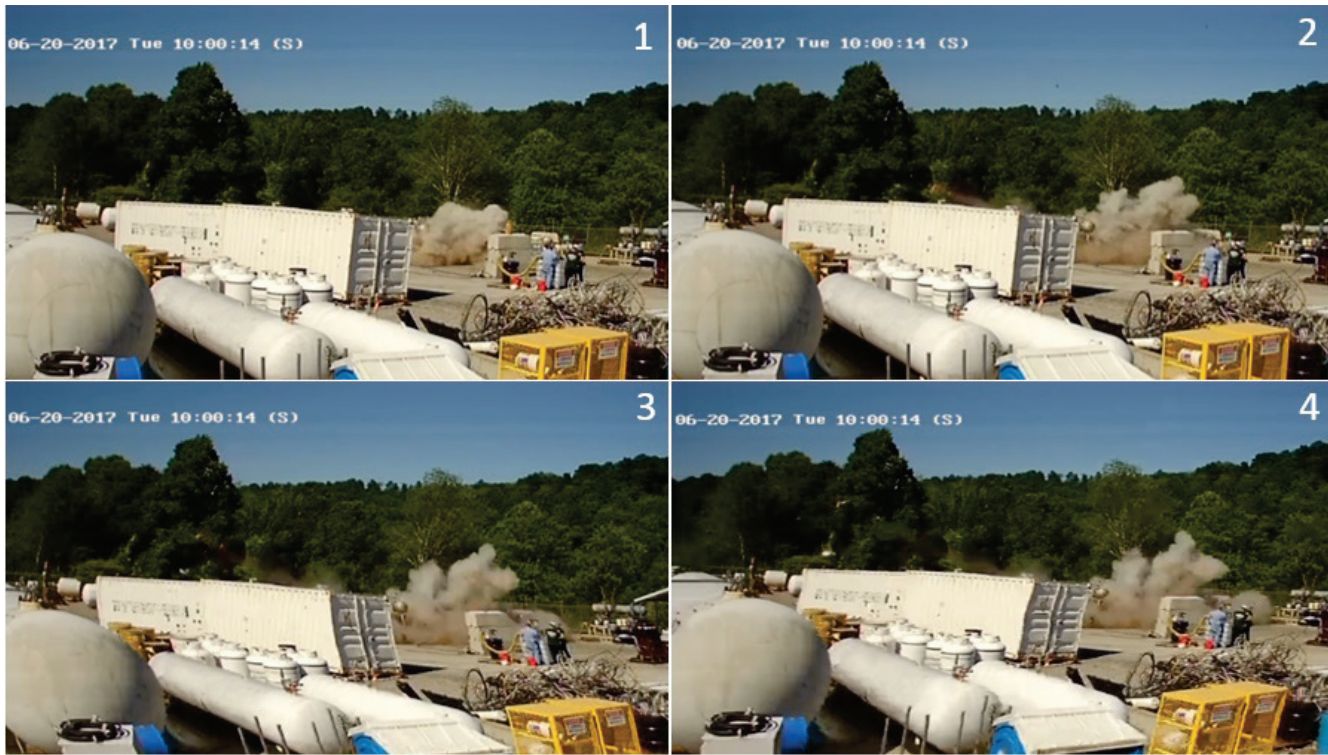


Figure 15. Surveillance Video Capturing June 20, 2017, Explosion. These still frames from an MRR surveillance camera capture the June 20, 2017, explosion. The MP odorizer involved in the explosion is partially obstructed from view, behind the white shipping container. No flames were visible in the surveillance footage. (Credit: MRR).





Figure 16. MP Odorizer Vessel That Exploded. This photo shows the MP odorizer that exploded on June 20, 2017. The back portion of middle chamber ruptured (see also Figure 17) and the front threaded section blew off. The aluminum tray and mechanical parts that were inside the middle chamber were expelled from the MP during the event. (Credit: SPSI).



Figure 17. Ruptured MP Odorizer Middle Chamber from June 20, 2017, Incident. This photo shows the post-incident condition of the rounded end of the middle chamber that ruptured in the June 20, 2017, explosion. (Credit: SPSI).

## 4.3 Post-Incident Investigation Activities

Following the June 20, 2017, incident, the CSB terminated all planned and future activities at the MRR Philippi site to protect the safety of CSB investigators. CSB investigators interviewed several SPSI personnel and were able to gain a better understanding of events leading up to the second incident and why SPSI felt its actions on June 20, 2017 to drain the remaining vessels were safe. According to interviews, following the May 24, 2017, incident, MRR planned to drain the liquid from the remaining MP odorizers to prevent another incident and to avoid concerning the public about a possible gas release due to the mercaptan odor. MRR attorneys hired SPSI to conduct this work. An SPSI worker informed the CSB that SPSI had initially planned to use linear shaped charge explosives<sup>a</sup> to cut a hole in the vessels, allowing the process water to empty directly to the ground, avoiding the need for people to be near the MP odorizers during the draining process. SPSI employees also said that because of community odor concerns, a decision was made not to use explosives to drain the odorizers because MRR “would not agree to doing the breach of the vessel that way.”<sup>b</sup>

The CSB learned that after MRR decided not to drain the remaining vessels using explosive charges, SPSI worked to identify the cause of the May 24, 2017 explosion. SPSI workers had observed that the middle chamber of 4 of the 11 remaining MP odorizers appeared to contain no liquid, based on the absence of visible liquid in the chambers’ sight

<sup>a</sup> A linear shaped charge is an explosive designed to produce a linear cutting action [38].

<sup>b</sup> MRR asserts while SPSI did discuss using explosives, MRR never prohibited SPSI from using explosives to drain the remaining MP odorizers.

glasses. The CSB learned that SPSI theorized that during the filling of those four vessels with the sodium hypochlorite solution, a closed valve between the top and middle chambers allowed a vapor pocket to remain inside the middle chamber. The company had also observed, on the MP odorizer that exploded on May 24, 2017, that the valve between the top and middle chambers was in the open position, counter to what MRR had communicated as the technique used to fill the vessels with sodium hypochlorite. SPSI technical staff identified the following potential scenario to explain the cause of the May 24, 2017 explosion:

- MRR personnel filled the MP odorizer with sodium hypochlorite solution, keeping the valve between the middle and top chambers closed. Air was trapped inside the MP odorizer by this closed valve, causing an air pocket to remain in the middle chamber of the odorizer.
- Inside the middle chamber is an aluminum tray. Aluminum is highly reactive with sodium hydroxide – a chemical present in sodium hypochlorite solutions.<sup>a</sup> Sodium hydroxide reacts vigorously with aluminum at room temperature to produce hydrogen gas.
- MRR personnel opened the valve between the top and middle chambers of the MP odorizer, allowing the sodium hypochlorite solution—containing sodium hydroxide—to contact the aluminum components in the middle chamber that were inside the trapped air bubble. Sodium hydroxide reacted with the aluminum to rapidly generate hydrogen, causing pressure to increase inside the closed MP odorizer. Because the MP odorizer lacked pressure relief protection, the unit exploded from the high pressure generated by the hydrogen gas.

