



U.S. CHEMICAL SAFETY AND HAZARD INVESTIGATION BOARD

INVESTIGATION REPORT



T2 LABORATORIES, INC.

RUNAWAY REACTION

(Four Killed, 32 Injured)



KEY ISSUES:

- REACTIVE HAZARD RECOGNITION
 - HAZARD EDUCATION
 - EMERGENCY PREPAREDNESS
- PROCESS DESIGN AND SCALE-UP



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List of Acronyms and Abbreviations

ABET	Accreditation Board for Engineering and Technology, Inc.
AIChE	American Institute of Chemical Engineers
ARSST	Advanced Reactive System Screening Tool
ATF	U.S. Bureau of Alcohol, Tobacco, Firearms, and Explosives
CCPS	Center for Chemical Process Safety
CFR	Code of Federal Regulations
CSB	U.S. Chemical Safety and Hazard Investigation Board
DHS-CSCD	U.S. Department of Homeland Security, Chemical Security Compliance Division
DIERS	Design Institute for Emergency Relief Systems
Diglyme	Diethylene glycol dimethyl ether
DOT	U.S. Department of Transportation
EHS	Extremely Hazardous Substance
EPA	U.S. Environmental Protection Agency
EPCRA	Emergency Planning and Community Right-to-Know Act
FDEP	Florida Department of Environmental Protection
HAZOP	Hazard and operability study
HAZWOPER	Hazardous Waste Operations and Emergency Response
IC	Incident Commander
JFRD	Jacksonville Fire and Rescue Department
JSO	Jacksonville Sheriff's Office
LEPC	Local Emergency Planning Commission
MCMT	Methylcyclopentadienyl manganese tricarbonyl
MCPD	Methylcyclopentadiene
MSDS	Material safety data sheet
NIMS	National Incident Management System
NIOSH	National Institute for Occupational Safety and Health
OSHA	U.S. Department of Labor, Occupational Safety and Health Administration
PHA	Process hazard analysis
psig	Pound-force per square inch gauge

PSM	OSHA Process Safety Management Standard
RMP	Risk Management Plan
RMR	Reactivity Management Roundtable
SACHE	Safety and Chemical Engineering Education Committee
SCBA	Self-contained breathing apparatus
SERC	State Emergency Response Commission
VSP2	Vent Sizing Package 2

Executive Summary

At 1:33 pm on December 19, 2007, a powerful explosion and subsequent chemical fire killed four employees and destroyed T2 Laboratories, Inc. (T2), a chemical manufacturer in Jacksonville, Florida. It injured 32, including four employees and 28 members of the public who were working in surrounding businesses. Debris from the reactor was found up to one mile away, and the explosion damaged buildings within one quarter mile of the facility.

On December 19, T2 was producing its 175th batch of methylcyclopentadienyl manganese tricarbonyl (MCMT). At 1:23 pm, the process operator had an outside operator call the owners to report a cooling problem and request they return to the site. Upon their return, one of the two owners went to the control room to assist. A few minutes later, at 1:33 pm, the reactor burst and its contents exploded, killing the owner and process operator who were in the control room and two outside operators who were exiting the reactor area.

The CSB found that a runaway exothermic reaction occurred during the first (metalation) step of the MCMT process. The CSB tested the T2 batch recipe to determine the most likely failure scenario. A loss of sufficient cooling during the process likely resulted in the runaway reaction, leading to an uncontrollable pressure and temperature rise in the reactor. The pressure burst the reactor; the reactor's contents ignited, creating an explosion equivalent to 1,400 pounds of TNT.

The CSB identified the following root cause:

T2 did not recognize the runaway reaction hazard associated with the MCMT it was producing.

The CSB identified the following contributing causes:

1. The cooling system employed by T2 was susceptible to single-point failures due to a lack of design redundancy.
2. The MCMT reactor relief system was incapable of relieving the pressure from a runaway reaction.

The CSB makes recommendations to the American Institute of Chemical Engineers and the Accreditation Board for Engineering and Technology, Inc.

1.0 Introduction

1.1 Summary

At 1:33 pm on December 19, 2007, an explosion and fire destroyed T2 Laboratories, Inc. (T2), a chemical manufacturer on the north side of Jacksonville, Florida (Figure 1). The explosion, which was felt and heard 15 miles away in downtown Jacksonville, killed four T2 employees, including a co-owner. It injured 32, including four T2 employees and 28 members of the public at surrounding businesses.



Figure 1. Aerial photograph of T2 taken December 20, 2007.

Debris from the explosion was found up to one mile away, and the blast damaged buildings within one quarter mile of the facility. The City of Jacksonville subsequently condemned buildings used by four of the businesses surrounding T2. Three of these businesses relocated operations while their buildings were repaired; the remaining business, a trucking company adjacent to T2, permanently closed due to lost business.

On December 19, T2 was producing methylcyclopentadienyl manganese tricarbonyl (MCMT) in a 2,450-gallon chemical batch reactor. At 1:23 pm, the process operator directed an outside operator to call the two owners, who were off site, to report a cooling problem and request they return. Upon their return, one of the owners went to the control room to assist. A few minutes later, at 1:33 pm, the reactor burst and its contents exploded, killing the owner and process operator in the control room and two outside operators who were exiting the reactor area.

Responding to the explosion and subsequent fire were the Jacksonville Fire and Rescue Department (JFRD); U.S. Naval Air Station Mayport Fire Department; Jacksonville International Airport Fire Department; Jacksonville Sheriff's Office (JSO); City of Jacksonville Environmental Resource Management Division; City of Jacksonville Planning and Development Department; Florida State Fire Marshal; Florida Department of Environmental Protection (FDEP); U.S. Bureau of Alcohol, Tobacco, Firearms, and Explosives (ATF); U.S. Environmental Protection Agency (EPA); U.S. Department of Homeland Security, Chemical Security Compliance Division (DHS-CSCD); U.S. Department of Labor, Occupational Safety and Health Administration (OSHA); and American Red Cross (ARC).

1.2 Investigative Process

Due to the multiple deaths, many injuries, and extensive community damage, the CSB launched an investigation on December 19, 2007. On December 20, the CSB investigation team arrived at the incident scene, joined Incident Command structure in accordance with the National Incident Management System¹ (NIMS), and began on-scene investigation activities. On December 21, 2007, JFRD extinguished the remaining smoldering fires onsite. JSO and ATF concluded that the incident was not a

¹ NIMS is a comprehensive nationwide incident response structure enabling all response entities to cooperate during incidents. DHS requires implementation of NIMS.

criminal act and Incident Command demobilized. The CSB investigation team remained, interviewing employees of T2, emergency responders, and officials from the City of Jacksonville. The team documented off-site damage, located and photographed reactor debris, and interviewed injured parties and eyewitnesses. JSO assisted the CSB in debris documentation and collection.

The CSB conducted laboratory testing of the chemical reaction used in the T2 process, recreated the most likely scenario, and calculated the pressure relief capacity necessary to safely vent the uncontrolled reaction. The CSB also conducted a community damage survey of the 32 structures damaged by the blast, using the data collected to estimate the amount of TNT necessary to produce a blast of equivalent magnitude.

1.3 T2 Laboratories, Inc.

T2 Laboratories, Inc. (T2)² was a small privately-owned corporation located in Jacksonville, Florida, that began operations in 1996. A chemical engineer and a chemist³ founded T2 as a solvent blending business and co-owned it until the incident. From 1996 to 2001, T2 operated from a warehouse located in a mixed-used industrial and residential area of downtown Jacksonville. T2 blended and sold printing-industry solvents; it also blended pre-manufactured MCMT to specified concentrations for Advanced Fuel Development Technologies, Inc. (AFD), a third-party distributor.

² In the course of designing and constructing the MCMT plant, the T2 owners formed two other business enterprises, which were eventually subsumed into T2. These ventures involved the same personnel; for simplicity this report refers to the company as T2 throughout. Following the incident, T2 has ceased production operations.

³ The T2 owners are herein referred to as “owner/chemical engineer” and “owner/chemist.”

In 2001, T2 leased a 5-acre site in a north Jacksonville industrial area and began constructing an MCMT process line. In January 2004, T2 began producing MCMT in a batch reactor.⁴ By December of 2007, MCMT production was the primary business operation. On the day of the incident, T2 employed 12 people and was producing its 175th MCMT batch (Batch 175).

1.4 Advanced Fuel Development Technologies, Inc.

Advanced Fuel Development Technologies, Inc. (AFD) is a Daytona Beach, Florida-based distributor of fuel additives, including MCMT. AFD customers include individual consumers, commercial facilities, and refineries. AFD also offers services in fuel development, testing, and custom formulation.

1.5 Methylcyclopentadienyl Manganese Tricarbonyl

Methylcyclopentadienyl manganese tricarbonyl (MCMT) is an organomanganese compound used as an octane-increasing gasoline additive. The Ethyl Corporation⁵ originally developed MCMT in the late 1950s. T2 manufactured and sold MCMT under the trade name Ecotane.

MCMT is a combustible liquid and is very toxic by inhalation or skin contact. Both the National Institute for Occupational Safety and Health (NIOSH) and OSHA set exposure limits for MCMT.⁶ Although MCMT decomposes quickly when exposed to light, the EPA designates MCMT as an extremely hazardous substance (EHS) (Section 6.2.2).

⁴ In batch reactions, process operators feed fixed amounts of raw materials into a reactor at specified times, according to a chemical recipe. The entire process occurs within the reactor, which is emptied between batches.

⁵ The Ethyl Corporation is now known as Afton Chemical, which is the only U.S. producer of MCMT.

⁶ NIOSH's recommended exposure limit is 0.2 milligrams per cubic meter average concentration over 10 hours. OSHA's permissible exposure limit is 5 milligrams per cubic meter at any one time.

1.6 City of Jacksonville

The City of Jacksonville, located in northeastern Florida, comprises approximately 840 square miles, has a population of more than 850,000, and is governed by a mayor and a 19-member City Council. The Jacksonville Fire and Rescue Department (JFRD) provides fire protection and emergency medical services. JFRD has approximately 1,200 salaried employees in six divisions: Operations, Rescue, Training, Fire Prevention, Administrative Services, and Emergency Preparedness. The divisions operate 56 stations including two hazardous materials stations. The Fire Prevention division had inspected T2 prior to the incident. Based on the chemicals that T2 reported storing, JFRD conducted hazardous materials response drills for emergencies involving sodium metal.⁷

⁷ Sodium metal is highly water-reactive and requires specialized firefighting strategies.

2.0 Incident Description

2.1 December 19, 2007 Incident

On the evening of December 18, 2007, a night shift process operator cleaned and dried the reactor in preparation for a new MCMT batch. At about 7:30 am on December 19, the day shift process operator began manufacturing Batch 175 from the control room adjacent to the process line. He likely followed the routine batch procedures, loading the reactor with the specified quantities of raw materials using an automated process control system (Section 3.2). An outside operator hand-loaded the reactor with blocks of sodium metal, then sealed the reactor. At about 11:00 am, the process operator began heating the batch to melt the sodium and initiate the chemical reaction, while monitoring the temperature and pressure on the process control screen.

