U.S. CHEMICAL SAFETY AND HAZARD INVESTIGATION BOARD

INVESTIGATION REPORT

TOXIC CHEMICAL VAPOR CLOUD RELEASE

(154 Treated, Five Hospitalized for Toxic Chemical Exposure)

MFG CHEMICAL, INC.

DALTON, GEORGIA

APRIL 12, 2004

KEY ISSUES:

- REACTIVE CHEMICALS PROCESS DESIGN
- PROCESS SCALE-UP
- EMERGENCY PLANNING AND RESPONSE

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Abstract

This report examines a toxic chemical release. On April 12, 2004, a runaway chemical reaction during the production of triallyl cyanurate at MFG Chemical, Inc. (MFG) in Dalton, Georgia, released highly toxic and flammable allyl alcohol and toxic allyl chloride into the nearby community, forcing the evacuation of more than 200 families. One worker received chemical burns and 154 people, including 15 police and ambulance personnel, required decontamination and treatment for chemical exposure. This report makes recommendations to the companies involved in the incident, as well as the local, county, and state agencies in charge of preparing emergency responses to chemical releases.

The U.S. Chemical Safety and Hazard Investigation Board (CSB) is an independent Federal agency whose mission is to ensure the safety of workers and the public by preventing or minimizing the effects of chemical incidents. The CSB is scientific investigative organization; it is not an enforcement or regulatory body. Established by the Clean Air Act Amendments of 1990, the CSB is responsible for determining the root and contributing causes of accidents, issuing safety recommendations, studying chemical safety issues, and evaluating the effectiveness of other government agencies involved in chemical safety. No part of the conclusions, findings, or recommendations of the CSB relating to any chemical incident may be admitted in evidence or used in any action or suit for damages arising out of any matter mentioned in an investigation report (see 42 U.S.C. § 7412[r][6][G]).

The CSB makes public its actions and decisions through investigation reports, summary reports, safety bulletins, safety recommendations, special technical publications, and statistical reviews. More information about the CSB is at www.csb.gov.

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Acronyms and Abbreviations

ACC	American Chemistry Council
ATSDR	Agency for Toxic Substances and Disease Registry
AHC	All Hazards Councils
AIChE	American Institute of Chemical Engineers
BTU	British thermal unit
CAER	Community Awareness and Emergency Response
CCPS	AIChE Center for Chemical Process Safety
CFR	Code of Federal Regulations
CSB	U.S. Chemical Safety and Hazard Investigation Board
DOT	U.S. Department of Transportation
EH&S	Environmental Health and Safety
EMA	Whitfield County Emergency Management Agency
EMC	Whitfield County Emergency Management Center
EMS	Hamilton Medical Center Emergency Medical Service (Paramedic and EMT ambulance service)
EMT	Emergency Medical Technician
EPA	U.S. Environmental Protection Agency
EPCRA	Emergency Planning and Community Right-to-Know Act
EPD	(Georgia) Environmental Protection Division of GDNR
GC/MS	Gas Chromatography and Mass Spectroscopy
GDNR	Georgia Department of Natural Resources
GEMA	Georgia Emergency Management Agency
GERC/SERC	Georgia (State) Emergency Response Commission
GPC	GP Chemical

HAZWOPER	Hazardous Waste Operations and Emergency Response
IC	Incident Commander
IChemE	Institute of Chemical Engineers
IDLH	Immediately dangerous to life or health
LEPC	Local Emergency Planning Committee
MFG	MFG Chemical, Inc.
MSDS	Material Safety Data Sheet
NAICS	North American Industrial Classification System
NIOSH	National Institute of Occupational Safety and Health
NFPA	National Fire Protection Association
OSHA	Occupational Safety and Health Administration
PEL	Permissible Exposure Limit
ppm	parts per million
PSM	Process Safety Management (29 CFR 1910.119)
R&D	Research and Development
RMP	Risk Management Plan (40 CFR 68, Subpart G)
SARA	Superfund Amendments and Reauthorization Act of 1986
SCBA	Self-Contained Breathing Apparatus
SOCMA	Synthetic Organic Chemical Manufacturers Association
TAC	Triallyl Cyanurate

Executive Summary

On the night of April 12, 2004, during an attempt to make the first production batch of triallyl cyanurate (TAC) at MFG Chemical, Inc. (MFG) in Dalton, Georgia, a runaway chemical reaction released highly toxic and flammable allyl alcohol and toxic allyl chloride into the nearby community. The fire department ordered an evacuation of residents and businesses within a half-mile of the facility. The release forced more than 200 families from their homes. One MFG employee sustained minor chemical burns and 154 people received decontamination and treatment at the local hospital for chemical exposure, including 15 police and ambulance personnel assisting with the evacuation. Five residents required overnight hospitalization for breathing difficulties. The reactor continued venting toxic vapor for nearly eight hours and the evacuation order lasted more than nine hours.

The U.S. Chemical Safety and Hazard Investigation Board (CSB) determined that the runaway chemical reaction rapidly pressurized the reactor causing the manway seal to fail, and then activated the overpressure safety device. Unable to contain the toxic vapor or stop the runaway reaction, the release continued until the chemical reaction ceased.

The CSB identified the following root causes of the incident:

- MFG did not understand or anticipate the reactive chemistry hazards. They did not make use of readily available literature on the hazards of reactive chemistry, or conduct a comprehensive literature search of the reactive chemistry specifically involved in manufacturing the product, which would have alerted them to the hazards involved in manufacturing TAC.
- MFG did not perform a comprehensive process design and hazard review of the laboratory scale-up to full production before attempting the first production run.

- MFG did not prepare and implement an adequate emergency response plan. They did not train or equip employees to conduct emergency mitigation actions.
- MFG did not implement the EPA Risk Management Program or the OSHA Process Safety Management program prior to receiving the allyl alcohol. The regulations require comprehensive engineering analyses of the process, emergency planning, a pre-startup safety review, and coordination with the local community before receiving the covered chemical at the site and introducing the covered chemical into the process.

The CSB makes recommendations to MFG to develop and implement written procedures requiring comprehensive hazard review for all process changes and new processes, develop a comprehensive emergency response plan and train the employees, as well as two additional recommendations addressing toll manufacturing services and regulatory compliance review.

Furthermore, the CSB makes recommendations to GP Chemical, Lyondell Chemical Company, the City of Dalton, Whitfield County, the Governor of the State of Georgia, and the Synthetic Organic Chemical Manufacturers Association.

1.0 Introduction

1.1 Background

An attempt to manufacture a new product resulted in a runaway reaction[1] that over-pressurized the reactor, activated the emergency vent, and released toxic vapor into the atmosphere, exposing and injuring facility employees, nearby residents, and emergency responders. The CSB concluded that this incident was avoidable. The company should have thoroughly investigated the hazards of the process and properly designed the emergency vent system to contain a potential release of the toxic vapor. Local emergency response agency all-hazard preparedness was not adequate for this event. The state emergency planning agencies could have assisted the local emergency response agencies in specific planning for hazardous chemical incidents.

This report presents the findings and specific actions that the parties who were directly involved in the incident should take to prevent a recurrence. Small and large businesses who use hazardous chemicals, especially those involving reactive chemistry should closely examine the lessons learned from this incident, particularly those involving hazard reviews, process design, and emergency planning. Furthermore, emergency response agencies should closely examine the lessons learned, especially those that address businesses, residents, and other community stakeholders involvement with emergency planning.