Based on this theory, SPSI personnel believed they understood the cause of the May 24, 2017, explosion and they developed a protocol to allow their personnel to safely drain the liquid from the remaining odorizers.<sup>b</sup> SPSI personnel told the CSB that MRR had never informed them that the remaining MP odorizers might contain methanol, diesel, kerosene, or other contaminants. As a result, SPSI specifically developed its protocol to drain the remaining MP odorizers while avoiding conditions that could generate hydrogen and thus create high pressure inside the equipment.

### 4.3.1 Purpose of Concrete Barriers

Figure 15 above shows three SPSI workers positioned behind one of three concrete barriers set up before the June 20, 2017, explosion. The CSB was not able to determine conclusively the intended purpose of these barriers. The MRR vice president of operations told the CSB that these barriers were in place to protect SPSI workers, but SPSI personnel statements, documents, and worker actions do not support that these barriers were intended to provide a worker protection safeguard.

When CSB investigators discussed the reason for the concrete barriers with MRR’s vice president of operations, he believed the barriers were “there for the protection of the people that were working there.” He added that, “they were

<sup>a</sup> The Chlorine Institute’s *Pamphlet 96, Sodium Hypochlorite Manual* identifies a number of metals that are incompatible with sodium hypochlorite, including aluminum and carbon steel. The manual cautions that mixing any of these metals with sodium hypochlorite may result in “[r]elease of oxygen gas, [that] generally does not occur violently. Could cause overpressure/rupture of a closed system.” None of the incompatible material scenarios described in the manual result in the generation of hydrogen gas [19, p. 110].

<sup>b</sup> SPSI’s draft protocol was dated June 9, 2017. On June 19, 2017, MRR legal counsel emailed the draft protocol to the lead CSB investigator while investigators were traveling from Denver to Philippi to conduct employee interviews related to the May 24, 2017 incident. The email from MRR legal counsel identified the protocol as a draft that might be modified as plans were finalized on June 20, 2017. MRR counsel did not provide sufficient time for CSB to review or comment on the draft protocol SPSI workers used to drain the remaining MP odorizers.

strategically placed because ... SPSI knew that they were going to have to go at several spots to remotely open valves and work on them.” The MRR vice president also explained that MRR did bring in the two 40-foot conex boxes (Figure 15) to protect their large mercaptan storage tank, but MRR also emptied all the mercaptan from this area before the June 20, 2017 activities.

When asked by CSB investigators if SPSI intended for these barriers to protect workers, SPSI’s business development and special project manager clarified that they were not. The SPSI manager said:

Those were put in place at the request of MRR’s vice president of operations. ... [We] knew we would be working within the physical boundaries of those retaining walls that were stacked up. ... The barriers were for the protection of their [MRR’s] other mercaptan tanks and areas of their facility that they had concern for outside of our work area.

The SPSI manager’s statement about the concrete barriers is consistent with the protocol SPSI developed to drain the process water from the MP odorizers. The protocol does not mention the concrete barriers, establish any type of exclusion zone near the MP odorizer, or suggest that SPSI workers would use the concrete barriers as a safeguard while performing the work. The SPSI manager’s statement is also consistent with the worker actions that took place on June 20, 2017. During the nearly five minutes from when SPSI started their activities to drain the process water from the MP odorizer up to the time of the explosion, only one of the four SPSI employees consistently remained behind the concrete barrier wall (Figure 18).



Figure 18. Concrete Barriers. This surveillance video image from June 20, 2017 at 9:56 a.m., shows only one of four SPSI workers positioned behind the concrete barrier. Two other concrete barriers were placed, but they are outside the view of this surveillance camera (Credit: MRR).

Based on SPSI worker actions captured by the surveillance video leading up to the explosion, MRR and SPSI needed to provide more barriers and strengthen their work plan for these concrete barriers to properly serve as a worker protection safeguard. Had MRR and SPSI established a more robust barrier system, such barriers may have helped to protect the SPSI field supervisor from being struck and fatally injured by the projectile when the MP chamber

exploded. The CSB notes, however, that the goal should be to protect people by preventing reactive chemical explosions. The confusion surrounding the purpose of the concrete barriers alone should have been enough for MRR and SPSI to pause, reevaluate the work plan using the hierarchy of controls,<sup>a</sup> and reconsider using explosive charges to protect people from being in the work area adjacent to the imminent hazard posed by these chemically treated MP odorizers.

## 4.4 Draining the Remaining MP Odorizers

Following the second incident, MRR hired an outside firm, Specialized Response Solutions (SRS), to vent and drain the liquid from the remaining 11 MP odorizers. SRS noted the following in its *Operations Safety Plan on MRR Vessel Control & Mitigation*:

With careful consideration of the events that have transpired at the MRR site in Philippi, WV, we feel there is an imminent threat to life safety as long as the vessels in question are sealed and not vented. Understanding the dynamics of catastrophic failure of pressure vessels, regardless of whether it is from an explosive compound or a rapid overpressure from a reaction, the impact to life safety remains the same. Understanding these factors, and the need to remove the life safety threat to further assess the compounds and chemistry involved with the over pressure events, we will operate under the same protective measures and practices used in explosive material operations.

SRS continued:

The use of explosive venting of the vessels at MRR provides the safest means to reduce the risk of another incident. Both incidents have resulted after manual manipulation, of some kind, of valves or fittings on the vessels. The use of explosive venting of large and small compressed gas vessels, is and has been used for at least 35 years and is the industry standard for reducing risk of catastrophic pressure vessel failure [Figure 19].