Once the sodium melted, at 210°F (98.9°C), the process operator likely started the mixer (agitator). Mixing the raw materials increased the reaction rate, creating heat. Heat from the reaction and the heating system continued raising the temperature in the reactor. At a reaction temperature of about 300°F (148.9°C), the process operator likely turned off the heating system as specified in the procedure, but heat from the reaction continued increasing the mixture temperature.

At a temperature of about 360°F (182.2°C), the process operator likely started cooling, using the process control system, as specified in the procedure. However, the mixture temperature in the reactor continued to increase.

At 1:23 pm, the process operator had an outside operator call the owners to report a cooling problem⁸ and request they return to the site. Upon their return, the owner/chemical engineer went to the control room to assist and the owner/chemist searched for the plant mechanic. Employees indicated that after visiting the control room, the owner/chemical engineer went to the reactor. He told an outside operator—who was coming to the control room to investigate multiple process alarms sounding—that he thought there would be a fire and motioned employees to get away. The owner/chemical engineer then returned to the control room.

By 1:33 pm, the reactor's relief system could no longer control the rapidly increasing temperature and pressure of the runaway reaction. Eyewitnesses from nearby businesses reported seeing venting from the top of the reactor and hearing a loud jet engine-like sound immediately before the reactor violently ruptured, its contents exploding. The explosion killed the owner/chemical engineer and process operator who were in the control room (50 feet from the reactor) and two outside operators who were leaving the reactor area (Figure 2). Another outside operator and the plant mechanic were injured. The owner/chemist was sheltered from the force of the explosion by a shipping container, but suffered a non-fatal heart attack during the incident.

⁸ Survivors' accounts indicate that the process operator (deceased) reported a cooling system problem.



Figure 2. Control room.

2.2 Emergency Response

At 1:33 pm, Jacksonville 911 dispatchers began receiving calls about the incident. The Jacksonville Fire and Rescue Department (JFRD) and Jacksonville Sheriff's Office (JSO) responded and set up unified Incident Command. Within 10 minutes of the incident, two JFRD hazardous materials stations dispatched.

JFRD completed a hazard analysis using material safety data sheets (MSDSs) from the T2 website.⁹ The incident commander (IC) ordered a half-mile evacuation radius, closing Faye Road and an adjacent railroad track. The IC ordered full personal protective equipment, including bunker gear¹⁰ and self-contained breathing apparatus (SCBA) for all personnel entering the area. About 90 firefighters from JFRD, the U.S. Naval Air Station Mayport Fire Department, and the Jacksonville International Airport Fire Department responded to the incident, battling the fire for many hours as stored solvents burned (Figure 3). Despite the large amounts of toxic MCMT and water-reactive sodium metal stored onsite, no responders were injured.



Photo JFRD

Figure 3. JFRD responders in SCBA battle fire.

⁹ T2 had not yet filed its annual Tier II report for the 2007 reporting year (Section 7.2).

¹⁰ Bunker or turnout gear refers to the set of firefighter protective clothing including flame-resistant pants, coat, and hood, gloves, helmet, and chemical-resistant boots.

The Jacksonville Planning and Development Department surveyed surrounding buildings and condemned unsafe structures, including the four businesses closest to T2. An environmental cleanup firm remained onsite for more than a month after the incident, providing site security, collecting and cataloging debris, and arranging for the removal of the remaining chemicals. As of the date of this report, soil and groundwater on the site remain contaminated with manganese and benzene. FDEP is closely monitoring site cleanup activities.

2.3 Injuries and Community Damage

The explosion killed four T2 employees and injured 32 workers at T2 and surrounding businesses. All of the people at T2 during the incident—eight T2 employees and one truck driver making a delivery—were injured or killed. The four fatally injured employees died of blunt force trauma as a result of the explosion. Another T2 employee was critically injured and hospitalized for several months.

The CSB conducted a community survey of the surrounding businesses to characterize injuries and structure damage (Figure 4). At the nine businesses within 1,900 feet of the reactor, the explosion injured 27 workers. Of those, 11 suffered lacerations and contusions, seven reported hearing loss, and five fell or were thrown by the force of the blast. The CSB survey team photographed and catalogued 32 damaged structures, some as far as 1,700 feet from T2.

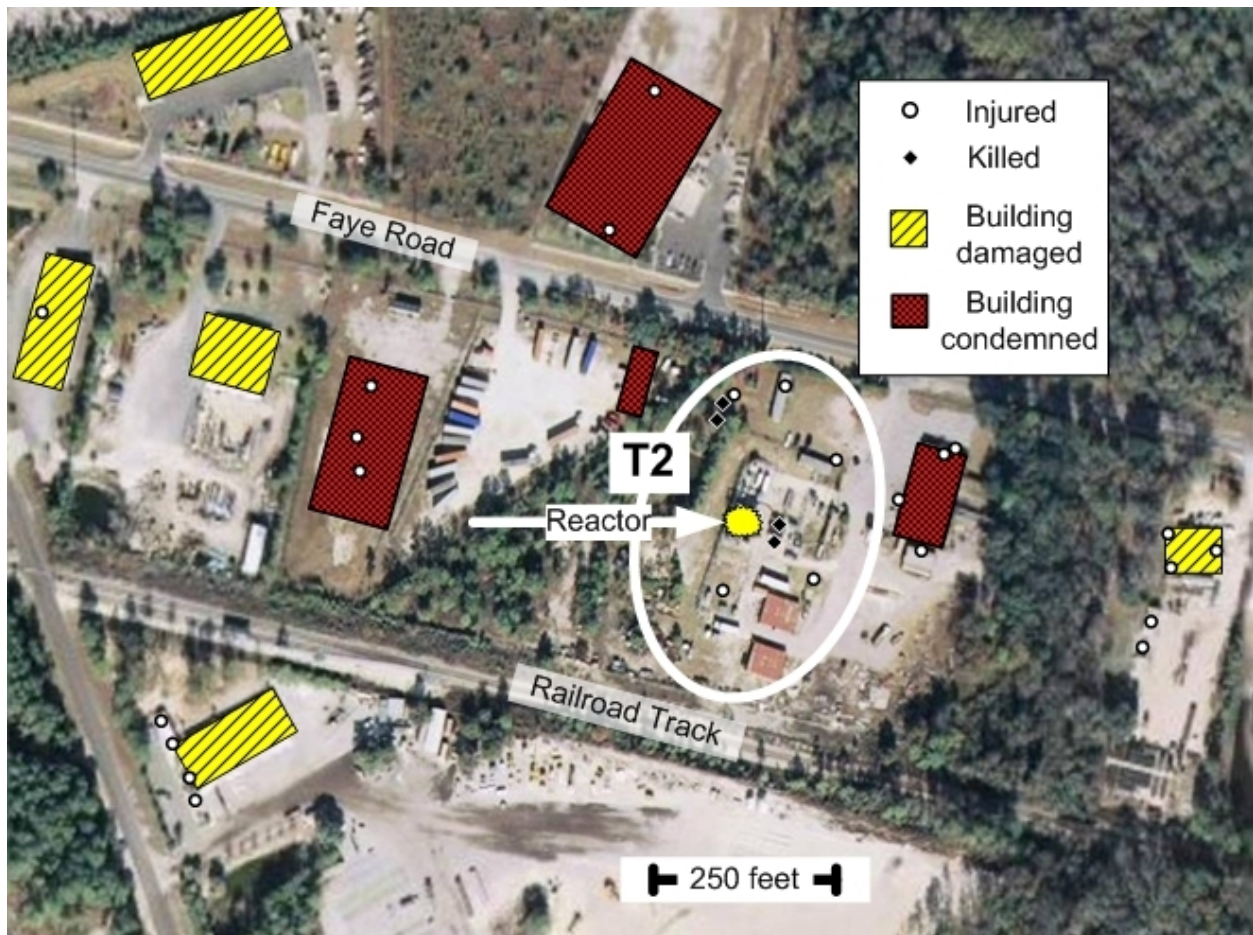


Figure 4. Injury and business locations.

The explosion leveled the plant, propelling debris in all directions. Two large steel support columns from the reactor structure traveled about 1,000 feet along Faye Road in both directions. A 2,000-pound section of the 3-inch-thick reactor head (Figure 5) impacted railroad tracks adjacent to T2, pushing a rail out of place, before impacting and damaging a building about 400 feet from the reactor. The explosion threw piping from inside the reactor hundreds of feet onto the other businesses and wooded areas surrounding T2. The 4-inch diameter agitator shaft from the reactor was thrown about 350 feet across Faye Road in two large pieces that imbedded in a sidewalk and the ground (Figure 6).



Figure 5. Portion of the 3-inch-thick reactor.



Figure 6. Agitator shaft pieces.

Businesses near T2 sustained heavy damage. Structures sustained window damage from the overpressure up to 1,700 feet away from T2. The explosion destroyed a trucking company office trailer located 250 feet from the reactor (Figure 7). If trucking company employees had been in the trailer at the time of the incident, it is likely that they would have been seriously injured or killed.¹¹ Two warehouses located about 400 to 500 feet from the reactor both sustained heavy damage; nine of the 25 employees at these two businesses were injured.

¹¹ Due to the upcoming holiday, trucking company employees had dismissed for the day shortly before the incident.



Figure 7. Trucking company trailer adjacent to T2.

3.0 T2 MCMT Process

3.1 Process Development

The president of Advanced Fuel Development Technologies (AFD) asked T2 to consider manufacturing MCMT in 1998. Although both of the T2 owners had prior chemical industry experience, neither had previously worked with reactive chemical processes; they waited two years before agreeing to pursue the project. Upon T2's agreement, the AFD president, a PhD chemist with more than 20 years' experience, provided patent literature¹² and research support to T2's owner/chemist. The owner/chemist then duplicated and tested the chemistry described in the patents and created a three-step process for making MCMT in the laboratory. Between 2000 and 2001, the owner/chemist ran about 110 test batches of MCMT in a one-liter reactor.

In 2001, T2 leased its Faye Road site, in an area zoned for heavy industry.¹³ With financial support from a number of investors including AFD,¹⁴ T2 designed and constructed a full-scale MCMT production plant. T2 hired consulting engineers to assist in the process design, control system engineering, and project management. Due to limited funding, T2 purchased and refurbished used equipment, including the 2,450-gallon high-pressure batch reactor used for the three-step MCMT reactions.

On January 9, 2004, T2 began manufacturing its first full-scale MCMT batch (Batch 1) in the new process line. Batch 1 produced an unanticipated exothermic reaction in the first step; T2 noted the

¹² Appendix B contains a list of patents T2 used in their research.

¹³ Although the site was properly zoned, T2 did not obtain all necessary permits prior to plant construction.

¹⁴ Several investors were involved in financing T2's initial plant production. However, no other entity retained financial interest or ownership at the time of the incident.

anomaly, adjusted the batch recipe and production procedures to include reactor cooling in the first step,¹⁵ and began a new production batch. Between February and May 2004, T2 manufactured nine more MCMT batches, adjusting the recipe and procedures between batches. Yields varied from no saleable product to about 70 percent saleable product.¹⁶ Batch 5 resulted in an uncontrolled (runaway) exothermic reaction in the first step. In Batch 10, the temperature also increased beyond expectations—though not as severely as in Batch 5—due to the exothermic reaction.