On the evening of April 12, 2004, MFG Chemical (MFG) was attempting to make the first production batch of triallyl cyanurate (TAC) at their Callahan Road facility in Dalton, Georgia. At approximately 9:30 PM, the reaction went out of control and over-pressurized a 4000-gallon

[1] A runaway reaction is a reaction that is out of control because the heat generation rate from the reaction exceeds the rate at which the heat is removed from the system by the cooling media and the surroundings (CSB, 2002).

reactor. The runaway reaction caused the release of highly toxic and flammable allyl alcohol vapor and toxic allyl chloride vapor into the community. The dense vapor continued to escape from the reactor for more than eight hours. Neither the Dalton Fire Department emergency responders nor MFG personnel had the personnel protective equipment required to enter the process area safely to attempt to stop the vapor release. The Dalton Fire Department promptly ordered an evacuation of all residents and businesses within a one-half mile radius of the facility. The Dalton Police Department then dispatched officers to the neighborhoods to alert the residents to evacuate.

More than 154 individuals, including police, ambulance crews, and residents, were overcome by the toxic vapor and required treatment at the hospital for respiratory distress, and eye and skin irritation. One MFG employee sustained minor chemical burns to his skin and was treated and released. Five residents required overnight hospitalization. The fire department cancelled the evacuation order at 7:00 AM, more than nine hours after the incident started.

The release exposed emergency responders, residents, and nearby businesses to toxic allyl alcohol and allyl chloride. Furthermore, the incident likely involved hazardous chemical reactions similar to incidents discussed in the U.S. Chemical Safety and Hazard Investigation Board (CSB) report, *Improving Reactive Hazard Management" (CSB, 2002).* Therefore, the CSB launched an investigation to determine the root and contributing causes and make recommendations to prevent similar occurrences.

1.2 Investigative Process

CSB investigators arrived on scene the morning of April 14, 2004. The investigation began with interviews with the MFG management and senior engineering personnel responsible for chemical process development, equipment, and the safety program at MFG. The CSB team then conducted a detailed examination of the process equipment, the chemical transport and storage tanker (isotainer), and the reactor cooling system. Investigators collected samples of the raw materials and residue from the reactor for analytical testing.

The investigation included interviews with personnel from the Dalton Fire Department including the fire chief, battalion chief, safety coordinator, deputy fire chief, and the on-scene incident commander. Investigators interviewed the Dalton Police Department lieutenant responsible for the Patrol Division, the captain of the Support Services Division, and many of the police officers exposed to the toxic vapor cloud during the community evacuation. They also interviewed the Whitfield County Emergency Management Agency director, hospital personnel responsible for decontaminating and treating the individuals at the hospital, and ambulance services personnel including the dispatcher and the emergency medical technicians (EMT) and paramedics exposed to the toxic vapor the night of the incident.

CSB investigators, assisted by individuals from the Whitfield County Health Department, Environmental Health Section conducted a door-to-door survey of 21 families evacuated from their residences, some of whom received decontamination and treatment at the hospital, and management personnel at local businesses in the evacuation area. Investigators interviewed the Georgia Department of Natural Resources on-scene investigator and management personnel in the Atlanta headquarters. CSB investigators also interviewed the president of GP Chemical, the company that contracted with MFG to manufacture the TAC, and personnel from Lyondell Chemical Company, the supplier of one of the raw materials used in the process. Officers from the Atlanta office of the Agency for Toxic Substances and Disease Registry (ATSDR) assisted the CSB by interviewing emergency room doctors and nurses at the Hamilton County Medical Center, the hospital where the people exposed to the toxic chemical underwent decontamination and treatment.

The CSB convened a public meeting in Dalton, GA on November 16, 2004 to present the preliminary incident summary to the community. The Board solicited comments from the residents and emergency response agencies regarding their experiences during the emergency. The Whitfield County Emergency Management Agency Director presented a summary of the emergency response actions during the incident and a representative from the Hamilton Medical Center presented their observations on hospital staff performance during the emergency.

The investigation team obtained the services of an engineering analysis and laboratory services consultancy to analyze the raw materials and recovered residue, and perform reactive chemistry testing of the chemical recipe[2] involved in the incident. The investigation team also contracted for modeling of the vapor cloud release.

1.3 Key Findings:

1. There was a runaway reaction at the MFG facility during the TAC synthesis. The runaway reaction resulted when operators added the entire quantity of each reactant, as well as the catalyst,[3] to the reactor at once, and were then unable to control the reaction rate.

2. MFG did not conduct an adequate evaluation of the reactive chemistry hazards involved in manufacturing triallyl cyanurate before attempting the first production batch. Readily available technical literature, including specific TAC synthesis accident histories would have alerted them to the reactive chemistry hazards involved.

[2] A recipe is a detailed instruction used to make a specific chemical. It typically includes equipment preparation prerequisites, raw chemical quantities, addition sequence, and critical process parameters such as timing, temperature, pressure, and flow. Recipes also usually contain warnings, cautions, and special personnel protective equipment need to manufacture the material.

[3] A catalyst is a substance that promotes or increases the rate of a chemical reaction without changing its own composition.

3. Lyondell Chemical (the allyl alcohol manufacturer) did not clearly communicate to MFG management or GPC (the allyl alcohol buyer) that MFG would be required to implement the EPA Risk Management Program regulation, including conducting appropriate design reviews and preparing comprehensive emergency plans, before receiving the allyl alcohol shipment at the MFG facility.

4. MFG did not develop the comprehensive process hazards analysis, pre-startup review, and emergency response elements required by the OSHA PSM standard and the EPA Risk Management Program regulation.

5. MFG and GPC did not apply industry best practices for toll manufacturing such as those provided in *Guidelines for Process Safety in Outsourced Manufacturing Operations* (CCPS, 2000). MFG did not share certain critical process safety information with GPC, and GPC did not ensure that MFG had addressed all hazards associated with the process before attempting to produce the first production batch.

6. MFG did not provide a hazardous vapor/liquid containment system on the reactor emergency vent. The runaway reaction released allyl alcohol and allyl chloride into the atmosphere and into a nearby creek.

7. The Whitfield County Emergency Response Plan did not include a community shelter-in-place or an effective evacuation plan, nor did it provide prompt notification to the affected residents and businesses.

8. The Dalton City and Whitfield County emergency response agencies did not have the hazmat team personal protective equipment and air monitoring devices needed to respond safely to the toxic chemical release.

9. The Dalton City Fire Department incident command did not direct all unprotected emergency response personnel to remain a safe distance away from the advancing toxic

vapor cloud. The incident command also allowed inadequately protected MFG employees to reenter the toxic vapor cloud.

10. The only decontamination station was more than five miles away from the perimeter of the evacuation zone, contributing to the spread of toxic material and exposure to additional personnel.

11. MFG employees conducted emergency response activities without the necessary procedures, training, or personnel protective equipment. One employee sustained chemical burns.

12. The State of Georgia has not established clear responsibility for oversight of the regulatory requirements contained in the Emergency Planning and Community Right-to-Know Act (EPCRA), and did not identify deficiencies in the Whitfield County Emergency Operations Plan.

1.4 Companies Involved

1.4.1 MFG Chemical, Inc.

MFG began operations in 1979. It employs approximately 35 personnel at two chemical manufacturing facilities, one located on Brooks Road and the other located on Callahan Road in Dalton, GA. Manufactured chemical products include emulsified mineral oils, phosphate esters, surfactants and sulfosuccinates (wetting agents), and various polymers. MFG produces many of these products in tolling arrangements[4] with other companies. The MFG analytical laboratory

[4] "Tolling" is a contractual agreement between two companies to produce material products. The toller, client, or both may provide the raw materials to the toller. The client usually retains ownership and controls the sale of the product. The toller usually provides the facility, equipment, labor, and other resources to manufacture the product.

performs product quality verification, and research and development for new or modified products. The Callahan Road facility (Figure 1) was selected to manufacture the TAC because it had a 4000-gallon, glass lined reactor (R4) and associated equipment needed for the chemical synthesis. It is approximately five miles southwest of the Brooks Road facility. The staff includes the president, plant manager, three Ph.D. organic chemists, and a chemical engineer. The chemical engineer is responsible for the safety and health program.