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<sup>a</sup> The hierarchy of controls is a concept that refers to the ranking of the safety potential of various strategies for hazard management from most to least effective. Even if a greater risk-reduction action, such as minimizing hazardous chemicals, is used, it is still important to maintain other, lower level, administrative controls, such as wearing adequate personal protective equipment (PPE). This way even if one risk reduction system fails, others are in place to prevent or minimize the incident's impact. Prevention and mitigation strategies represent the safeguards designed to eliminate, prevent, reduce, or mitigate a scenario; they are also referred to as barriers, layers of protection, lines of defense, or control measures [53, pp. 34-35].



Figure 19. Explosive Venting. These drone video images show the explosive venting used to cut holes in a group of MP vessels to drain the vessels while minimizing risk to people. The bottom right image shows a fire that erupted from flammable liquids that drained from some of the MP vessels. (Credit: MRR).

SRS subcontracted to another company, Explosive Service International (ESI), to make the vessels safe for SRS to dispose of. ESI prepared an *Explosive Blast Plan* for MRR that explained how it would conduct this work. ESI's plan was to use proprietary precision explosive cutting tools to cut two-inch holes in each vessel to allow SRS to conduct a final remediation procedure at the site (Figure 20). ESI noted that this method would provide minimal exposure to contract personnel. ESI also explained that it would use proprietary conical shape charges for the operation – 178 precision explosives charges would be used on vessels above ground during daylight hours.

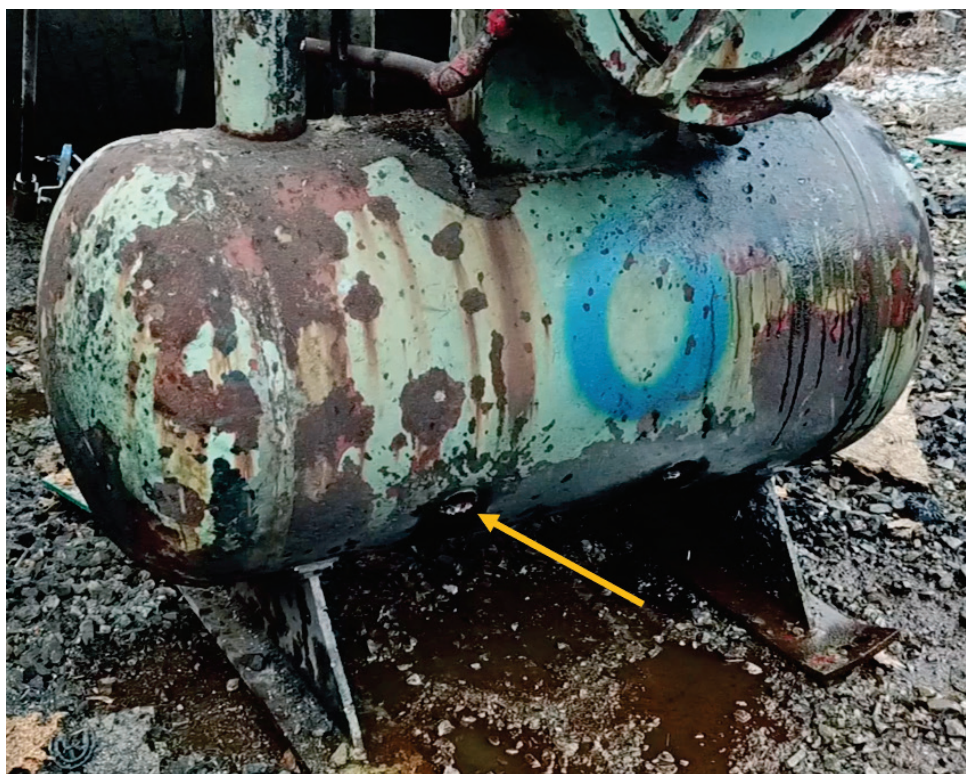


Figure 20. Drain Hole. This drone image shows one of the holes cut by the explosion venting process used to drain the bottom chamber of an MP vessel. (Credit: MRR).

Before starting the explosive venting process, MRR issued a “Public Safety Information Memo” to the Barbour County, West Virginia, Sheriff’s Office, which shared the memo on its Facebook page. The memo notified the community that MRR intended to control and mitigate a small quantity of natural gas odorizing vessels at its facility in a safe manner [10]. The memo informed the public that during operations certain residences and businesses located within one-half mile of the site would be evacuated during blasting operations, and certain roads would be closed. SPSI had not used explosives to drain the MP vessels because of community odor concerns, yet MRR’s public memo did not alert the community to potential odor concerns related to SRS’s explosive venting operation.

The explosive venting work to drain and dispose of these vessels took place during a two-week period from December 4 to December 15, 2017.

## 5 Incident Analysis

Given the general lack of evidence, it is unclear what exact chemical reactions took place within the two MP odorizers in May and June to cause them to rupture violently. It is likely, however, that the explosions were caused by uncontrolled chemical reactions. At no point in MRR’s decommissioning or chemical treatment process were the contents inside either vessel tested to determine what was initially present. Furthermore, due to MRR’s operational practices at its Philippi facility, it cannot be conclusively determined what exactly was added to either vessel, in what quantity, or when. Despite this uncertainty, it appears an unexpected chemical reaction occurred, resulting in the rupture of the two MP odorizers. The equipment came from different facilities in different states and the chemicals used in their operation prior to coming to MRR could not be determined.

MRR personnel knew that adding sodium hypochlorite to mercaptan would result in an exothermic reaction. Workers reported that after bleach was added to the MP odorizers at the Philippi site, the tanks would get hot to the touch, indicating that a chemical reaction was occurring. It is also known that both explosions occurred during activities to drain process water from the MP odorizers after they had been filled at least a month prior. In both cases, the work activities disturbed the contents of the MP odorizer.

## 5.1 MRR Practices

Good practice safety guidance is available to help companies effectively manage reactive chemical hazards. For example, the Center for Chemical Process Safety (CCPS) published *Essential Practices for Managing Chemical Reactivity Hazards*. In introducing its 2003 text, CCPS stated:

The objective of the publication is to provide guidance, to any facility with chemical reactivity hazards, on ways to effectively address the difficult challenge of preventing loss, injury or environmental harm from uncontrolled chemical reactions. This publication is not intended to provide the only guidance on how to safely manage chemical reactivity hazards, but it does represent the result of a consensus of the development committee representing a number of chemical companies and consulting organizations [11, p. viii].