On May 24, 2004, following Batch 11, T2's owner/chemical engineer sent a memo to investors declaring successful plant startup and full-scale MCMT production. Although all of the investors had ended their involvement by late 2004, T2 continued producing and selling MCMT on an irregular basis, relying upon sales to pay for more raw materials. On July 28, 2005, producing Batch 42, T2 increased batch size by one-third. T2 manufactured batches from 2005 until the incident (Batch 175) at this larger size.

A process operator ran each step of the batch reaction from a control room adjacent to the process line. The T2 plant manager, a chemical engineer, began working as a process operator in 2004. In 2006, T2 hired two additional chemical engineers to run the process throughout multiple weekday shifts. Each batch required about 48 hours to manufacture. By December 2007, client demand had increased, and T2 produced three batches a week.

3.2 Manufacturing Process

T2 manufactured MCMT in three steps that occurred sequentially within a single process reactor (Figure 8). The National Annealing Box Company of Washington, Pennsylvania, originally constructed the

¹⁵ The process design already included reactor cooling, which was required in later production steps.

¹⁶ A 70 percent MCMT process yield was a good outcome based on the owner/chemist's research.

reactor in 1962 for an internal pressure of 1,200 psig.¹⁷ T2 purchased the reactor in 2001 and contracted a firm specializing in pressure vessels to refurbish, modify, and test the reactor. The modifications included replacing and adding of piping nozzles and reducing the maximum allowable working pressure from 1,200 psig to 600 psig.¹⁸

A 4-inch¹⁹ vent pipe that made two 90-degree pipe bends before connecting to a 4-inch rupture disk provided overpressure protection for the reactor. Employees stated that the rupture disk was set at 400 psig. A pressure control valve installed in a 1-inch vent pipe, which branched off of the 4-inch vent pipe below the rupture disk, controlled reactor pressure.

The MCMT process required both heating and cooling. A heating system circulated hot oil through 3-inch piping installed around the inside of the reactor. A cooling jacket covered the lower three quarters of the reactor. A pipe from the city water system connected to the bottom of the jacket through a control valve and a common supply/drain connection. Water was injected into the jacket and allowed to boil; steam from the boiling water vented to atmosphere through an open pipe connected to the top of the jacket.

¹⁷ National Annealing designed and fabricated the reactor in accordance with the 1959 version of the American Society of Mechanical Engineers (ASME) Boiler and Pressure Vessel Code.

¹⁸ Although the nameplate pressure was reduced this had little effect on the inherent pressure-retaining ability of the reactor.

¹⁹ All piping sizes presented in this report are nominal pipe size (NPS).

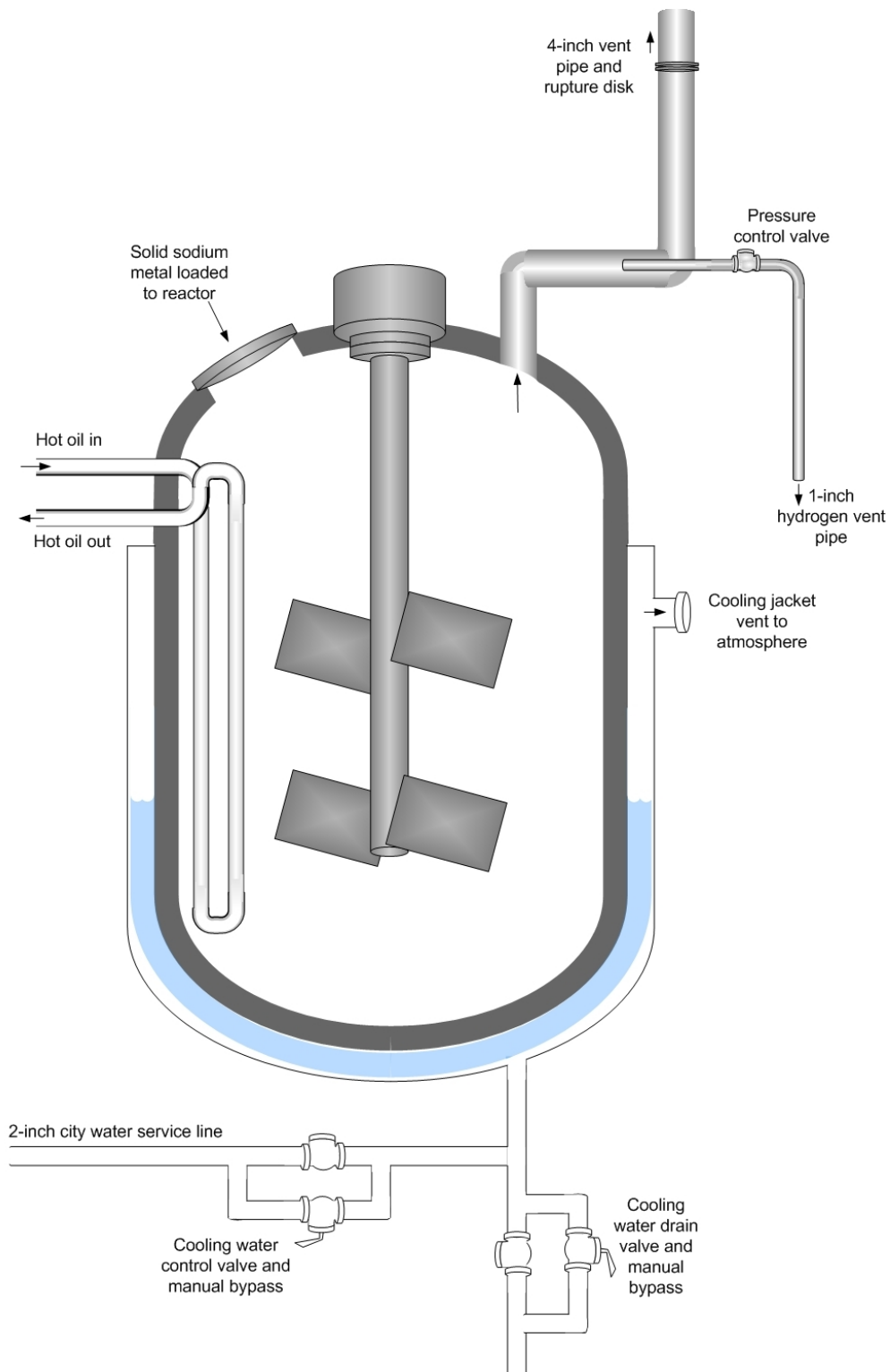
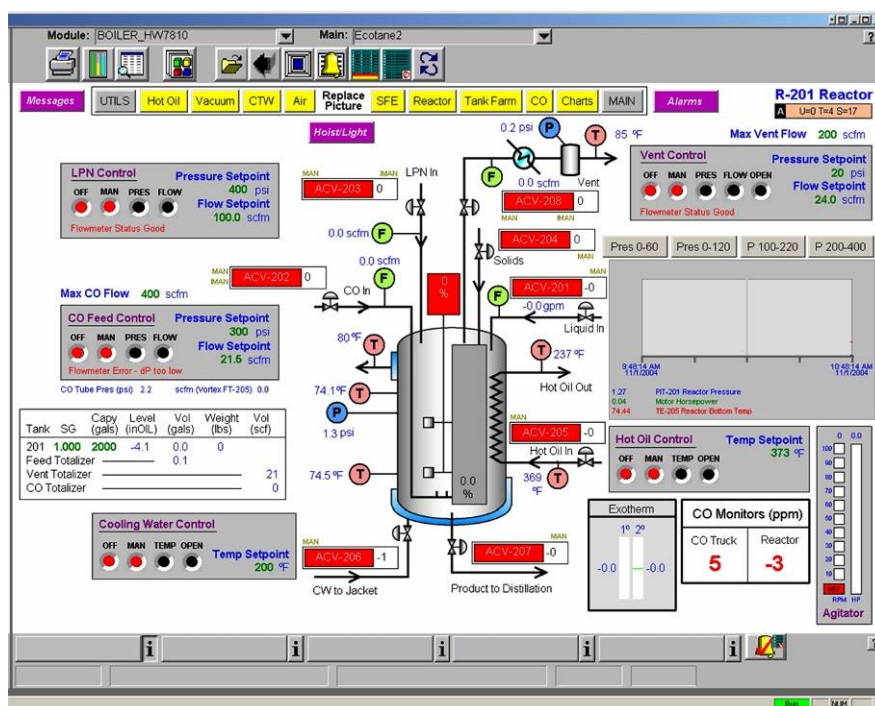


Figure 8. Reactor cross-section.

Each MCMT production step required the process operator to add raw materials and adjust heating, cooling, and pressure using a computerized process control system (Figure 9). On December 19, 2007, the incident occurred during the first (metalation) step of the reaction. The second and third steps of the reaction, which did not occur on December 19, 2007, were also conducted within the reactor. Appendix A discusses the complete reaction chemistry.



T2 screen capture

Figure 9. Process control system screen.

In the first reaction step (called metalation), the process operator fed a mixture of methylcyclopentadiene (MCPD) dimer²⁰ and diethylene glycol dimethyl ether (diglyme) into the reactor. An outside operator then hand-loaded blocks of sodium metal through a 6-inch gate valve on top of the reactor, closing the

²⁰ MCPD dimer is a molecule consisting of two identical MCPD molecules.

valve when complete. The process operator began heating the mixture with the hot oil piping system, setting reactor pressure control at 50 psig (3.45 bar) and hot oil temperature control at 360°F (182.2°C).

Heating the mixture began the metalation reaction by melting the sodium and splitting each MCPD dimer molecule into two MCPD molecules. The melted sodium then reacted with the MCPD to form sodium methylcyclopentadiene, hydrogen gas, and heat. The hydrogen gas vented to the atmosphere through the pressure control valve and 1-inch vent line.

Once the mixture temperature reached 210°F (98.9°C), the process operator started the agitator. The mixing and higher temperature both increased the metalation reaction rate. At a reaction temperature of about 300°F (148.9°C), the process operator turned off the hot oil system; heat generated by the metalation reaction continued to raise the mixture temperature.

At a temperature of about 360°F (182.2°C), the process operator initiated the control system cooling program, which intermittently injected water into the jacket based on the rate of reaction temperature increase. The operating procedures used at the time of the incident included no emergency instructions for loss of cooling. However, earlier procedures—which included emergency instructions—directed the operators to fully open the water supply valve and the manual bypass valve. A secondary (backup) source of water stored on site was not immediately available to the process operator in an emergency.

4.0 Incident Analysis

The incident at T2 was one of the most energetic explosions investigated by the CSB. The CSB estimated the energy release of this explosion to be equivalent to 1,400 pounds of TNT (Appendix B). The blast occurred due to a runaway chemical reaction that generated high temperature and pressure in the reactor. Runaway chemical reactions are extremely dangerous, but their causes are well documented.²¹ The CSB evaluated possible causes of the runaway reaction, including

- cross-contamination of the reactor,
- contamination of raw materials,
- wrong concentration of raw materials,
- local concentration of chemical within the reactor,
- application of excessive heat, and
- insufficient cooling.