MFG is a member of the Synthetic Organic Chemical Manufacturers Association (SOCMA) and actively participates in trade shows and other industry activities.

1.4.2 GP Chemical

MFG agreed to produce TAC in a tolling agreement with GP Chemical (GPC). GPC started business in 1990 to develop new chemical processes, and market and sell chemical products. It employs three full-time individuals in the New Jersey office. One is a chemist with more than 15 years of experience with producing specialty chemicals. GPC is a 50% owner of a chemical manufacturing facility in Tennessee. The Tennessee facility also serves as a pilot plant for developing new chemical products.

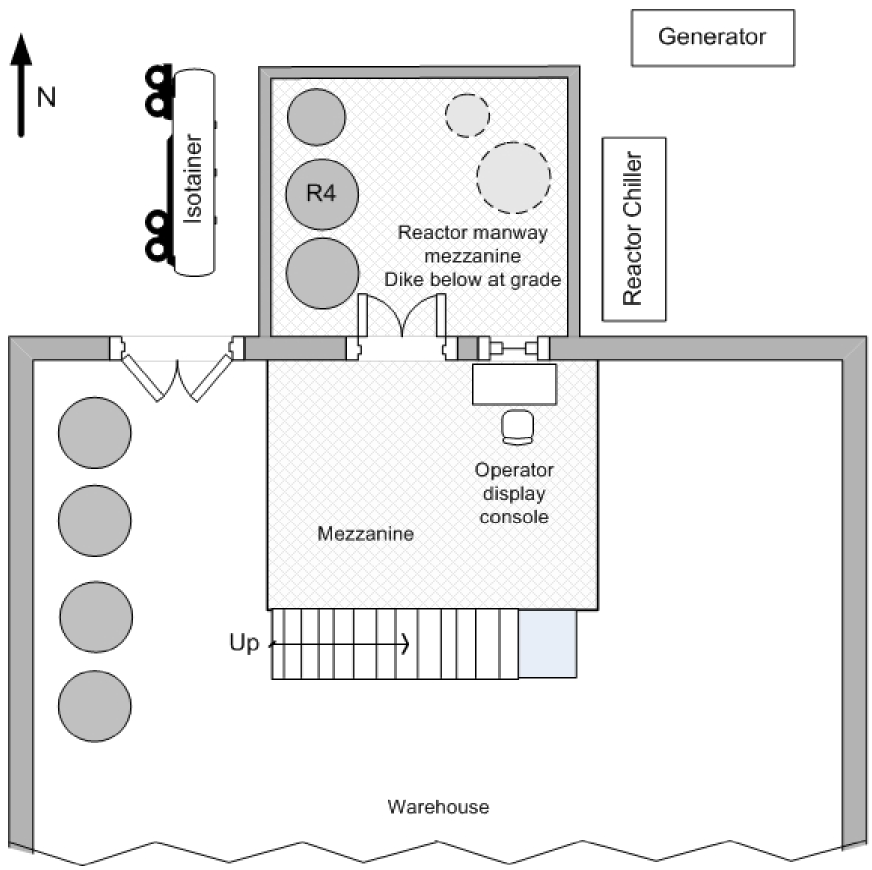

Figure 1. MFG Callahan Road facility layout.

GPC began discussions with MFG in late 2002 to procure tolling services for TAC, a chemical used in the manufacturing of rubber and other polymers. The two companies began discussing the details of the manufacturing process, which included selecting raw material suppliers, handling production quantities, and delivery schedules. GPC (the client) issued a purchase order to MFG (the toller) in January 2004 for the manufacture of the first production quantity of TAC.

1.4.3 Lyondell Chemical Company

GPC contracted with Lyondell Chemical Company (Lyondell) to provide the allyl alcohol to MFG. Headquartered in Houston Texas, Lyondell is a worldwide producer of basic chemicals and derivatives and is the sole manufacturer of allyl alcohol in the United States.

Lyondell maintains a product stewardship program[5] for all hazardous chemicals that they manufacture. Three months before delivering the allyl alcohol, Lyondell personnel visited the MFG facility and conducted an assessment to evaluate the preparedness of MFG to handle a large quantity of allyl alcohol safely. Lyondell concluded that MFG could safely handle production quantities of allyl alcohol after they made improvements in fire suppression equipment, and provided additional personal protective equipment and training to employees who would be working with the chemical. On April 4, 2004, GPC issued a purchase order to Lyondell to supply 35,000 pounds (4940 gallons) of allyl alcohol to MFG. An isotainer of allyl alcohol arrived on April 12, 2004, a few hours before the incident occurred, and was parked adjacent to the reactor (Figure 2).

[5] Product stewardship is a product-centered approach to environmental protection. It calls on those in the product lifecycle—manufacturers, retailers, users, and disposers—to share responsibility for reducing the environmental impacts of products. Source: EPA website, June 2005.

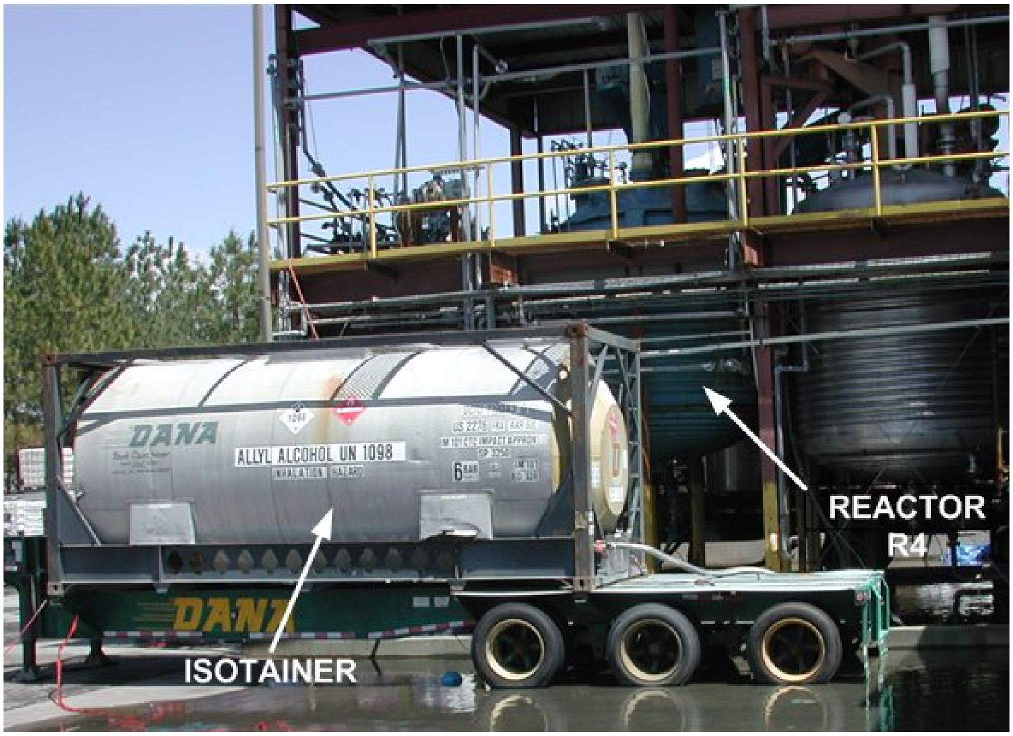

Figure 2. Isotainer (tanker) used to ship 35,000 lbs of allyl alcohol (looking east).