In *Reactive Hazards* (a CSB safety video produced in 2007), Dennis Hendershot, a chemical process safety consultant, described what companies need to do to prevent reactive chemistry hazards: “The most important thing to managing reactive chemistry hazards is that you have to have a thorough and complete understanding of your chemistry under design conditions and also under all foreseeable abnormal conditions” [12]. Ultimately, MRR’s failure to understand and manage its reactive chemistry hazards led to both the May 24, 2017, and June 20, 2017, incidents.

MRR’s lack of robust process safety management systems and inconsistent operational practices made it difficult for the CSB to understand what specific reactive chemistry occurred. As discussed earlier, the site relied on spray painting the vessels to document where each vessel was in the process. Post-incident analysis showed that this procedure was inconsistently carried out and potentially gave contradictory information. Also, while MRR had a general treatment procedure for tanks, it had no formal procedure addressing how to chemically treat and drain the MP odorizers. In addition, although the general tank procedure called for filling the tanks with sodium hypochlorite only up to the 10 percent level, the MP odorizers were completely filled with liquid.

Even though these pressure vessels were filled with reactive liquid chemicals, no overpressure protection was provided for them.<sup>a</sup> MRR’s vice president of operations stated that when such vessels were in odorizing service, the industry often treated them as an extension of the process, which therefore did not require additional protection from a pressure relief device.<sup>b</sup> He added that during the sodium hypochlorite treatment process, the vessels typically pressured up to about five psig, and then an MRR technician would close and seal the vessel. Over time, as the vessel cooled, it would actually operate under slight negative pressure (that is, at a slight vacuum). Also, although the MP vessels were never

<sup>a</sup> MRR asserts that it is important for readers of this CSB report to know “that the [MP odorizer] vessels are only closed after an extended filling process, being open to atmosphere for 45 minutes to an hour.”

<sup>b</sup> Some companies do equip their odorizers with relief devices. MRR technicians removed these devices before transporting the equipment for chemical treatment because of concerns that the valve could be a weak point that would allow an odor event to occur should a transportation accident happen.



completely empty during transportation, MRR did not believe that transportation regulations required relief protection for these vessels. The CSB notes, however, that if SPSI's theory was correct, and the May 24, 2017, incident was caused by hydrogen generation (Section 4.3), a pressure relief device might have prevented the vessel rupture. Overpressure protection is further discussed in Section 5.2.

For treating tanks, MRR normally kept the sodium hypochlorite in the tanks for only one to two days. When treating the MP odorizers, however, MRR allowed them to sit for over a month, potentially allowing unstable chemicals to form. MRR lacked controls, such as established limits for how long to keep the MP odorizers full of sodium hypochlorite to control for any unintended chemical reactions. Also, MRR did not control the sodium hypochlorite dilution.<sup>a</sup> Workers established the dilution quantities roughly, based on estimating the volume of large, partly filled totes. In addition, an MRR technician told the CSB that to "save a buck or two," they sometimes use rainwater recovered from the ground inside tank containment areas instead of city water to dilute the hypochlorite. Using rainwater from storage tank containment areas could introduce contaminants into MRR's chemical treatment process. In an interview with CSB investigators, MRR's vice president of operations acknowledged that he was aware of the practice of using water out of storage tank dikes and using this rainwater as dilution water for the sodium hypochlorite.

No formal or documented risk assessment was conducted before MRR began its decommissioning process for odorant equipment, and no formal or documented risk assessment was done before establishing the MP odorizer decommissioning process. No compatibility studies were completed prior to treating equipment, and MRR conducted no studies to determine the exothermic rates of reaction for adding different solutions of bleach to different mercaptan odorant mixtures. Had a risk assessment been done and laboratory testing been carried out to identify any unwanted chemicals formed as a byproduct, it is possible that MRR could have identified the reactive chemicals that formed to cause the incidents, and could have developed a treatment process to prevent their formation.

## 5.2 Overpressure Protection

As previously stated, MRR's chemical treatment method was intended to completely fill the MP odorizers with liquid sodium hypochlorite, and then seal the vessels without providing any overpressure protection, such as a pressure relief valve.<sup>b</sup> The MP odorizers were designed and built as pressure vessels using the American Society of Mechanical Engineers (ASME) *Boiler and Pressure Vessel Code*. The applicable section of this code for pressure vessels is *Section VIII – Rules for Construction of Pressure Vessels, Division I*, which covers "the design, fabrication, inspection, testing, and certification of pressure vessels operating at either internal or external pressures exceeding 15 psig" [13].

The ASME *Boiler and Pressure Vessel Code* requires that all pressure vessels "shall be provided with overpressure protection" [14]. Furthermore, the code requires the user to identify all overpressure scenarios, establish how the

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<sup>a</sup> The Chlorine Institute's *Pamphlet 96, Sodium Hypochlorite Manual* provides guidance on diluting sodium hypochlorite solutions. Among other things, this guidance covers dilution water and says that, "Soft water (well or tap) should be used which can be generated using an ion exchange softening unit that uses salt (sodium chloride) as the regenerate." In addition, to ensure stability of the final product, the guidance highlights the importance of testing and adjusting the pH and excess caustic to ensure the solution contains excess alkalinity [19, p. 99]. The CSB is not aware of any MRR practices or testing to evaluate or adjust its diluted sodium hypochlorite solutions.

<sup>b</sup> The Chlorine Institute's *Pamphlet 96, Sodium Hypochlorite Manual* recommends use of overpressure protection where sodium hypochlorite can be trapped between valves or blinds. The guidance also cautions that sodium hypochlorite gasses can cause significant pressure buildup in the trapped section [19, p. 39].

equipment will be protected for each scenario, and ensure that the required overpressure protection is properly installed before initial operation [15].

West Virginia and 10 other states, however, have not adopted this pressure vessel code [16].<sup>a</sup> In 2009, former CSB Chairman John Bresland discussed this gap and implored the remaining states to adopt the long-standing pressure vessel code to help prevent accidents. Chairman Bresland stated:

There are only eleven states that do not require companies to follow the Pressure Vessel Code of the American Society of Mechanical Engineers (ASME). I ask all jurisdictions to adopt the Pressure Vessel Code and related boiler standards. Lives will be saved as a result [17].