The CSB determined contamination scenarios to be unlikely. The T2 owner/chemist stated that batch-to-batch contamination of the reactor had previously occurred, resulting in low yields or batch polymerization. Additionally, T2 had experienced a runaway chemical reaction on its first production batch in a clean reactor. Contamination of the raw materials was similarly unlikely, as all of the raw materials used on the day of the incident came from shipments that had been used in previous successful batches.

²¹ *Lees' Loss Prevention in the Process Industries* (3rd edition)

Based on the reaction chemistry, raw material concentration abnormalities were not credible failure scenarios. Of the raw materials used, only an increase in the amount of sodium would have accelerated the reaction rate. Sodium was hand-loaded by operators in the form of one four-drum pallet per batch, making amount variation extremely unlikely. Varying local concentrations of chemicals within the reactor would reduce rather than accelerate reaction rate, since uniform distribution of the three metalation reaction raw materials results in the maximum reaction rate.

Heat was applied to the mixture using the hot oil system; had heating continued beyond 300°F (148.9°C), the CSB calculated that the cooling system would have easily overwhelmed it. The capacity of the cooling system was more than 10 times greater than the maximum capacity of the hot oil system.

The CSB determined insufficient cooling to be the only credible cause for this incident, which is consistent with witness statements that the process operator reported a cooling problem shortly before the explosion. The T2 cooling water system lacked design redundancy, making it susceptible to single-point failures including

- water supply valve failing closed or partially closed.
- water drain valve failing open or partially open.
- failure of the pneumatic system used to open and close the water valves.
- blockage or partial blockage in the water supply piping.
- faulty temperature indication.
- mineral scale buildup in the cooling system.

Interviews with employees indicated that T2 ran cooling system components to failure and did not perform preventive maintenance. On at least one prior occasion since 2006, the reactor cooling drain valve had failed during operations and required repair. Additional credible cooling system failures include formation of mineral scale inside the jacket that could interfere with system heat removal capacity

or loose scale blocking the inlet/drain pipe and causing it to stick open. Although a control system malfunction or operator error might also contribute to insufficient reactor cooling, there is no evidence to indicate that either of these occurred.

The CSB contracted laboratory testing of the batch recipe used by T2 on the day of the incident (Appendix C). The results of this testing showed that the standard T2 chemical recipe, without sufficient cooling, was capable of producing the extreme temperature and pressure necessary for the violent reactor failure on December 19, 2007.

When the CSB conducted tests in a closed (sealed) test cell, two exothermic reactions were observed using the T2 recipe. The first exothermic reaction occurred at about 350°F and was the desired reaction between the sodium and the MCPD. A second and more energetic exothermic reaction occurred when the temperature exceeded 390°F (198.9°C); this reaction was between the sodium and the diglyme solvent. The pressure and temperature rise during the second exothermic reaction were about 32,000 psig per minute (2,206 bar per minute) and 2340°F per minute (1300°C per minute), respectively, and burst the test cells.

Using the data obtained from these tests, the CSB determined that it is unlikely that an overpressure relief device of any size set at 400 psig could have prevented failure of the reactor once the second exothermic reaction began. Failure could only be prevented by relieving at a lower pressure during the first exothermic reaction and allowing the MCPD and diglyme solvent to boil and vent, removing both heat and reactants. Had T2 set its 4-inch reactor rupture disk at 75 psig, rather than the 400 psig used, the runaway reaction likely would have been relieved during the first exothermic reaction, precluding the second exothermic reaction. This could have prevented the catastrophic reactor failure that occurred.

5.0 Reactive Hazard Analysis

Companies developing chemistry for commercial production, like T2, must fully research the hazards involved. Hazards may be identified in each phase of commercial development, from laboratory testing to plant operations, and actions taken to assess risk and mitigate or eliminate potential consequences. Many guidelines, including free resources, address these topics (Section 7.0).

5.1 T2 Research and Development

T2 developed its MCMT chemistry based primarily on patents granted in the late 1950s and early 1960s (Appendix D). While patents document process chemistry, they generally do not document process hazards. All three steps of the MCMT process involved toxicity, flammability, or reactivity hazards. Hazardous chemicals used or generated during production steps included sodium metal, carbon monoxide, hydrogen, and organometallic compounds. A literature search performed by the CSB found little published information on the production of MCMT other than the patents, and no published information specific to its reactivity hazards.

A lack of available process hazard information makes laboratory testing especially important. The T2 owner/chemist performed laboratory testing in a 1-liter glass reactor to establish the MCMT process chemistry and determine maximum product yield. He reported that he never observed extreme exothermic behavior during testing and that test temperatures never exceeded 380°F (193°C). By not investigating the reaction's behavior at higher temperatures, the owner/chemist did not observe evidence of exothermic runaway potential.

Cooling requirements in the one-liter laboratory reactor did not accurately indicate the amount of cooling needed in the full-scale T2 reactor. Although the laboratory reactor required occasional heating and did

not require cooling, T2 employees reported that additional cooling was determined to be necessary during multiple process upsets in early production batches.

Other CSB investigations (Section 5.4) have found that reliance on laboratory testing can lead to dangerous underestimation of full-scale batch temperatures and has been a principle factor in accidents involving reactive chemistries. *Designing and Operating Safe Chemical Reaction Processes* (HSE, 2000) discusses the importance of proper scale-up design of process equipment and the potential for incidents to occur in full-scale processes that have appeared uneventful in laboratory testing.

5.2 Process Hazard Analysis

Process hazard analysis (PHA) in the development phase helps establish operating limits and identify operating strategies to prevent runaway reactions. PHAs for batch reactor systems should evaluate potential process deviations and equipment malfunctions, including agitator failure, loss of cooling, contamination, and mischarging feed stocks, all of which are common causes of runaway reactions.

One of T2's design consultants identified the need to perform a hazard and operability study (HAZOP, a type of PHA) during scale-up. A comprehensive HAZOP likely would have identified the need for testing to determine the thermodynamic and kinetic nature of the reaction, as well as the limitations of the cooling and pressure relief systems. CSB found no evidence that T2 ever performed the HAZOP.

Similarly, T2 sized the reactor relief devices based on anticipated normal operations, without considering potential emergency conditions. T2 employees stated that the owner/chemical engineer sized the rupture disk based on the maximum expected hydrogen gas generation during normal operation. T2 could not provide any documents related to the sizing and set point of the rupture disk. However, there was no evidence that T2 evaluated a runaway reaction as a possible overpressure source.

5.3 T2 Incident History

The runaway reaction on December 19, 2007, was not the first unexpected exothermic reaction that T2 experienced; three of the first 10 MCMT batches resulted in unexpected exotherms.²² Each of these occurred during metalation, and in each instance the batch recipe was slightly different. T2 did not repeat batch recipes to isolate the problem, instead changing recipes in each of the first 10 batches.²³ T2 announced successful commercial operation to its stakeholders after Batch 11.

In 2005, at Batch 42, T2 increased the batch size by one third. There are no records of additional chemical or process analysis conducted as part of this recipe change, which may have introduced significant new risks. A greater volume of reactants increased the energy that the reaction could produce, and likely altered cooling and pressure relief requirements.

When the MCMT process yielded unexpected results in early batches, T2 did not halt production, investigate causes, and redesign the process. Instead, T2 attempted to control unexpected reaction results on-line through operator controls or minor alterations to continue running the process as it was already constructed. As demand grew, T2 increased batch size and frequency with no additional documented hazard analysis.

5.4 Reactive Hazard Recognition

Chemists and chemical engineers involved in developing and operating the T2 MCMT process were unaware of the need to perform runaway reaction testing, address emergency relief, and identify and evaluate the causes of process upsets. Unexpected exothermic reactions were managed as they occurred,

²² These exothermic behaviors were either stronger than T2 expected, or occurred at unexpected steps in the reaction.

and T2 employees expected that the owner/chemical engineer could control any future incidents, as evidenced by the call to request his assistance shortly before the incident. Although the owner/chemical engineer told employees he thought a fire would occur, none of the T2 employees appreciated the potential for a catastrophic explosion.

The CSB has investigated four previous runaway reaction incidents caused in part by not recognizing the reactive hazard. The incidents were

- an explosion at Morton International, Inc. in Paterson, New Jersey on April 8, 1998;
- an explosion at Concept Sciences, Inc. in Hanover Township, Pennsylvania on February 19, 1999;
- a toxic vapor cloud release at MFG Chemical, Inc. in Dalton, Georgia on April 12, 2004; and
- a flammable vapor release and explosion at Synthron, LLC in Morganton, North Carolina on January 31, 2006.

These incidents, summarized in Appendix E, and the one at T2 are responsible for a combined 10 deaths and over 200 injuries.

5.5 Hazard Education

The T2 owner/chemical engineer had a bachelor's degree in chemical engineering and was active in his university's chemical engineering curriculum advisory board. However, reactivity hazard awareness is not currently a fundamental component of chemical engineering curricula. Although both the owner/chemical engineer and owner/chemist held bachelor's degrees and had prior chemical industry experience, neither had previously worked with reactive chemical processes. Hence, they were ill-prepared to appreciate and recognize the reactivity hazards of the MCMT process.

²³ The fire following the December 19, 2007 explosion destroyed documentation on later batches and batch recipes.

In 2006, the Mary Kay O'Connor Process Safety Center²⁴ surveyed 180 chemical engineering departments at U.S. universities to determine whether process safety was part of their chemical engineering curricula. Of the universities surveyed, only 11 percent required process safety education in the core baccalaureate curriculum. An additional 13 percent offered an elective process safety course. The survey did not specifically address reactivity hazard awareness education; however, a sampling of curricula indicates that the inclusion of reactivity hazards in chemical engineering education is limited at best.

Accreditation of U.S. engineering programs, including chemical engineering, is a voluntary, peer-reviewed process to assure consistent curricular quality. Baccalaureate programs are accredited by the Accreditation Board for Engineering and Technology, Inc. (ABET) based on recommendations from profession-specific industry groups. ABET reviews and approves chemical engineering programs based on criteria recommended by the American Institute of Chemical Engineers (AIChE). There is no requirement for accredited baccalaureate chemical engineering programs to include process safety or reactive hazard awareness in their curricula.

²⁴ The Mary Kay O'Connor Process Safety Center is part of the Texas Engineering Experimental Station at Texas A&M University.

6.0 Regulatory Analysis

6.1 Occupational Safety and Health Administration

The OSHA Process Safety Management (PSM) standard²⁵ requires employers to implement a management program to prevent or minimize the consequences of catastrophic releases of hazardous chemicals. PSM applies to facility processes that include 10,000 pounds or more of flammable liquids or gases in one location, and to listed toxic chemicals at or above certain threshold quantities. Key elements of the management system required for covered processes include conducting PHAs, implementing and maintaining written operating procedures, conducting periodic operator training, and implementing a management of change program.

T2 did not use or store any listed chemicals subject to PSM coverage. Although the PSM standard is also applicable to processes with at least 10,000 pounds of flammable liquids and gases, OSHA tested a mixture of the chemicals used in the metalation step and determined that the mixture did not meet the OSHA definition of “flammable liquid”²⁶ and coverage of this process step was not required.