1.5 Chemical Characteristics

1.5.1 Allyl Alcohol

The National Fire Protection Association (NFPA) classifies allyl alcohol as a Class IB, extremely flammable liquid. The flashpoint[6] is 70° F and the flammable limits[7] range from 2.5% to 18% by volume. Allyl alcohol is toxic and poses a severe inhalation hazard, high skin absorption hazard, and high ingestion hazard. It is corrosive to the eyes and is a severe skin irritant. The Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) is 2.0

[6] Flashpoint is the minimum temperature at which a liquid will give off sufficient vapors to form an ignitable mixture with air near the surface, but will not sustain combustion.

[7] Flammable limit is the lower or upper concentration of vapor in air at which propagation of flame will occur in the presence of an ignition source.

parts per million (ppm) based on an eight-hour time weighted average. The National Institute of Occupational Safety and Health (NIOSH) lists 20 ppm as Immediately Dangerous to Life or Health (IDLH). Smell does not provide adequate warning of potentially hazardous air concentrations because odor thresholds are imprecise and the allyl alcohol PEL is within the odor threshold range of 1.4 ppm and 2.1 ppm (AIHA, 1989).

OSHA and EPA both regulate allyl alcohol. When used in quantities of 10,000 pounds or greater, allyl alcohol is an OSHA Process Safety Management (PSM) regulated flammable liquid (Section 4.1.1). It is an EPA Risk Management Program regulated toxic chemical when used in quantities of 15,000 pounds or greater (See Section 4.2.2).[8]

1.5.2 Cyanuric chloride

Cyanuric chloride is a fine white, crystalline powder with a pungent odor that strongly irritates the skin, mucous membranes, respiratory, and gastrointestinal tracts. It is highly reactive. Cyanuric chloride has no specified occupational exposure limits, nor is it covered in the PSM or Risk Management Program regulations.

1.5.3 Allyl Chloride

Allyl chloride is a colorless highly flammable and toxic liquid. It is extremely irritating to the respiratory system, eyes, and skin. The odor threshold ranges from one to five parts per million. The vapor is heavier than air.

[8] To protect the workers in the facility, the OSHA PSM standard regulates flammable liquids as a group based on the flammable characteristics of the liquid, and 137 specifically named toxic chemicals. To protect the environment and the public, the EPA Risk Management Program regulates 63 specifically named flammable gasses and volatile liquids, and 77 specifically named toxic chemicals.

1.6 Triallyl Cyanurate Process Development

1.6.1 GP Chemical Studies

A company interested in a multi-year contract to purchase large quantities of TAC from a U.S.-based manufacturer contacted GPC. GPC identified an expired American Cyanamid patent that provided a straightforward method to manufacture TAC and produced one laboratory-scale test batch in a three-liter flask to confirm that the basic recipe would produce a product that met the quality standards established by their customer.

GPC identified two important manufacturing considerations: 1) the chemical reaction liberated significant heat. Controlling the heat would require an adequate cooling system as well as slow, controlled addition of the chemicals, and 2) the fine powder form of one of the chemicals in the recipe required careful addition to control the reaction rate. GPC discussed these issues with MFG management and concluded that they understood the issues.

GPC began negotiations with MFG in late 2002 to manufacture TAC at their Dalton, GA facility. They signed a confidentiality agreement, the only formal contractual document executed for the tolling activity. It included a provision for MFG to hold confidential from GPC certain refinements or improvement in the catalyst used in the process. The agreement also provided for GPC to review the final chemical recipe prior to the first production batch. They did not arrange for GPC to observe or participate in the first TAC production batch.

GPC and MFG met in August 2003 where they discussed methods for controlling the rate of addition of the dry powder chemical into the reactor. They discussed the reactor cooling system performance requirements at a meeting the following December. The companies verbally agreed on other key elements, including financial arrangements for the temporary reactor cooling system and the purchase of the raw materials. GPC issued a purchase order to MFG in January 2004 to produce the first 20 tons of TAC, with the expectation of subsequent purchase orders after the acceptance of the first batch by their customer. They indicated that their customer was anxious for the delivery of large quantities of TAC.

1.6.2 MFG Studies

MFG personnel conducted a literature search to confirm that there were no patent restrictions that could adversely affect their TAC production. However, they did not conduct detailed literature research addressing the reactive chemistry hazards involved in the process (Section 5.3).

1.6.2.1 TAC Synthesis

MFG intended to synthesize triallyl cyanurate by reacting cyanuric chloride with allyl alcohol in the presence of a catalyst.

Allyl Alcohol + Cyanuric Chloride + Catalyst → TAC + Hydrogen Chloride + Catalyst

The reaction produces hydrogen chloride (HCl) as a by-product. In order to ensure complete conversion of the cyanuric chloride, the procedure specified an excess amount of allyl alcohol.[9] MFG planned to synthesize fixed-volume batches of TAC using a 4000-gallon reactor equipped with an external cooling-jacket (See Figure 2).

The procedure specified a slow addition of a caustic soda solution to the batch after thoroughly mixing the reactants. The caustic soda would neutralize the HCl produced in the synthesis reaction. MFG personnel understood that the neutralization reaction was very exothermic (i.e., heat generating), so they planned to circulate coolant through the reactor jacket to prevent the mixture from overheating. MFG did not anticipate that the reaction between the allyl alcohol and

[9] "Excess" as used in the chemistry context, is a means of driving a reaction to a desired endpoint. It does not imply that the amount of allyl alcohol was excessive in a safety context.

the cyanuric chloride was also highly exothermic and could generate significant heat (Section 1.8.2). The MFG laboratory test results indicated the heat generated during the neutralization step would require the highest rate of reactor cooling.

After the synthesis and neutralization were complete, the addition of an inhibitor to the batch would prevent polymerization of the TAC. Next, heating the batch would distill off the excess allyl alcohol. Finally, MFG would ship the washed, dried, and packaged TAC.

1.6.2.2 Batch Recipe Refinement

In the first half of 2003, MFG conducted laboratory scale testing of TAC recipes, but only for improving the yield and minimizing production cost. MFG and GPC discussed various techniques to control the maximum temperature from the exothermic reaction, including rearranging the sequence of chemical addition into the reactor and providing an adequately sized a reactor cooling system. However, despite the laboratory experiments, patent research, and discussions between the two companies, they never learned of the significant potential for an exothermic decomposition reaction.

MFG performed three batch tests in the 30-gallon reactor (Figure 3), but the final production batch procedure was different from the test batch procedures. The first two batches did not use a catalyst. They both used an incremental chemical addition sequence that included neutralizing the mixture with caustic soda at each increment. They added cyanuric chloride then caustic soda in small increments while maintaining the batch temperature below 95 °F. The third test batch loaded the entire quantity of allyl alcohol, cyanuric chloride, and the catalyst, then controlled the batch temperature below 50 °F, which was easy to accomplish in the 30-gallon reactor. The second and third test batches used recycled allyl alcohol from the first test batch, not fresh allyl alcohol.

The procedure used to attempt the full-scale TAC production in the 4000-gallon reactor was similar to the third 30-gallon reactor test, but used only fresh allyl alcohol and did not limit the batch temperature. The production procedure did not specify the incremental addition and neutralization steps used in the first two test batches. The production batch procedure contained no chemical addition rate restrictions, critical for controlling the reaction rate even though management had discussed the issue with GPC.