Installing a spring-loaded safety relief valve on the equipment is a typical approach used to protect pressure vessels from overpressure.<sup>b</sup> Given the lack of certainty around the reactive chemistry that caused both the May 24, 2017, and June 20, 2017, explosions at MRR, however, the CSB cannot definitively say that these incidents could have been prevented by equipping the MP odorizers with typical spring-loaded safety relief valves. In fact, a safety relief valve may not be capable of reacting quickly enough to protect the equipment from the rapid pressure increase generated by an explosion originating inside a vessel.

The American Petroleum Institute (API) publishes API Standard 521(API 521), *Pressure-relieving and Depressuring Systems*. This industry standard specifies requirements and gives guidance in examining the causes of overpressure and for determining relief rates. API 521 explains that while spring-loaded safety relief valves can protect equipment from most common overpressure scenarios, these devices may react too slowly to protect from an explosion originating inside a pressure vessel. Using the example of a typical combustion reaction, API 521 states:

If overpressure protection is to be provided against internal explosions caused by ignition of vapor-air mixtures where the flame speed is subsonic ([in other words,] deflagration but not detonation), rupture disks or explosion vent panels, not relief valves, should be used. These devices respond in milliseconds. In contrast, relief valves react too slowly to protect the vessel against the extremely rapid pressure buildup caused by internal flame propagation [18, p. 29].

For the design of explosion-relief systems, API 521 directs the designer to the National Fire Protection Agency's (NFPA) *Standard on Explosion Protection by Deflagration Venting*, NFPA 68 [18, p. 29]. API 521 also informs the user that NFPA 69, *Standard on Explosion Prevention Systems*, details alternative means of explosion protection "including explosion containment, explosion suppression, oxidant-concentration reduction, and so forth" [18, p. 29].

The CSB notes that the complexity of applying explosion venting or explosion prevention systems for the MP odorizers would likely far exceed the complexity needed to modify and simply eliminate the explosion conditions created by MRR's chemical treatment process. As will be further discussed in Section 8, modifying the chemical treatment process to eliminate the conditions that could create an explosion appears to be precisely the path MRR has taken post-incident through changes made to the company's odorization equipment treatment process.

<sup>a</sup> West Virginia requires the ASME *Boiler and Pressure Vessel Code* for most steam boilers [44].

<sup>b</sup> See [What Are Safety Relief Valves?](#), a video explaining what safety relief valves are and how they work [45].

## 5.3 Physical Evidence

Physical evidence from the May 24, 2017, and June 20, 2017, incidents show differences in the aluminum MP odorizer components. For example, aluminum components from the May 24, 2017, incident have a general corrosion appearance while aluminum parts from the June 20, 2017, incident show signs of melting from heat (Figure 21). These differences could be related to how much exposure the aluminum parts had with the sodium hypochlorite and whether or not liquid was present in chamber two, affecting how much these parts were heated by the explosion. It is also possible that the physical difference in the aluminum parts may indicate that the reactive chemical mechanism involved was not the same.



Figure 21. Aluminum Parts. The picture on the left shows an aluminum part from the MP odorizer involved in the May 24, 2017, incident that appears to have general corrosion. The photo on the right shows an aluminum part from the MP odorizer involved in the June 20, 2017, incident that appears to show signs of melting from heat. (Credit: MRR (left), SPSI (right)).

## 5.4 Test Results

Chemical analysis was conducted on contents of the ruptured MP odorizers after both the May and June 2017 incidents. This analysis showed that unintended chemical reactions were likely occurring during the cleaning process that contributed to the ruptures.

The MP odorizer involved in the May 24, 2017, incident contained reaction products and byproducts expected from the reaction of sodium hypochlorite with mercaptans.<sup>a</sup> However, the testing of the June 20, 2017 ruptured vessel contents also showed chemicals that would not be expected, such as long-chain hydrocarbons (e.g., nonane and decane) and benzene components. These unexpected chemicals show that some other reactions were likely occurring, or unexpected chemicals were in the vessel before chemical treatment.

MRR hired a contractor to perform testing on liquid samples from the MP odorizer involved in the June 20, 2017, incident. The liquid was observed to have two layers (which had not been observed in other process water totes), and both liquid layers were analyzed in a laboratory. The bottom liquid phase was typical of what was observed in other process water totes. The top liquid phase had a chemical profile similar to diesel fuel, with long-chain hydrocarbons

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<sup>a</sup> Testing results from the bottom chamber of the MP odorizer involved in the May 24, 2017 incident showed the presence of tertiary butyl alcohol in the sample. The testing did not identify the presence of methanol.

present. The contractor could not see any liquid under the aluminum tray when looking into the vessel through the sight glass, but the tray may have been blocking the view of a small amount of liquid inside the second chamber.

Post-incident, various totes of process water were also tested with gas meters, and multiple totes indicated the presence of flammable material that, based on MRR's statement regarding the effectiveness of the cleaning process, should not have been present.

## 5.5 Potential to Form Explosive Compounds During Treatment

Other than the mercaptan odorant, other chemicals including methanol, diesel, and kerosene, could be present in odorization equipment. MRR's vice president of operations was aware of potential customer practices in which, at times, methanol might be added to reduce the freezing point of wet mercaptan or customers might try to save money on odorant cost by diluting the odorant with diesel or kerosene. In addition, Peerless odorization equipment training documents describe the practice of adding kerosene to odorization equipment.

The Chlorine Institute's *Pamphlet 96, Sodium Hypochlorite Manual* identifies a number of organic compounds that are incompatible with sodium hypochlorite, including methanol, fuels, and fuel oils such as diesel or kerosene. The manual warns that mixing any of these chemicals with sodium hypochlorite may result in the "Formation of explosive compounds" [19, p. 110].

The *Chemical Reactivity Worksheet* is a free software program that can be used to find out about the chemical reactivity of common hazardous chemicals [20]. Using the *Chemical Reactivity Worksheet* to evaluate mixtures of sodium hypochlorite with methanol, diesel, or kerosene shows that sodium hypochlorite is incompatible with these chemicals, that "hazardous reactivity is expected," and that the reaction "may be particularly intense, violent, or explosive."<sup>a</sup>

When asked whether the potential presence of methanol, diesel, or kerosene, in the odorization equipment created any potential concerns with MRR's chemical treatment process, MRR's vice president of operations said, "I'm not aware of any." Other MRR employees were either unaware of the potential for methanol, diesel, or kerosene to be present in the odorization equipment or were unaware that these chemicals could form explosive compounds when mixed with sodium hypochlorite.