²⁵ 29 CFR 1910.119.

²⁶ OSHA defines a flammable liquid as “any liquid having a flashpoint below 100°F (37.8°C), except any mixture having components with flashpoints of 100°F (37.8°C) or higher, the total of which make up 99 percent or more of the total volume of the mixture.”

6.2 Environmental Protection Agency

6.2.1 Risk Management Planning

EPA Risk Management Program²⁷ regulations cover specifically listed chemicals that pose a significant hazard to communities should accidental releases occur, including 77 toxic chemicals, 63 flammable chemicals, and some explosives.²⁸ Facilities subject to these regulations must submit a Risk Management Plan (RMP) addressing

- accidental release prevention and emergency response programs,
- site activities, regulated chemicals used, and their quantities;
- worst-case and alternative release scenarios, including distance the chemicals could travel and possible mitigation measures;
- five-year accident history; and
- planned changes to improve safety.

RMP elements must specifically address potential community impact, environmental damage, and site coverage under other regulatory programs. T2 did not use or produce any RMP-covered chemicals and was not required to register with or submit plans and release analyses to EPA.

²⁷ 40 CFR 68

²⁸ Explosives defined by the Department of Transportation as Class 1.1.

6.2.2 Emergency Planning and Community Right-to-Know

The Emergency Planning and Community Right-to-Know Act (EPCRA) requires annual reporting from facilities storing or processing listed Extremely Hazardous Substances (EHSs).²⁹ Facilities possessing chemicals on the EHS list must submit these annual reports, called Tier II reports, to the State Emergency Response Commission (SERC) and local emergency planning committees (LEPCs), listing the chemicals and their quantities on site.

EPCRA Tier II reporting requirements are designed to inform emergency responders of potential hazards should a chemical incident occur at a facility. Emergency responders should be familiar with the hazards of EPCRA-listed chemicals, but are dependent upon facilities to accurately convey which chemicals are present on their sites.

Of the chemicals T2 used, only the MCMT is EHS-listed. T2 produced thousands of pounds of MCMT per batch and stored thousands more pounds prior to shipment offsite, and therefore was required to submit an annual Tier II report to the LEPC and SERC. Although T2 did submit annual Tier II reports, they did not include MCMT. This incomplete report did not warn emergency responders of the MCMT, which is toxic by ingestion, inhalation, and skin absorption.

6.3 T2 Regulatory Compliance

T2 hired a consultant to analyze regulatory programs that might apply to its MCMT production facility. The consultant addressed EPA and FDEP programs for air, water, waste, hazardous chemicals, and

²⁹ The list of EHSs appears in Appendices A and B of 40 CFR 355.

storage tanks.³⁰ The consultant prepared, and T2 submitted to FDEP, tank registrations, storm water discharge general permit registration,³¹ and annual Tier II reports. T2 also submitted Tier II reports to the LEPC, although these, as discussed above, did not reflect the EHS-listed MCMT.³²

Although the consultant T2 hired had primary expertise in environmental regulations, he briefly addressed OSHA requirements. The consultant informed T2 that it must develop a hazard communication program,³³ which should include employee training, chemical labeling, and provision of MSDSs for all chemicals onsite. The consultant listed other OSHA requirements that would likely apply to T2, including

- confined space programs,
- lock-out/tag-out programs,
- personal protective equipment, and
- additional employee training.

The consultant recommended that T2 hire an additional consultant with OSHA expertise to address these and other OSHA regulations. There is no documentation that T2 further addressed potential OSHA requirements.

³⁰ Programs included SPCC planning,

³¹ This filing was a Notice of Intent (NOI) to use a Multi-Sector General Permit (MCGP), in accordance with FDEP implementation of National Pollutant Discharge Elimination System (NPDES) regulations.

³² It is likely that T2's consultant excluded the MCMT from the Tier II reports due to an oversight. He compiled the report based upon a list of raw materials provided by T2, and was unaware that T2 was manufacturing a toxic chemical.

³³ OSHA Hazard Communication Standard, 29 CFR 1910.1200

7.0 Reactive Hazard Resources

A number of resources are available to chemical manufacturers designing reactive processes. In 2002 the CSB published a comprehensive report, *Improving Reactive Hazard Management*, documenting the rate, types, and causes of reactive incidents and providing recommendations to improve regulatory coverage. The American Institute of Chemical Engineers (AIChE) has actively promoted reactivity hazard education, operating groups specifically tailored to provide reactivity safety and design information to students and process engineers

7.1 The CSB Reactives Study

The CSB found that reactive incidents are a serious problem in the U.S., and that both management system and regulatory improvements are needed to help facilities control reactive hazards. The report studied reactive incidents, causal factors, and preventive measures, and outlined the screening, hazard identification, hazard review, operating procedures, and training needed to prevent reactive incidents.³⁴

The report documented 167 serious reactive incidents in the United States between January 1980 and June 2001 that resulted in 108 deaths, hundreds of injuries, and significant public impacts. Ongoing CSB monitoring indicates that reactive incidents—such as the T2 explosion—continue to occur.

The report also found that 70 percent of reactive incidents occurred in the chemical manufacturing industry, with 35 percent due to runaway reactions like the one that occurred at T2.³⁵ While 42 percent of

³⁴ Available for download at <http://www.csb.gov>.

³⁵ Of reactive incidents, 25 percent originate in reactors, with the rest occurring in a wide range of equipment.

reactive incidents resulted in fires and explosions, another 37 percent caused toxic emissions. Many reactive incidents occurred at small manufacturing sites like T2.

More than 50 percent of the 167 incidents documented in the CSB report involved chemicals not covered by existing OSHA Process Safety Management (PSM) or EPA Risk Management Program regulations (Section 7). The CSB recommended that EPA and OSHA expand reactive hazard coverage under these regulations. EPA now requires reporting of reactive chemical incidents under RMP reporting rules and OSHA has taken steps to increase industry awareness of reactive hazards, but neither has fully implemented the CSB recommendations.

7.2 Reactive Hazard Reference Materials

Numerous publications document safe practices for reactive hazard management. The reference section of this report lists resources that are widely available to plant designers and operators. Both OSHA and EPA maintain web pages dedicated to reactive chemical hazards.³⁶ These pages provide information on recognizing and safely managing reactivity hazards as well as links to additional information, case studies, and screening tools. In addition, an AIChE-published reference book, *Essential Practices for Managing Chemical Reactivity Hazards*, was developed by the Center for Chemical Process Safety (CCPS, discussed below) with support from EPA, OSHA, the American Chemistry Council, and the Society of Chemical Manufacturers and Affiliates (formerly the Synthetic Organic Chemical Manufacturers Association). This publication is available online free of charge at <http://info.knovel.com/ccps/>; the online version includes the full text and interactive support software.

³⁶ The EPA Reactive Chemical Hazards web page is http://www.epa.gov/oem/content/learning/chemical_hazards.htm; the OSHA Chemical Reactivity Hazards web page is <http://www.osha.gov/SLTC/reactivechemicals/index.html>.

7.3 American Institute of Chemical Engineers

AIChE is a professional organization that provides chemical process safety guidance through education, training, and outreach. Two AIChE groups, the Design Institute for Emergency Relief Systems (DIERS) and the Center for Chemical Process Safety (CCPS), are active in improving reactivity hazard management and education.

7.3.1 Design Institute for Emergency Relief Systems

DIERS is a non-profit organization formed by AIChE in 1976 to promote improved emergency relief design. Presently more than 230 domestic and international member companies interested in design, use, or manufacture of emergency relief systems comprise the DIERS Users Group, which meets semiannually.

DIERS methodology has earned broad industry acceptance and recognition. OSHA's PSM regulation recognizes AIChE/DIERS technical reports as "generally recognized and accepted good engineering practice." OSHA has also recommended using DIERS methodology for reevaluation of relief sizing following a runaway reaction incident.

DIERS Users Group publications address screening and management of chemical reactivity hazards, reactivity test apparatus design and evaluation, scale-up, and design of emergency relief systems. As of the date of this report, the DIERS Users Group was revising the second edition of the CCPS book *Guidelines for Pressure Relief and Effluent Handling Systems* to include technology updates, simplify the text, and provide an advanced software tool for pressure relief design.

7.3.2 Center for Chemical Process Safety

CCPS identifies and addresses process safety needs within the chemical, pharmaceutical, and petroleum industries. CCPS members define, develop, and publish engineering and management best practices to prevent or mitigate catastrophic releases of chemicals.

In 1992, CCPS's Safety and Chemical Engineering Education (SChE) Committee began providing chemical process safety teaching materials for undergraduate chemical engineering curricula. SChE products address hazards of chemical reactivity, inherently safer design, risk assessment, simplified relief design, and other process safety topics. Two SChE products address runaway reactions; one of these provides information on experimental characterization and vent sizing using the Advanced Reactive System Screening Tool (ARSST) (Appendix C discusses the CSB's use of the ARSST).

In 2004, CCPS formed the Reactivity Management Roundtable (RMR) to assimilate, implement, maintain, and update effective practices for managing chemical reactivity. RMR provides reactivity hazard recognition and management resources to companies with limited technical sophistication. RMR is developing web-based tools that use decision trees to identify potential chemical reactivity hazards.

In 2008, SChE began a Student Certificate of Safety Achievement Program which is available free to student members of U.S. universities' AIChE chapters. Two certificate modules, in addition to the general module, address runaway reactions and chemical reactivity hazards. The program issued about 800 certificates in its first year.

8.0 Key Findings

1. On December 19, 2007, an explosion at T2 Laboratories, Inc., killed four, injured 32, and destroyed multiple businesses.
2. The explosion was due to a runaway exothermic reaction that occurred in a chemical batch reactor during the production of methylcyclopentadienyl manganese tricarbonyl (MCMT).
3. The runaway reaction occurred during the first, metalation, MCMT process step.
4. A desired exothermic reaction in the metalation step ran away due to a cooling system failure, leading to a second (undesired) exothermic reaction.
5. The reactor cooling system lacked design redundancy and was susceptible to single-point failure. No emergency source of cooling existed.
6. The T2 owner/chemical engineer designed the pressure relief system for normal operating conditions, and it was unable to relieve the second exothermic reaction.
7. The T2 owners were likely unaware of the second exothermic reaction that occurred in the batch recipe at high temperatures.
8. Neither of the T2 owners had prior reactive chemistry experience.
9. Most baccalaureate chemical engineering curricula in the U.S. do not specifically address reactive hazard recognition or management.

9.0 Root and Contributing Causes

9.1 Root Cause

T2 did not recognize the runaway reaction hazard associated with the MCMT it was producing.

9.2 Contributing Causes

The cooling system employed by T2 was susceptible to single-point failures due to a lack of design redundancy.

The MCMT reactor vessel relief system was incapable of relieving the pressure from the runaway reaction.

10.0 Recommendations

American Institute of Chemical Engineers

2008-03-I-FL-R1

Work with the Accreditation Board for Engineering and Technology, Inc. to add reactive hazard awareness to baccalaureate chemical engineering curricula requirements.

2008-03-I-FL-R2

Inform all student members about the Process Safety Certificate Program and encourage program participation.