Controlling the temperature of the reacting chemicals was significantly more difficult in the 4000-gallon reactor than in the 30-gallon reactor. The heat removal capacity of a reactor equipped with an external jacket is directly proportional to the ratio of the jacketed surface area to the reactor volume. This surface-to-volume ratio decreases as the reactor volume increases,[10] thus the ability to remove excess heat may be significantly less in a large production reactor compared to the bench-scale reactor. Scaling to the 4000-gallon production reactor made controlling the batch temperature much more difficult.

[10] This assumes that both the small and large reactor have a similar height-to-diameter ratio, percent of jacketed surface area on the reactors, and agitator mixing characteristics.

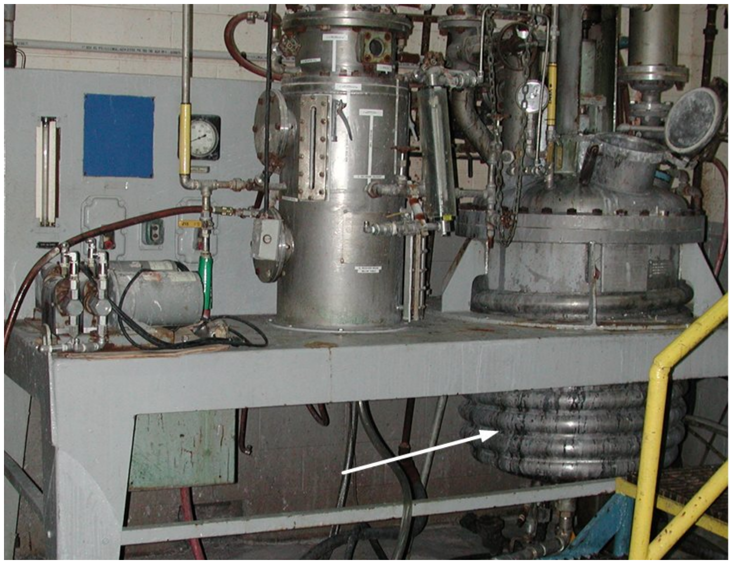

Figure 3. Small batch test reactors. Reactor cooling jacket (arrow) is similar to the 4000-gallon production reactor.

1.7 Pre-Startup Hazard Planning

1.7.1 Lyondell Allyl Alcohol Product Stewardship

Recognizing the toxic and flammable hazards associated with allyl alcohol, Lyondell published the *Allyl Alcohol Product Safety Bulletin* (Lyondell, 2004), a 74-page guide for handling, transporting, and using allyl alcohol. The bulletin discusses physical and chemical hazards; exposure limits, detection, and first aid; engineering safeguards and fire safety; hazard communication; and storage and transportation. It only briefly summarizes the OSHA and EPA regulations specifically applicable to allyl alcohol. It only lists PSM in Product Storage, Section 8 and References, Appendix V. The EPA Risk Management Program regulation is in the Regulatory Summary, Appendix VI but the appendix does not list PSM. A discussion of these regulations is in Section 4.0 of this report.

Lyondell conducted a site review at the MFG facility in January 2004, four months before delivering the allyl alcohol. A representative from the Lyondell, Houston logistics department, the technical services manager at the allyl alcohol manufacturing plant, and the allyl alcohol unit process specialist, met with the MFG personnel for about three hours to review the site safety program and evaluate the capabilities of MFG for handling large quantities of allyl alcohol. They also provided a copy of the product safety bulletin to MFG.

The team leader used a checklist, developed by the Lyondell European business unit, to guide the assessment. However, it lacked U.S.-specific elements such as the OSHA PSM and EPA Risk Management Program regulations. Furthermore, the checklist only addressed Lyondell's concerns about the safe handling of allyl alcohol; it did not address any process design and emergency containment considerations, or production issues involving the use of the allyl alcohol.

Lyondell and MFG did not discuss the PSM standard or the Risk Management Program regulations during the site visit, or at any other time prior to the April 2004 incident. Only one of the assessment team members was even aware of the PSM program requirements. All three stated in interviews that they were not aware that the Risk Management Program regulation applied to allyl alcohol.

The assessment team concluded that Lyondell would permit MFG to receive and handle the allyl alcohol upon completion of two important actions:

- Require MFG employees who would connect the isotainer to the process equipment and transfer the allyl alcohol to wear positive pressure air purifying respirators or full face respirators equipped with organic cartridges to protect them from toxic vapor exposure,

- Notify the Dalton City Fire Department of the intent to use allyl alcohol and confirm that the fire department had foam fire suppression capabilities.

Although MFG implemented the prerequisites, the safety program provisions only addressed small allyl alcohol releases. MFG management informed Lyondell that they would rely on the Dalton City Fire Department to handle any large allyl alcohol release. Lyondell then approved the allyl alcohol delivery to MFG.

1.7.2 MFG Safety Program

MFG routinely used flammable and toxic chemicals in their manufacturing facilities and employed a full-time engineering and compliance manager to oversee the worker safety and environmental compliance programs. They conducted training with the affected employees whenever they planned to handle new chemicals. The training addressed the contents of each material safety data sheet (MSDS) and any special precautions.

As a member of the Synthetic Organic Chemical Manufacturers Association (SOCMA), MFG used the Responsible Care program self-evaluations to review their safety programs. They conducted self-assessments for the Process Safety program, the Environmental Health & Safety (EH&S) program, the Product Stewardship program, and the Community Awareness and Emergency Response (CAER) program. Each self-assessment concluded their programs were adequate.

Management was aware of the PSM standard but reported that they never handled any of the listed toxic chemicals or covered flammable liquids in quantities above the regulatory threshold limits prior to receiving the allyl alcohol. Management also reported that they had never applied the EPA Risk Management Program regulation to any chemicals at the facility.

MFG did not implement a PSM program for the TAC process (Section 4.1.1). They concluded that maintaining the quantity of allyl alcohol used in the TAC batch below the 10,000-pound flammable liquid threshold quantity was sufficient to avoid implementing a PSM program.[11] Furthermore, they concluded that although the isotainer was connected to the process, the allyl alcohol in the isotainer[12] met the flammable exemption provided in §1910.119 (a)(ii)(B).[13]

1.7.2.1 On-site Safety Upgrades

MFG prepared a written procedure for the operations personnel to use when transferring the allyl alcohol into the process equipment. The procedure required each employee assigned to transferring the allyl alcohol from the isotainer to the reactor to wear full-face respirators with organic cartridges and acid-resistant clothing, gloves, and boots. The procedure did not contain any requirement for the employees to measure the allyl alcohol vapor concentration in the air; critical data needed to determine if the personal protective equipment (PPE) they were using would provide adequate protection in the event of a significant spill. Furthermore, management had not purchased air-monitoring devices suitable for detecting allyl alcohol nor did they purchase "Level A" personal protective equipment[14] if the vapor concentration level necessitated its use.

MFG purchased a 125-pound portable foam fire extinguisher and provided training to the employees who would be conducting the TAC production activities. They also contacted the

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[11] OSHA has provided in the Preamble to the final PSM rule and in interpretation letters that reducing the quantity of a covered chemical or flammable liquid to a quantity less than the threshold quantity is an acceptable technique for excluding the process from PSM compliance.

[12] In a 1994 PSM interpretation letter, OSHA advised that a commercial tank motor vehicle is subject to OSHA standards, rather than the DOT regulations once the commercial tank motor vehicle is no longer "considered 'in transit' by DOT." (OSHA, 1994). DOT provided additional clarification to the applicability of the Hazardous Material Regulations (49 CFR Subchapter C) such as cargo tanker unloading in the Final Rule promulgated in October 2003 (DOT, 2003).