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<sup>a</sup> The *Chemical Reactivity Worksheet* also shows that "aluminum and its alloys are incompatible with sodium hypochlorite solutions" [20].

## 6 CSB Reactive Hazards Study

### 6.1 Applicable Key Findings

Chemical reactions allow for a diversity of manufactured products. However, chemical reactivity can lead to significant hazards if not properly understood and controlled. Chemical reactions can rapidly release large quantities of heat, energy, and gaseous byproducts. Uncontrolled reactions have led to serious explosions, fires, and toxic emissions. The impacts may be severe in terms of death and injury to people, damage to physical property, and effects on the environment. Therefore, safely conducting chemical reactions is a core competency of the chemical manufacturing industry.

Recognizing this hazard, the CSB released a report in September 2002 titled *Improving Reactive Hazard Management* [21], which detailed findings related to understanding and controlling the hazards of reactive chemistry. The objectives of the report included determining the impacts of reactive chemical incidents, examining how industry, the U.S. Occupational Safety and Health Administration (OSHA), and the U.S. Environmental Protection Agency (EPA) address reactive hazards; and developing recommendations for reducing the number and severity of reactive chemical incidents.

The 2002 CSB report issued multiple key findings, many of which are applicable to the MRR incidents, including these:

- Of the 167 serious incidents in the United States involving uncontrolled chemical reactivity from January 1980 to June 2001, over 50 percent involved chemicals not covered by existing OSHA or EPA process safety regulations [21, p. 5].
- Reactive hazards are diverse. The 167 incidents analyzed included over 40 different chemical classes (i.e., acids, bases, monomers, oxidizers, etc.), several types of hazardous chemical reactivity (chemical incompatibility, runaway reactions, or sensitive materials), a diverse range of chemical process equipment involved including storage tanks and transfer equipment. These incidents resulted in a variety of consequences from fire and explosions to toxic gas emissions [21, p. 7].
- Approximately 70 percent of the 167 incidents occurred in the chemical manufacturing industry. Thirty percent involved a variety of other industrial sectors that store, handle, or use chemicals in bulk quantities [21, p. 8].
- Unique aspects of reactive hazards should be examined during a process hazard analysis (PHA), such as the need for reactive chemical test data, and methods available to identify and evaluate worst-case scenarios involving uncontrolled reactivity [21, p. 9].
- Integration of reactive hazard information into process safety information, operating procedures, training, and communication practices is vital to handling reactive chemicals safely [21, p. 9].

The report highlighted that inadequate process safety management practices are often cited as the cause of reactive incidents and that it is vital to maintain robust practices when handling reactive chemicals. As a result of recommendations made in the CSB's 2002 report, the Center for Chemical Process Safety (CCPS) produced a book in

2003 titled *Essential Practices for Managing Chemical Reactivity Hazards* [11], which provided technical guidance for identifying, addressing, and managing chemical reactivity hazards.

The table below summarizes some of the necessary systems the CSB and CCPS identified for the safe operation of reactive materials and how these systems were implemented by MRR. If MRR had implemented the findings and performed hazard identification and evaluations on the process prior to conducting the decommissioning work, it is likely the company would have determined safer methods for performing the work activities and prevented these incidents.

Reactive Safety Management Principles	Guidance Summary	MRR Activities around MP Odorizer Decommissioning and Chemical Treatment
Hazard Identification (CSB)	A structured approach to identifying and understanding the reactive hazards of chemicals used alone or in combination is needed.	No formal hazard identification process was in place to understand reactive hazards in decommissioning process.
Information (CCPS)	Know if you have the potential for uncontrolled reactions to take place, how such reactions might be initiated, how to recognize uncontrolled reactions, and what safeguards are in place to prevent uncontrolled reactions.	No formalized safeguards were put in place to prevent uncontrolled reactions.
Collection of Reactivity Hazard Information (CCPS)	Gather chemical reactivity data on the chemicals likely to be present at your facility. Include a means of detecting and checking any new or variant chemicals brought on site for the first time.	At no point in time were the contents inside vessels tested to check what chemicals were present prior to decommissioning or chemically treating.
Testing for Chemical Reactivity (CCPS)	An understanding of the inherent chemical energy present and conditions under which it can be released is needed. Literature sources or lab testing can provide the needed information.	No testing was conducted to determine the heat of reaction of the decommissioning process or to understand reaction byproducts.
Hazard Evaluation (CSB)	Set up a system for investigating reactive hazards, assessing the potential consequences of uncontrolled reactions, and establishing a safe design and operating basis.	No risk assessment (PHA) was conducted for the MP chemical treatment process, and no formalized risk assessment was conducted for chemically treating any vessels.
Consequence Assessment (CCPS)	Model possible scenarios that could lead to uncontrolled reactions, to understand what consequences (potential releases from the system) could occur.	No modeling was conducted to attempt to understand what was occurring within the vessels during the decommissioning process.

Reactive Safety Management Principles	Guidance Summary	MRR Activities around MP Odorizer Decommissioning and Chemical Treatment
Management of Change (CSB)	Establish a procedure to re-evaluate reactive hazards when changes occur throughout the life cycle of a chemical process	No formal analysis was conducted to determine how to chemically treat MP odorizers differently than single storage tanks. MP odorizers were filled completely, which was a deviation from the normal process, but no Management of Change was conducted.
Personnel Training and Procedures (CSB)	The program should include written operating procedures and consideration of the potential for human error in reactive systems.	No written procedure was developed to detail how to chemically treat or safely decommission MP odorizers. The only procedure was for a generic storage tank.

## 6.2 Regulatory Analysis

More robust safety management systems in place at MRR could have prevented both incidents as well as protected the safety of the workers and the public from the hazards of exploding pressure vessels. It appears that neither the OSHA Process Safety Management (PSM) Standard<sup>a</sup> nor the EPA Risk Management Plan (RMP) Rule<sup>b</sup> applied to MRR’s deodorizing process. This conclusion is based on MRR’s deodorizing practices; OSHA’s citations following the May 24, 2017, and June 20, 2017, incidents; the lack of an RMP filed with the EPA; and the fact that the quantities of the hazardous chemicals involved in the deodorizing process appear to fall below OSHA and EPA threshold limits.