Accreditation Board for Engineering and Technology, Inc.

2008-03-I-FL-R3

Work with the American Institute of Chemical Engineers to add reactive hazard awareness to baccalaureate chemical engineering curricula requirements.

By the

U.S. Chemical Safety and Hazard Investigation Board

John S. Bresland

Chair

Gary Visscher

Member

William Wark

Member

William Wright

Member

Date of Board Approval

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Appendix A
MCMT Process Chemistry

T2 manufactured MCMT in three steps. The first step of the reaction required heating to initiate the reaction. After that, all three steps were exothermic (heat-producing) and required cooling.

In the first step (called metalation), molten metallic sodium was reacted with methylcyclopentadiene (MCPD) in the presence of a diethylene glycol dimethyl ether (diglyme) to form sodium methylcyclopentadiene and hydrogen gas. This was accomplished by adding metallic sodium to a mixture of MCPD dimer³⁷ and diglyme, then heating the mixture. Heating melted the sodium and split the MCPD dimer molecules into two MCPD molecules that reacted with the sodium. T2 vented the hydrogen gas produced by this step to the atmosphere.

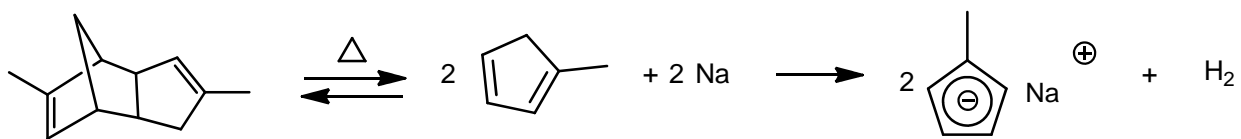


Figure 10. MCMT metalation reaction.

In the second step (called substitution), T2 added manganese chloride (dry powder) to the reactor. The manganese chloride reacted with the sodium methylcyclopentadiene in the reactor to form manganese dimethylcyclopentadiene and sodium chloride.

³⁷ MCPD dimer is a molecule consisting of two identical MCPD molecules.

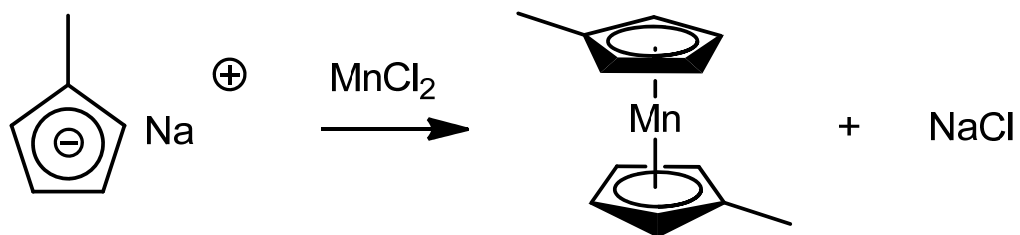


Figure 11. MCMT substitution reaction.

In the final step (called carbonylation), T2 added carbon monoxide gas to the bottom of the reactor, bubbling the gas through the manganese dimethylcyclopentadiene under pressure. In this step, one of the methylcyclopentadiene molecules on each manganese dimethylcyclopentadiene molecule was replaced with three carbon monoxide molecules, forming the MCMT.

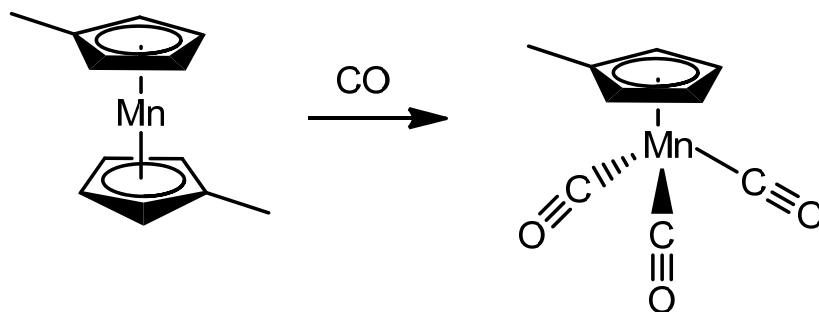


Figure 12. MCMT carbonylation reaction.

Following the carbonylation step, the process operator distilled the mixture to remove the MCMT and the diglyme. The remaining (waste) methylcyclopentadiene and sodium chloride was removed as a solid.

The diglyme was recovered and reused in the process.

Appendix B

Explosive Severity and Damage Characterization

The methodology used to estimate TNT equivalence involved analyzing observed building damage; this method assumes the applied blast energy from the explosion source has the same characteristics as a blast energy from an equivalent TNT charge. The average charge weight obtained from the observed building damage was 1,420 lb TNT.

Free-field pressure and impulse at various distances from the T2 explosion site were calculated based on the average estimated charge weight (Table 1). Figures 19 and 20 show the free-field pressure and impulse values at various distances plotted on a map of the Faye road area.

Table 1. Distance to Pressure Contours from Explosion Center for 1,420 lb TNT Yield.

Free-Field Pressure (psi)	Distance from the Source (ft)	Corresponding Free-Field Impulse (psi-ms)
0.25	1,559	7.14
0.5	863	13
1	511	21.9
1.5	372	29.8
2	299	36.8
3	225	48.4
5	162	65.8
10	110	92.6
25	70.6	136.6

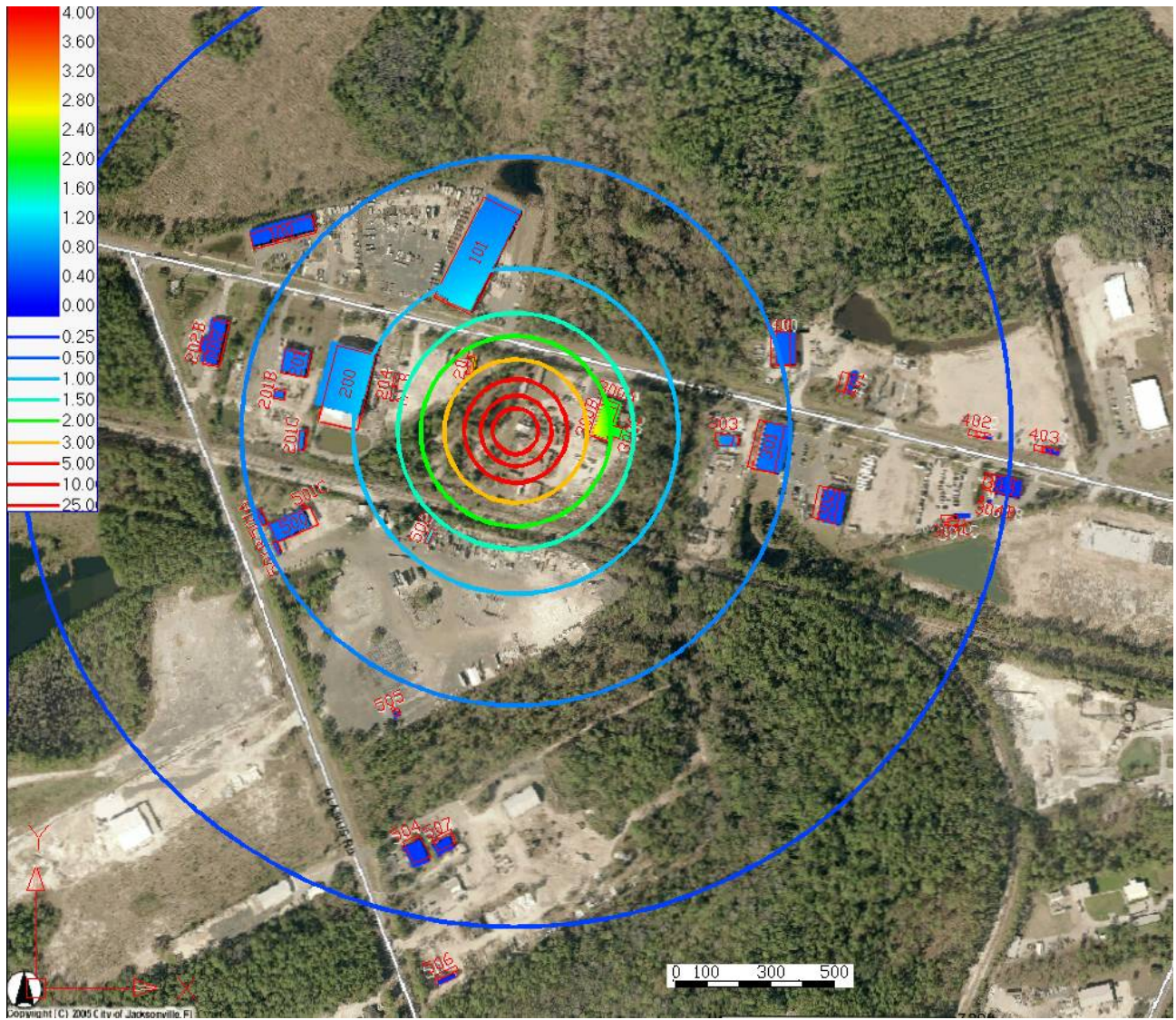


Figure 13. Free-Field Pressure Contours for Estimated TNT Yield of Explosion.