[13] The flammable liquid exemption applies to a qualified atmospheric tank containing a qualified flammable liquid regardless if it remains connected to the process (OSHRC Docket No. 95-0341, Secretary of Labor vs. Meer).

[14] Level A protection includes totally encapsulating chemical protective clothing and self-contained breathing apparatus as required by 29 CFR 1910.120.

Dalton City Fire Department and confirmed that the nearest fire station (Station 2) had foam fire suppression equipment useable in the event of a spill or fire involving allyl alcohol.

1.7.2.2 MFG – Dalton Fire Department Planning

The planned use of allyl alcohol for the TAC process would result in a significant increase in the quantity of flammable liquid stored on site at the facility. MFG management told CSB investigators that they assumed that the fire department would provide all emergency response tasks in the event of a significant release. Their procedure and training only covered very small releases. However, the fire department told investigators that their discussions with MFG management clearly explained that the fire department was not qualified or equipped to respond to a toxic chemical release[15] and that the company would have to make provisions for such an event.

MFG management provided a copy of the Lyondell allyl alcohol product safety bulletin to the fire department and verbally informed them of their intent to handle allyl alcohol. They also agreed to notify them after the allyl alcohol isotainer arrived on site, but before connecting it to the reactor. The fire department agreed that they would send a representative to the facility, only to become familiar with the placement of the isotainer and discuss emergency response activities with operators and supervisors before they started the production run. However, MFG did not notify the fire department when the allyl alcohol arrived, so the fire department site visit did not occur.

[15] Although the Dalton City Fire Department at one time maintained a HAZMAT response team, the fire department disbanded it due to city funding limitations.

1.8 Process Controls and Cooling System

1.8.1 Process Instruments

The operator console was located approximately 20 feet south of the reactor on the mezzanine floor inside the building. It was equipped to monitor only two process parameters; the weight of the chemicals measured by the load cells,[16] and the temperature inside the reactor. The reactor pressure was only available at a pressure gauge mounted on the reactor. It was not possible to read the pressure gauge from the console or the building door (See Figure 1). The agitator speed controller was also located at the console.

1.8.2 Reactor Cooling System

Early discussions between GPC and MFG included the possibility that the primary (TAC synthesis) reaction could generate significant heat. However, when MFG prepared the detailed procedure, they did not perform the necessary cooling system analysis for the primary reaction. The process engineer performed only a calculation to estimate the total heat load on the reactor during the hydrogen chloride neutralization step. The engineer then gave the chiller specification to GPC who contacted an equipment rental company to provide the portable chiller system. GPC did not confirm the cooling system design basis used by MFG and assumed that they had properly considered the heat load of the primary reaction.

The chiller system arrived late in the morning of Monday, April 12, 2004 (Figure 4). The vendor technician made the necessary piping connections to the reactor cooling-jacket, started the system, and verified that it was operating properly. He then instructed the MFG personnel how to

[16] Load cells are electronic weight scales placed beneath the reactor support legs. The weight of the chemicals is equal to the total weight minus the weight of the empty reactor and attached equipment.

start and stop the system. Since the TAC procedure did not specify any cooling system adjustments, the chiller system was not set up to provide for easy adjustments.

Figure 4. Portable cooling system used to cool the reactor. Generator (left), and chiller (right).

1.9 Chemical Addition Sequence

1.9.1 Dry Chemical Loading

The operators loaded the dry-powder cyanuric chloride into the reactor on Friday, April 9, 2004 three days before the allyl alcohol and the temporary reactor cooling system arrived. They wore the personal protective equipment recommended on the MSDS. The reactor load cells on the reactor (Figure 5) measured the weight of the chemical specified in the procedure. The operators closed the reactor manway and installed some of the hold-down clamp bolts (Figure 6), after which a nitrogen gas blanket was established. The dry-powder chemical remained in the reactor throughout the weekend.

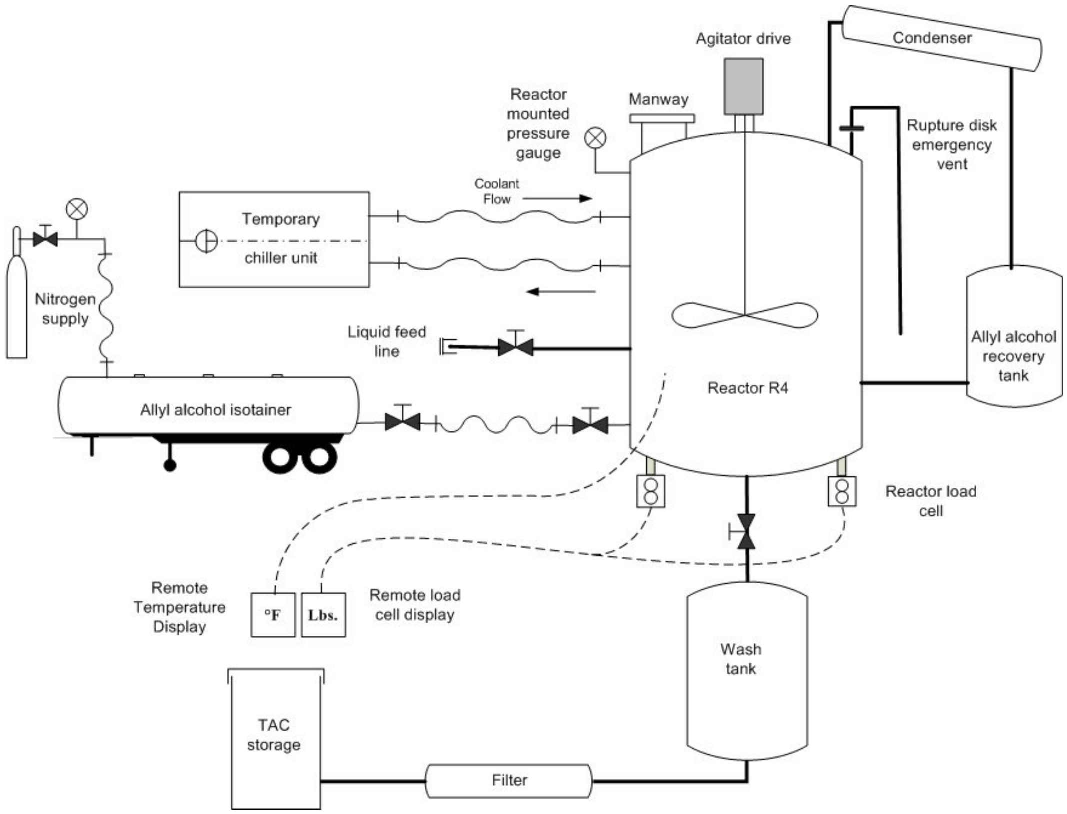

Figure 5. Basic TAC process diagram.

1.9.2 Allyl Alcohol Delivery and Connection to the Process

The allyl alcohol isotainer arrived in the afternoon on Monday, April 12 and was parked adjacent to the reactor (Figure 7). The engineering and compliance manager met with the operators and discussed the precautions and personnel protective equipment required for the allyl alcohol transfer into the reactor. They then connected the transfer hose to the process piping. The operators concluded the chiller was providing sufficient cooling to the reactor because the reactor interior temperature reading was 32° F and the reactor cooling-jacket and chiller piping were frost covered. They were finally ready to proceed with the remaining steps in the procedure.

Figure 6. The18-inch reactor manway.

Figure 7. Isotainer (right) positioned adjacent to the process equipment.