In the CSB’s 2007 safety video, *Reactive Hazards*, process safety expert and university professor Daniel Crowl stated, “[W]e cannot avoid reactive chemical hazards; however, chemical plant accidents involving reactive hazards are unacceptable. The technology and the management systems do exist to produce these products safely.”<sup>c</sup> As will be shown, current federal process safety regulations do not require companies with processes like MRR’s to develop and implement process safety management systems to effectively control reactive chemical hazards. And although good practice guidance for managing reactive chemical hazards does exist to allow companies to voluntarily establish these more robust safety management systems, as former CSB Chairperson Carolyn Merritt stated, “[T]he problem with voluntary programs is that not everybody volunteers” [22].

### 6.2.1 OSHA PSM Standard

The CSB’s 2002 report on chemical reactive hazards concluded that, “The OSHA PSM Standard has significant gaps in coverage of reactive hazards because it is based on a limited list of individual chemicals with inherently reactive properties” [21, p. 56]. The report stated that two elements are particularly relevant to reactive hazards – Process

<sup>a</sup> 29 C.F.R. § 1910.119.

<sup>b</sup> 40 C.F.R. § 68.150.

<sup>c</sup> See [CSB Safety Video: Reactive Hazards](#) at 19:08 [12].

Safety Information (PSI; 29 C.F.R. § 1910.119 (d)) and Process Hazard Analysis (PHA; 29 C.F.R. § 1910.119 (e)) [21, p. 56 ].

These observations are consistent with what the CSB found regarding the incidents at MRR – neither sodium hypochlorite nor tertiary butyl mercaptan (based on the amount involved in the deodorizing process) is covered under the OSHA PSM standard.<sup>a</sup> Therefore, OSHA must resort to citing companies for safety-related violations under its General Duty Clause following an incident involving one of these chemicals. This approach is reactive and not well suited for accident prevention.

OSHA investigated both incidents at MRR and issued citations. Following the May 24, 2017 incident, OSHA issued two serious citations to MRR for a total of \$19,013 in penalties [23]. These citations cited OSHA’s Hazard Communication standard and Medical Services and First Aid standard. After the June 20, 2017, incident, OSHA issued a serious citation to SPSI with a \$12,675 penalty, stemming from OSHA’s General Duty standard [24].

## 6.2.2 EPA RMP Rule

Regarding the EPA’s RMP Rule<sup>b</sup> and its regulation of reactive hazards, the CSB 2002 study noted:

When developing the list of substances, EPA considered only the inherent characteristics of a chemical that indicate a severe threat due to exposure. Well-defined criteria were used for toxicity and flammability. However, because of the complexities of site-specific factors and process conditions, EPA was unable to determine any inherent characteristic as an indicator of reactivity. EPA concluded that there was “insufficient technical information for developing criteria for identifying reactive substances.” Consequently, the January 1994 RMP list of 130 chemicals does not contain any substances listed due to reactive hazards... [21, p. 60].

The study concluded that “the EPA Accidental Release Prevention Regulations (40 CFR Part 68) have significant gaps in coverage of reactive hazards...” [21, p. 87].

As a result, the CSB issued a recommendation to the EPA to improve coverage and regulation of reactive chemicals. The EPA amended its RMP Rule in January 2017 and later rescinded most of these amendments in November 2019, but neither rulemaking effort revised the EPA’s List of Regulated Substances to include reactive chemicals [25, p. 10], [26, p. 1], and [27]. Meanwhile, the CSB has seen that reactive chemical incidents continue to occur, such as the two explosions at MRR, and the CSB maintains that this safety issue remains an important shortcoming with the EPA’s Accidental Release Prevention Requirements (40 CFR Part 68).

The CSB now reiterates (see Section 9.1) these recommendations to OSHA and the EPA to help prevent future reactive chemical incidents. The CSB continues to advocate for covering reactive chemicals by both the PSM Standard and the RMP Rule.

<sup>a</sup> 29 C.F.R. § 1910.119 (Appendix A).

<sup>b</sup> MRR was not required to submit an RMP to EPA and did not have one at the time of the incidents.