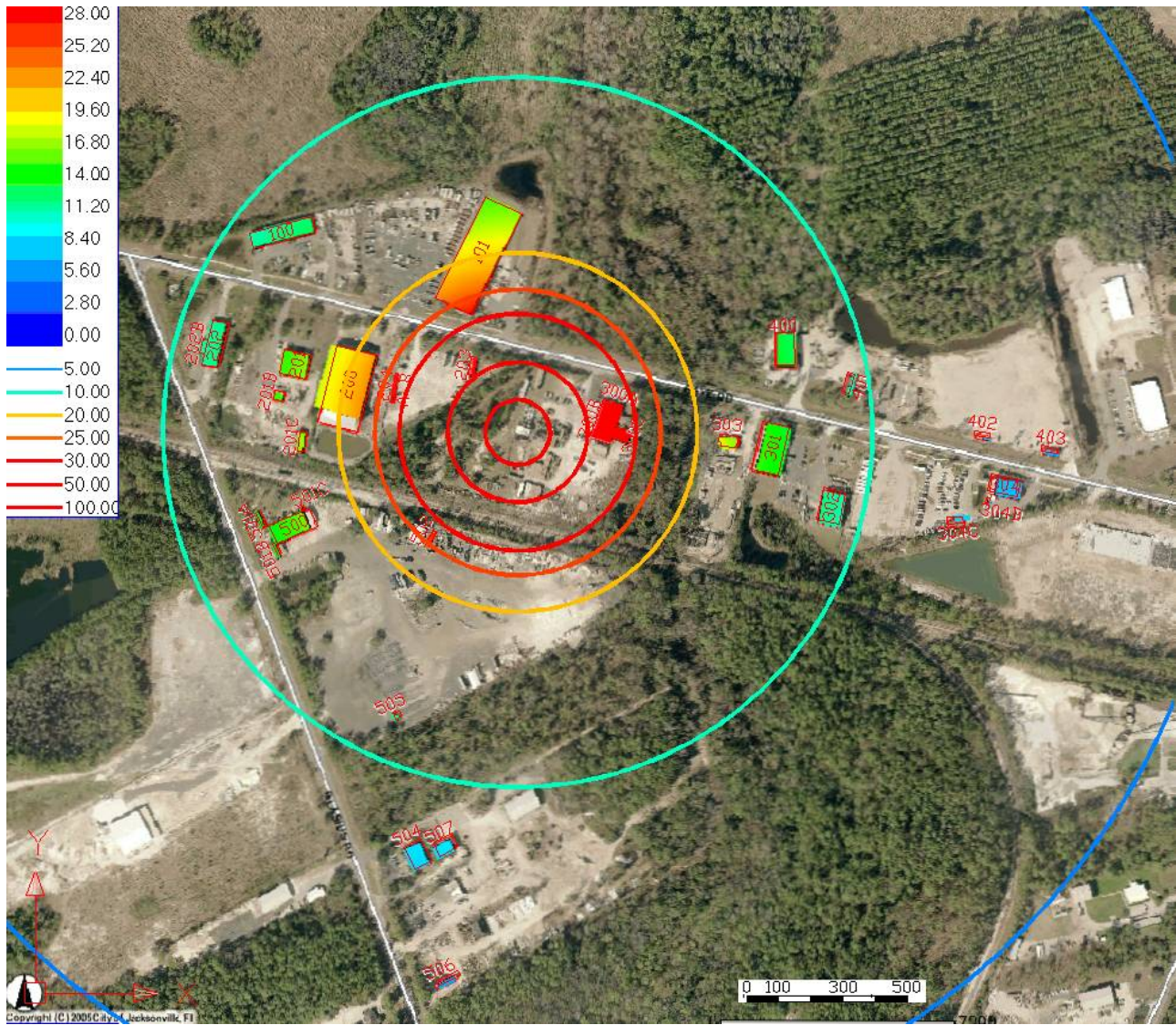


Figure 14. Free-Field Impulse Contours for Estimated TNT Yield of Explosion.

Appendix C
MCMT Chemical Testing

1.0 Test Description

The CSB performed 12 laboratory tests based on the T2 chemical recipe on the day of the incident, six using the Advanced Reactive System Screening Tool (ARSST) and six using the Vent Sizing Package 2 (VSP2).³⁸ These systems minimize heat loss through the cell walls to better predict behavior in large vessels, which have much smaller surface-to-volume ratios. All tests were conducted inside a larger containment vessel for safety.

Initial tests were conducted in the ARSST, which uses a small sample size and is open to the containment vessel, to minimize the hazards associated with the potentially destructive chemistry. In these tests, some MCPD and diglyme solvent evaporated because of the open-cell configuration. Two successive exotherms, the second larger, were observed and most pronounced in tests with lower MCPD concentration and excess sodium. The ARSST testing identified conditions required to initiate this second exotherm, but was unable to explore the full runaway potential of the reaction.

Therefore, to more closely match the conditions at T2, the CSB ran a second series of six tests using the larger VSP2 test cell (Figure 15).

³⁸ Both the ARSST and VSP2 are commercially available test apparatus for thermal hazard evaluation testing.



Figure 15. New VSP2 Test Cell.

The VSP2 mimics the T2 facility's physical arrangement more closely and can accommodate more intense stirring to improve mixing of the chemical components. The VSP2 also incorporates baffles in the test cell which provide turbulence and shear in the liquid. These features reduced the molten sodium droplet size and increased contact between the molten sodium and the MCPD, similar to the mixer in the T2 reactor.

In the VSP2 apparatus, a 116 ml test cell is loaded with the raw materials, stir bar, and temperature and pressure measurement devices. The test cell is contained in a protective pressure vessel (containment vessel) that can accommodate high temperature and pressure in the event the test cell ruptures. Tests were either open to containment vessel or sealed in the test cell. A sealed test cell prevents evaporation into the containment vessel, which would have had an undesired cooling effect. This test mimics an event such as a closed vent or undersized relief system.

For the first two VSP2 tests, the test cell was open to the containment vessel and results similar to the ARRST tests were obtained. The CSB conducted the remaining four VSP2 tests in a closed (sealed) test cell. A second and more energetic exothermic reaction was observed when the temperature exceeded 390°F (198.9°C) in two test that used the T2 recipe. The pressure and temperature rise during the second exothermic reaction was about 32,000 psig per minute (2,206 bar per minute) and 2340°F per minute (1300°C per minute) respectively and burst the test cells (Figure 16). The other two tests performed using only sodium and diglyme solvent, suggest that this second more energetic exothermic reaction is a reaction between the sodium and diglyme solvent.



Figure 16. Burst VSP2 Test Cell.

The results of this testing show that the standard T2 chemical recipe is capable of producing the reactor failure observed on December 19, 2007. Using the data obtain from these tests, the CSB determined by calculation failure of the reactor from this second exothermic reaction could not have been prevented by an overpressure relief device. Failure could only be prevented by relieving pressure before the second exothermic reaction and allowing the MCPD and Diglyme solvent to boil and vent. Allowing the MCPD and diglyme to boil and vent removes heat from the mixture and reactants from the reactor. For T2 this would have required a rupture disk set at 75 psig in lieu of the 400 psig disk that was used.

2.0 Test Data

Table 2 presents a summary of the VSP2 test conditions and results.

Table 2. VSP2 Test Results.

VSP2 Run Number	Chemical Components	Test Conditions	Peak Temperature	Peak Pressure	Conclusion
1	Normal recipe	Open to containment	698.4°F 370.2°C	97 psig 6.69 bar	Similar to ARSST
2	Normal recipe	Open to containment	671.4°F 355.2°C	78 psig 5.38 bar	Similar to ARSST
3	Normal recipe	Closed	887.4°F 475.2°C	1512 psig 104.2 bar	Test cell rupture
4	Sodium and Diglyme. No MCPD	Closed.	NA	NA	Leak developed in test cell
5	Sodium and Diglyme. No MCPD	Closed	1281.6°F 694.2°C	1598 psig 110.2 bar	Test cell rupture
6	Normal recipe	Closed	1222.2°F 661.2°C	1788 psig 123.3 bar	Test cell rupture

In VSP2 Run 5, the CSB tested the following chemical recipe:

Table 3. Run 5 Recipe.

Chemical	Actual Charge (g)	Weight Percent of Charge
Sodium	9.412	18.86
Diglyme	37.624	75.38
Mineral Oil ³⁹	2.877	5.76
Total Sample	49.912	100.00

Patent literature⁴⁰ suggests that a sodium-diglyme reaction occurs slightly above T2's normal process temperature. The CSB tested the sodium-diglyme system and determined a strong exothermic reaction can occur between sodium and diglyme at temperatures above 390 °F (198.9°C). T2 conducted the first process step at about 350°F (176.7°C), resulting in a margin of safety of only 40 °F (22.2°C) below the more energetic reaction.

³⁹ Sodium metal arrives packed in mineral oil to prevent oxidation and limit moisture contact with the metal. Some mineral oil is transferred into the test cell with the sodium. The mineral oil does not participate or interfere with the reactions.

⁴⁰ US Patent 2,942,040. Manufacture of Sodium Cyclopentadiene from Cyclopentadiene Dimer, June 21, 1960.

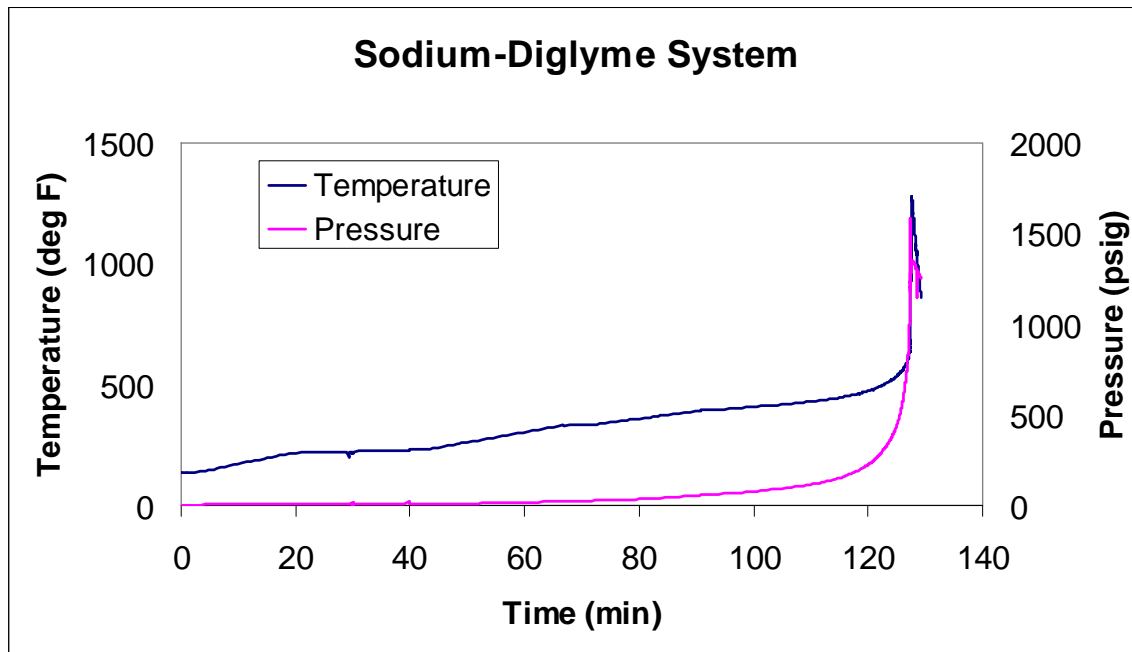


Figure 17. Sodium Diglyme Test Results.

In the VSP2 Runs 3 and 6, the CSB tested T2's normal chemical recipe. The recipe used in Run 6 is shown in Table 4 and the results in Figure 18:

Table 4. Run 6 Recipe.