1.9.3 Final Chemical Addition

The operators pumped the entire quantity of liquid catalyst through the liquid feed line into the dry chemical already in the reactor. They then transferred the allyl alcohol into the reactor by pressurizing the isotainer with nitrogen.

After a few minutes of transferring allyl alcohol into the reactor through the transfer piping, they concluded that it was going to require many hours to complete the transfer at the established flow rate. Because the procedure did not restrict the allyl alcohol fill-rate, the operators increased the nitrogen pressure to speed the transfer. At the higher flow rate, they completed the transfer in less than an hour. The operators closed both transfer-hose isolation valves, but left the hose attached to the equipment. The reactor agitator had been started sometime during the transfer operation to mix the chemicals (See Figure 5).

2.0 Incident Description

2.1 Process Upset

A short time after loading the allyl alcohol, the operators noticed that the reactor temperature had increased from 32° F to about 72° F, presumably due to the addition of the warm allyl alcohol. Ten minutes later, the operators noted that the temperature had already climbed to 103° F. The temperature continued to increase rapidly to 118° F, well above the peak temperature of about 100° F that they expected. Unknown to the engineers and operators, it was almost at the temperature at which the exothermic decomposition reaction occurs (Section 3.1.2). Rapidly increasing pressure in the reactor caused the manway gasket to blow out (See Figure 6). Dense, white vapor immediately began to spray out of the manway. The rupture disc (Figure 8) blew open about 30 seconds later, sending additional white vapor out of the end of the 4-inch vent pipe near the base of the reactor. The last observed reactor temperature was 124°F.

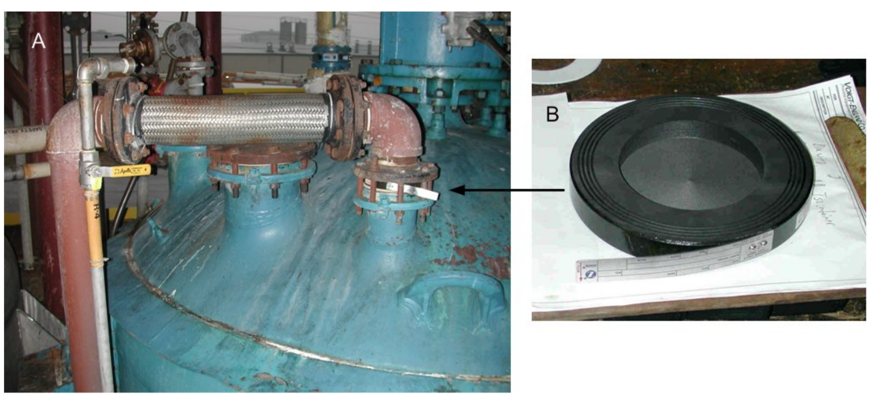

Figure 8. Overpressure rupture disc and vent pipe on top of reactor. An exemplar of the rupture disc (right).

2.2 Facility Evacuation

Operators initially considered approaching the reactor manway to attempt to reseal the gasket, but the leak was too large to stop and the venting vapor was moving toward them. With the two reactants and the catalyst fully charged into the reactor, no ability to increase the cooling rate, no emergency dilution system, and no reactor vent scrubber,[17] they had no choice but to evacuate the area. All seven personnel safely evacuated the facility as the vapor cloud rapidly expanded and began drifting off site to the north and east.

A 9:34 PM call informed the Whitfield County 911 Emergency Management Center that a "chemical release involving allyl alcohol" was occurring at the MFG Callahan Road facility. The emergency operator notified the Dalton City Fire Department dispatcher that there had been a "chemical spill" and the fire department should respond.

2.3 Emergency Response

The event timeline is shown in Figure 9. The following is a discussion of the significant events during the emergency response and community impact from the toxic vapor release.

2.3.1 First Responder Actions

The Whitfield County Emergency Management Center (EMC) dispatcher informed the fire crew that they were to respond to a “hazmat spill inside the building" at the facility. The dispatcher advised them that the material spilled was “alloy" alcohol. Responding firefighters unknowingly

[17] A reactor vent scrubber, neutralizes toxic material released from the reactor vent. The reactor vented directly to the ground under the reactor.

drove through the dense vapor cloud that was drifting over Lakeland Road, east of the facility (Figure 10).[18] The acrid odor immediately irritated their eyes and nostrils.

Concluding that the incident was much more serious than merely a "spill", they directed the other responding unit to take an alternate route to the facility and requested the dispatcher to call a chief officer to the incident scene. They also requested the dispatcher to alert the police department to dispatch police in preparation for a possible evacuation of the residents. Fire crews also requested that the police close Lakeland Road, north and south of the facility. About ten minutes had elapsed from the start of the vapor release.

Placing the community's wellbeing above their own safety, emergency responders entered the already-contaminated neighborhoods to alert the residents to evacuate the area. None of the responding police officers had the training or safety equipment needed to enter the neighborhoods but there was no other available notification method. The first police officer in the area immediately reported that there was a "real thick chemical odor" in the area. The police sergeant in command directed four police units to evacuate nearby apartments while directing other units to evacuate a nearby subdivision. The sergeant instructed one patrol officer to go door-to-door to alert residents because his vehicle PA system was not working. Another patrol officer requested the dispatcher to ask the fire department if there was need for any type of protective equipment, but he never received a reply. All of the responding officers were reporting significant noxious odors.

An ambulance crew, responding to a 911 call from a resident, informed the dispatcher that a strong chemical odor was noticeable as soon as they entered the neighborhood. Overcome by the

[18] The fire crew told CSB investigators that they saw what appeared to be low-lying fog caused by the cool, rainy weather drifting across the street as they approached the facility.

vapor while walking from the ambulance to the residents' home, the EMT and paramedic retreated from the neighborhood.

The crew soon pulled off the road and radioed the dispatcher to request assistance. The toxic vapor affected both the EMT and the paramedic, but only the EMT experienced a severe reaction that required long-term treatment. A second ambulance crew arrived and transported the stricken EMT and four residents who had stopped and requested medical aid to the hospital.

2.3.2 Initial On-Site Response Activities

MFG personnel informed the fire department Incident Commander (IC) that the reactor had overheated and they expressed concern that it needed cooling. They advised the IC to spray water on the releasing vapor cloud and reactor and recommended the evacuation of the community downwind.

The first responding fire department lieutenant addressed the immediate concerns of the emergency responders and community. He notified the dispatcher that "a precautionary evacuation of nearby residents might be needed" and reported the hazard placard identification number on the side of the isotainer to the dispatcher, confirming that allyl alcohol was the likely chemical involved.[19] He then established an incident command post outside the fence, at the southwest corner of the facility. The dispatcher then informed the IC that the DOT *Emergency Response Guidebook* (Guide 131)[20] advises an evacuation distance of 4/10^{ths} of a mile for a large, nighttime allyl alcohol spill. The IC directed the police to alert and evacuate the residents and businesses within a half mile downwind, north and east of the facility.

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[19] The allyl alcohol hazard placard identification number is 1098.

[20] The Emergency Response Guidebook provides first responders with specific or generic hazards of the materials involved, and methods to protect themselves and the general public during the initial response to a release.