## 7 Causal Analysis

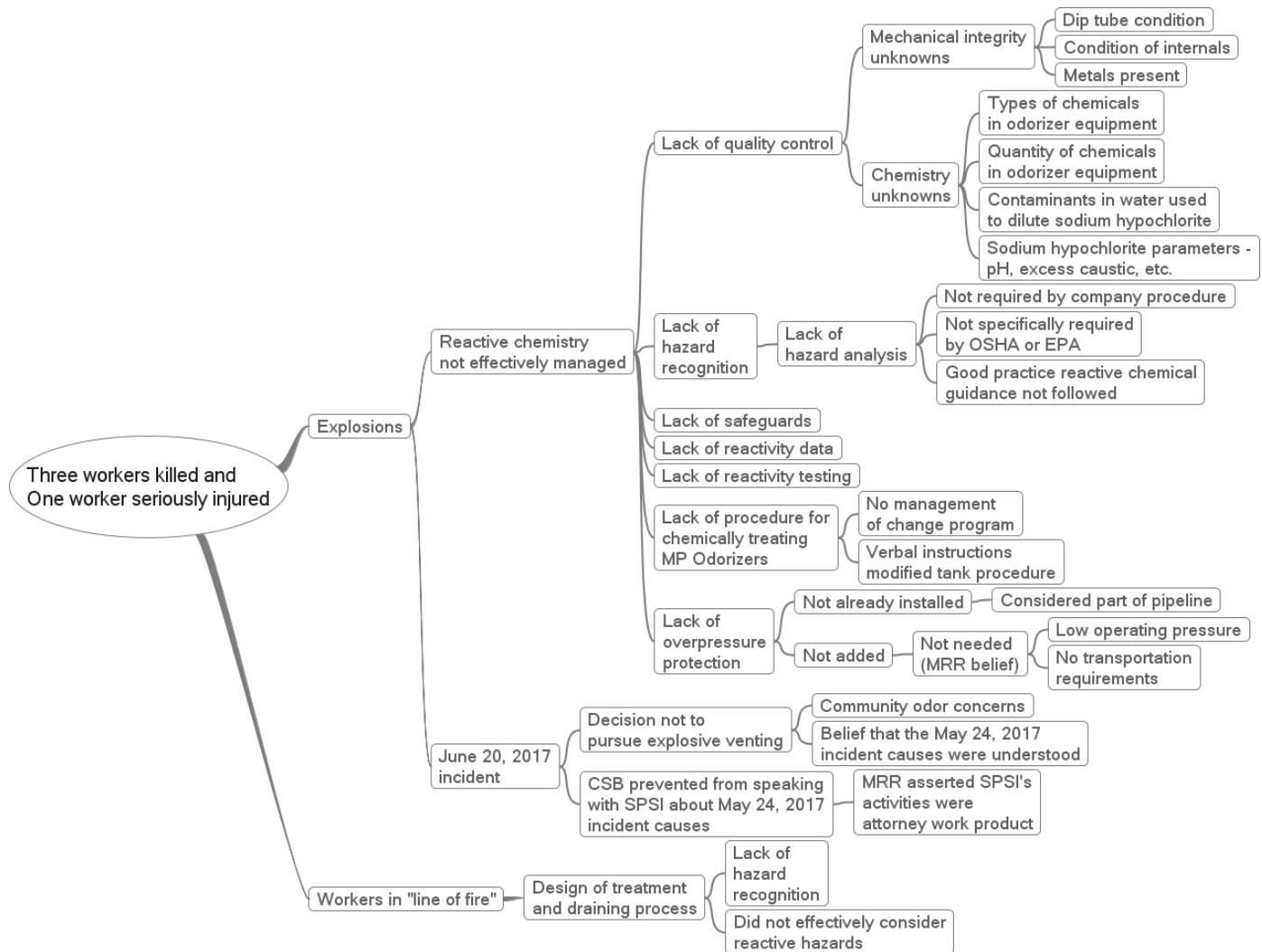


Figure 22. Causal Analysis. This image shows a simplified version of the CSB causal analysis. (Credit: CSB).

## 8 MRR Post-Incident Actions

### 8.1 MRR Theories on Reactive Chemistry Involved in the Incidents

In November 2019, MRR provided the CSB with some additional theories that the company developed on the potential chemistry involved with the incidents. MRR noted that its chemical treatment of mercaptans with sodium hypochlorite will produce sulfonic acid. MRR also identified the three “most likely” reactive chemical mechanisms that could produce reactive or flammable gases, including:

1. Sodium hydroxide from the sodium hypochlorite solution reacting with aluminum to produce hydrogen;<sup>a</sup>
2. Catalytic decomposition of sodium hypochlorite to produce oxygen; and
3. Reaction of sodium hypochlorite with an acid, such as sulfonic acid, to produce chlorine.

In addition, MRR identified two reactive chemical mechanisms that could produce hazardous byproducts. These include:

1. Hypochlorous acid reacting with mercaptan to produce an alkyl hypochlorite; and
2. A reaction between hypochlorous acid and an alcohol to produce an alkyl hypochlorite.

## 8.2 New Process for Removing the Mercaptan Smell from Odorization Equipment

MRR is still conducting decommissioning and deodorizing processes. In November 2019, the company asserted that after the catastrophic incidents in 2017, they stopped using reactive chemicals including sodium hypochlorite and now employ a proprietary process to remove the mercaptan smell from decommissioned odorization equipment. MRR communicated to the CSB that a third-party engineering firm assisted in engineering, validating, and testing the process for safety. MRR provided the CSB with a letter from the third-party engineering firm that suggests the new proprietary process is highly dependent on administrative controls. Among other things, the third-party engineering firm stated, “We believe the system can be safely operated by MRR, based on MRR implementing the operating practices recommended during the [two-day] project safety review.” MRR states that it is entirely compliant with all regulations and certifications, and the company is backed by a \$5,000,000 environmental, general and comprehensive insurance policy [28].

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<sup>a</sup> MRR stated that the company hired a consultant to perform testing and conduct research into the reaction chemistry and concluded that, “the exposure of sodium hypochlorite to aluminum does not produce a rapid generation of hydrogen gas. A slow reaction does occur; but this reaction is slow and would not be expected to produce a rapid pressure rise that would cause over pressurization of the MP vessels within seconds or minutes.”

## 9 Recommendations

### 9.1 Previously Issued Recommendations Reiterated in This Report

The U.S. Chemical Safety and Hazard Investigation Board reiterates the following previously issued safety recommendations:

#### 9.1.1 Occupational Safety and Health Administration:

##### **2001-01-H-R1**

Amend the Process Safety Management Standard (PSM), 29 CFR 1910.119, to achieve more comprehensive control of reactive hazards that could have catastrophic consequences.

- Broaden the application to cover reactive hazards resulting from process-specific conditions and combinations of chemicals. Additionally, broaden coverage of hazards from self-reactive chemicals. In expanding PSM coverage, use objective criteria. Consider criteria such as the North American Industry Classification System (NAICS), a reactive hazard classification system (e.g., based on heat of reaction or toxic gas evolution), incident history, or catastrophic potential.
- In the compilation of process safety information, require that multiple sources of information be sufficiently consulted to understand and control potential reactive hazards. Useful sources include:
  - Literature surveys (e.g., Bretherick's Handbook of Reactive Chemical Hazards, Sax's Dangerous Properties of Industrial Materials).
  - Information developed from computerized tools (e.g., ASTM's CHETAH, NOAA's The Chemical Reactivity Worksheet).
  - Chemical reactivity test data produced by employers or obtained from other sources (e.g., differential scanning calorimetry, thermogravimetric analysis, accelerating rate calorimetry).
  - Relevant incident reports from the plant, the corporation, industry, and government.
  - Chemical Abstracts Service.
- Augment the process hazard analysis (PHA) element to explicitly require an evaluation of reactive hazards. In revising this element, evaluate the need to consider relevant factors, such as:
  - Rate and quantity of heat or gas generated.
  - Maximum operating temperature to avoid decomposition.
  - Thermal stability of reactants, reaction mixtures, byproducts, waste streams, and products.
  - Effect of variables such as charging rates, catalyst addition, and possible contaminants.

- Understanding the consequences of runaway reactions or toxic gas evolution.

## 9.1.2 Environmental Protection Agency (EPA):

### **2001-01-H-R3**

Revise the Accidental Release Prevention Requirements, 40 CFR 68, to explicitly cover catastrophic reactive hazards that have the potential to seriously impact the public, including those resulting from self-reactive chemicals and combinations of chemicals and process-specific conditions. Take into account the recommendations of this report to OSHA on reactive hazard coverage. Seek congressional authority if necessary to amend the regulation.

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