Chemical	Actual Charge (g)	Weight Percent of Charge
Sodium	5.147	10.59
MCPD Dimer	21.164	43.55
Diglyme (95% purity)	20.690	42.58
Mineral Oil	1.591	3.28
Total Sample	48.592	100.00

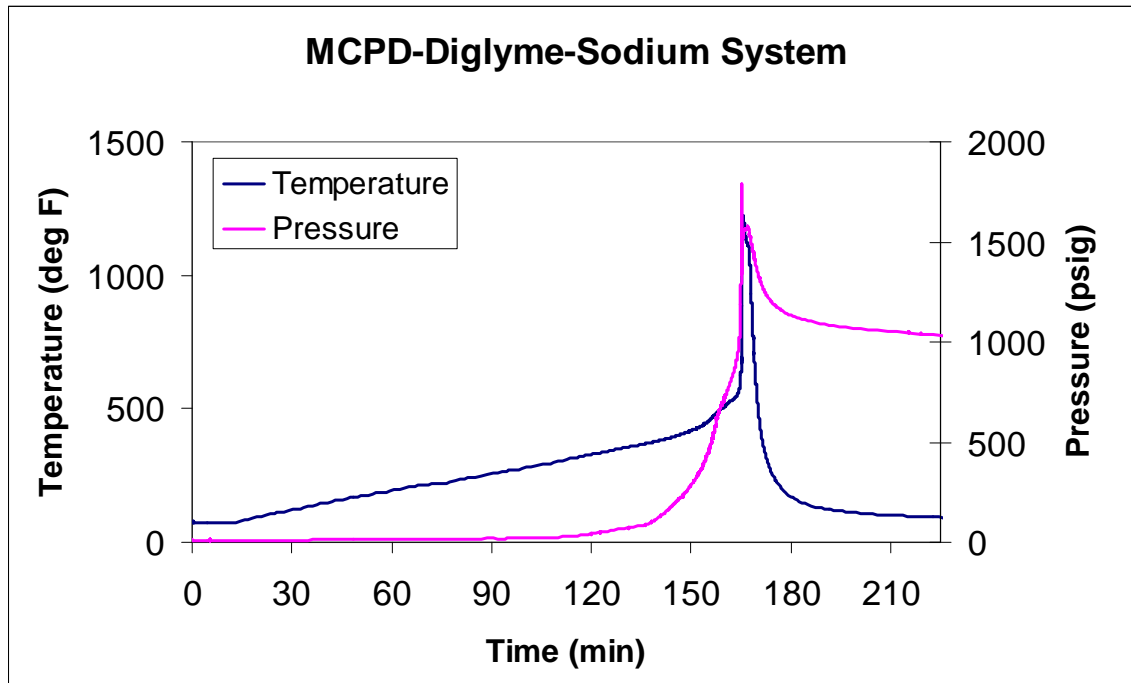


Figure 18. MCPD Diglyme Sodium Test Results.

The peak rate of temperature rise for the final test is 2340°F/minute (1300°C/minute) and the peak rate of pressure rise is 32,000 psi/minute (2206 bar/minute). In the closed system, a strong exothermic reaction occurs using the normal T2 chemical recipe.

Appendix D
MCMT-Related Patents

U.S. Patent 2,557,744. Preparation of a Metal Carbonyl from Tungsten or Molybdenum Oxychloride, June 19, 1951.

U.S. Patent 2,680,756. Dicyclopentadienyliron and Process of Making the Same, June 8, 1954.

U.S. Patent 2,680,758. Dicyclopentadienylnickel and Method, June 8, 1954.

U.S. Patent 2,694,721. Condensation Products of Bis-cyclopentadienyl Iron and Aldehydes, November 16, 1954.

U.S. Patent 2,810,736. Cyclopentadienyliron and Hydrocarbon Substituted Cyclopentadienyliron Carbonyl Compounds, October 22, 1957.

U.S. Patent 2,818,416. Cyclomatic Compounds, December 31, 1957.

U.S. Patent 2,818,417. Cyclomatic Compounds, December 31, 1957.

U.S. Patent 2,839,552. Cyclomatic Manganese Compounds, June 17, 1958.

U.S. Patent 2,868,816. Process for the Preparation of Cyclopentadienyl Manganese Tricarbonyl Compounds, January 13, 1959.

U.S. Patent 2,870,180. Process for the Preparation of Hydrocarbon Manganese Carbonyl Compounds, January 20, 1959.

U.S. Patent 2,898,354. Process for the Preparation of Cyclomatic Manganese Tricarbonyls, August 4, 1959.

U.S. Patent 2,915,440. Cyclopentadienyl Manganese Compounds, December 1, 1959.

U.S. Patent 2,915,539. Process for the Preparation of Cyclopentadienyl Manganese Tricarbonyl Compounds, December 1, 1959.

U.S. Patent 2,915,504. Manufacture of Cyclopentadienyl Manganese Carbonyl Compounds, December 8, 1959.

U.S. Patent 2,915,505. Manufacture of Cyclopentadienyl Manganese Carbonyl Compounds, December 8, 1959.

U.S. Patent 2,915,506. Manufacture of Cyclopentadienyl Manganese Compounds, December 8, 1959.

U.S. Patent 2,942,040. Manufacture of Sodium Cyclopentadiene from Cyclopentadiene Dimer, June 21, 1960.

U.S. Patent 2,960,514. Manufacture of Cyclopentadienyl Manganese Carbonyl Compounds, November 15, 1960.

U.S. Patent 2,964,547. Process for the Preparation of Manganese Cyclopentadienyl Tricarbonyl Compounds, December 13, 1960.

U.S. Patent 2,987,528. Manufacture of Cyclopentadienyl Manganese Compounds, June 6, 1961.

U.S. Patent 2,987,529. Use of Transition Metal Carbonyls in the Manufacture of Cyclopentadienyl Manganese Tricarbonyl, June 6, 1961.

U.S. Patent 2,987,530. Use of Transition Metal Carbonyls as Catalysts in the Manufacture of Cyclopentadienyl Manganese Tricarbonyl, June 6, 1961.

U.S. Patent 2,987,531. Preparation of Cyclopentadienyl Manganese Compounds from Tris (Cyclopentadienyl) Group III-A Metal Compounds, June 6, 1961.

U.S. Patent 3,040,077. Preparation of Cyclopentadienyl Manganese Tricarbonyls, June 19, 1962.

U.S. Patent 3,041,155. Fuel and Anti-Knock Compositions, June 26, 1962.

U.S. Patent 4,946,975. Process for Making Methycyclopentadienyl Manganese Tricarbonyl Compounds, August 7, 1990.

U.S. Patent 5,026,885. Process for Preparing Transition Metal Cyclopentadienyl Manganese Carbonyl Compounds, June 25, 1991.

U.S. Patent 5,281,733. Process for Producing MMT, January 25, 1994.

Appendix E
Similar Incidents

1.0 Morton International, Inc. Explosion and Fire

On April 8, 1998, an explosion and fire occurred during the production of Automate Yellow 96 Dye at the Morton International Inc. plant in Paterson, New Jersey. The explosion and fire were the consequence of a runaway reaction, which overpressurized a 2,000-gallon chemical vessel and released flammable material that ignited. Nine employees were injured. The incident caused the hospitalization of two employees, the release of chemicals into the community, and damage to the plant.

The investigation team determined that the Yellow 96 reaction accelerated beyond the heat-removal capability of the reactor. The resulting high temperature led to a secondary runaway decomposition reaction causing an explosion, which blew the hatch off the reactor and allowed the release of the reactor contents. The initial runaway reaction was most likely caused by excessive reactor heating and delayed use of the cooling water system. The reactor's cooling system could not control the exothermic reaction and had no emergency shutdown or quenching function.

The CSB investigation found that Morton had not adequately evaluated or controlled the hazards of the Yellow 96 production process. Neither a preliminary assessment conducted in 1990 nor a subsequent hazard analysis five years later considered the possibility of a runaway chemical reaction—one of the most common reactive hazards. As a result, the reactor was not provided with sufficient cooling capacity or adequate emergency shutdown or venting systems. Morton's analyses never considered possible scenarios—such as excessive heat input or inadequate cooling—that could trigger a runaway reaction.

2.0 Concept Sciences Inc. Hydroxylamine Explosion

On February 19, 1999, a process vessel containing several hundred pounds of hydroxylamine exploded at the Concept Sciences Inc. (CSI) production facility near Allentown, Pennsylvania. CSI employees were

producing the facility's first full-sized batch of hydroxylamine (HA). After the distillation process of an HA and potassium sulfate solution was stopped, the HA in the process tank and associated piping explosively decomposed, most likely due to high concentration and temperature. The explosion killed four CSI employees and a manager of an adjacent business. Two CSI employees survived the blast with moderate-to-serious injuries. Four people in nearby buildings were injured. The explosion also caused significant damage to other buildings in the light industrial use business complex where CSI was located and shattered windows in several nearby homes.

CSI had developed the HA production process through laboratory-scale experimentation in 1997, then constructed a 10-gallon pilot plant. In July 1998, CSI set up a full production facility in a multi-tenant building. The production parameters that CSI designed for the reaction involved a high concentration of HA, which could result in exothermic decomposition forming explosive crystals—despite available MSDS information regarding the fire and explosion hazards of such high concentrations.

The CSB found that CSI had not systematically evaluated the reactive hazards of the process during production development phases, determined the magnitude of the hazard, nor identified control measures. An adequate reactive chemical hazard evaluation and process hazard analysis (PHA) would have helped CSI quantify, evaluate, and mitigate the hazards of HA production. Such analyses might have even caused management to question whether its planned process presented substantial or unacceptable risks to employees and to the community.

3.0 MFG Chemical Inc. Toxic Gas Release

On April 12, 2004, a runaway reaction over-pressurized a chemical reactor at the MFG Chemical manufacturing plant, releasing toxic allyl alcohol vapor into the community. The resulting toxic cloud sent 154 people to a local hospital, forced the evacuation of nearby residents, and killed vegetation and aquatic life near the plant.

MFG was producing its first batch of triallyl cyanurate (TAC) in a batch reactor as part of a tolling arrangement with a third-party company. The CSB investigation found that MFG had not thoroughly researched the reactive hazards of the process before scaling up from laboratory tests to full production. Although literature on the hazards of TAC manufacturing was readily available, MFG's literature search focused on patent restrictions rather than the reactive chemistry hazards of the process.

Although MFG had tested the reaction at the bench scale, these tests were designed to maximize yield and minimize production cost, and did not indicate that the process included an additional highly exothermic decomposition reaction which would require additional cooling. MFG tested three batches in a 30-gallon reactor, but then used a different batch recipe in the full production batch. A comprehensive process design and hazard review of the scale-up was not performed, and MFG did not appreciate the significant difference in heat removal capacity of the 4,000-gallon reactor compared to the 30-gallon reactor.

The CSB concluded that this incident could have been avoided had MFG thoroughly investigated the hazards of the process and properly designed the emergency vent system to contain a potential release of the toxic vapor.

4.0 Synthron, LLC Chemical Explosion

On January 31, 2006, a runaway chemical reaction and subsequent vapor cloud explosion and fires killed one worker, injured 14 (two seriously), damaged structures in the nearby community, and destroyed the facility at Synthron, LLC in Morganton, North Carolina. At this facility, Synthron manufactured a variety of powder coating and paint additives by polymerizing acrylic monomers in a 1,500 gallon reactor.

The company had received an order for slightly more of an additive than the normal size recipe would produce. Plant managers scaled up the recipe to produce the required larger amount of polymer, and added all of the additional monomer needed into the initial charge to the reactor. This more than doubled

the rate of energy release in the reactor, exceeding the cooling capacity of the reactor condenser and causing a runaway reaction. The reactor pressure increased rapidly. Solvent vapors vented from the reactor's manway, forming a flammable cloud inside the building. The vapors found an ignition source and exploded.

The CSB investigation found that although Synthron combined monomers and reaction initiators in the presence of flammable solvent to produce polymer products, it had failed to identify the hazards associated with this type of chemistry. Additionally, process safety information was poorly documented, product recipes were changed without systematic review, and automatic safeguards to prevent or mitigate the effects of runaway reaction were not in place. When performing reactive chemistry, companies must be aware of the hazards involved and take action to minimize potential consequences of all identified hazards.