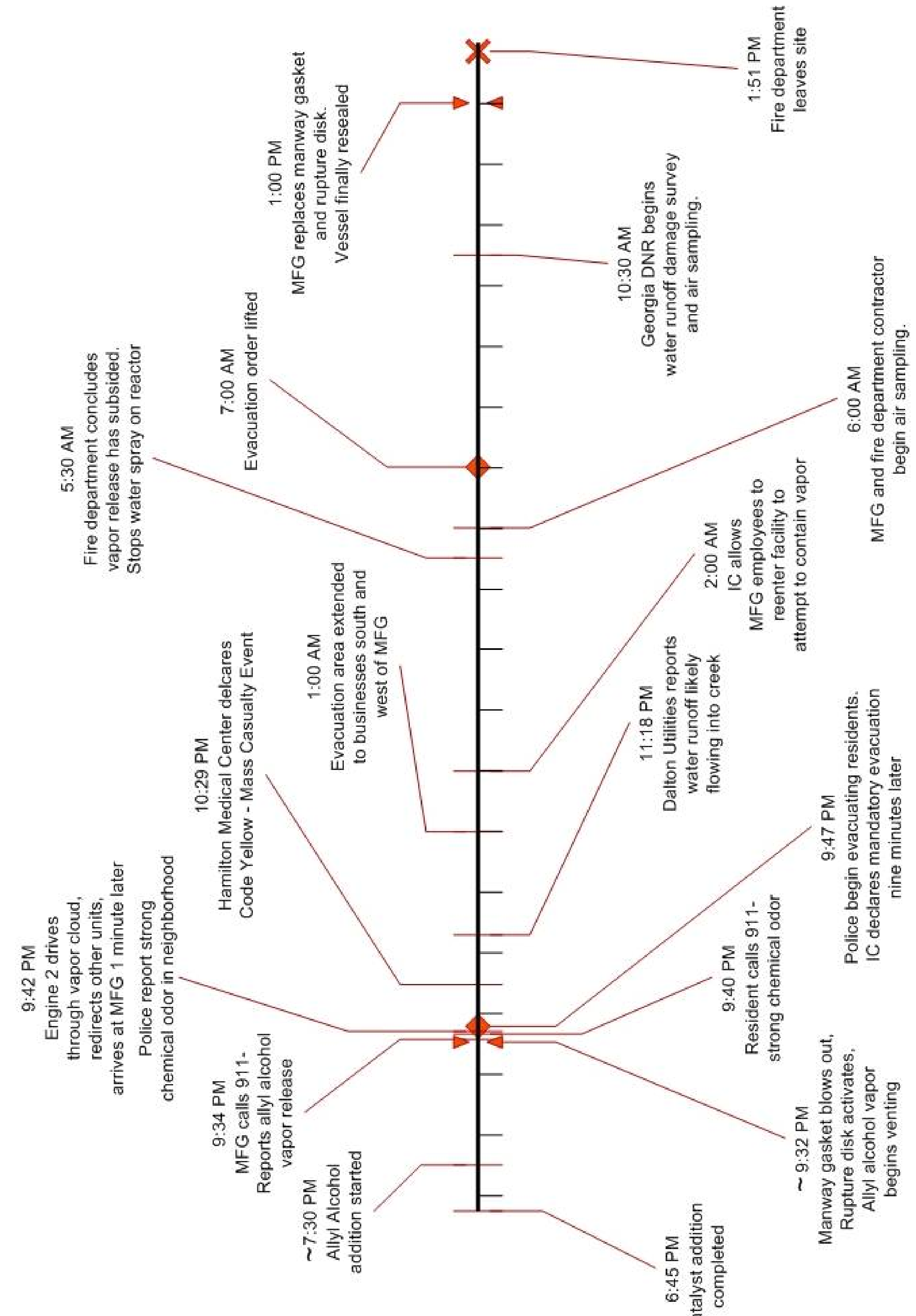

Figure 9. Event Timeline (Scale: 60 minutes / division).

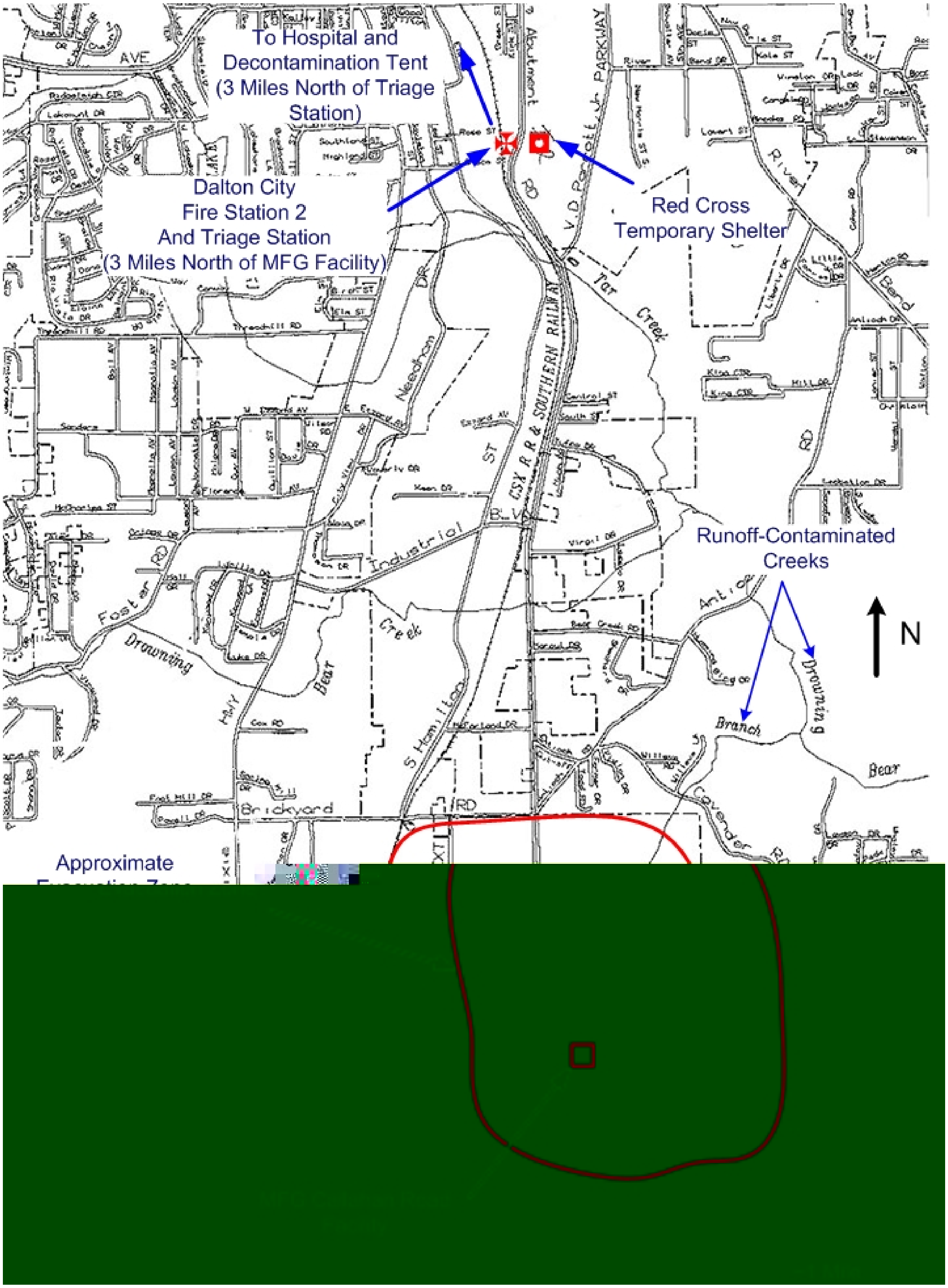

Figure 10. Map showing MFG and nearby neighborhoods. Wind out of the south.

One of the MFG chemists called the Lyondell Emergency Response Manager in Houston, TX shortly after the fire department arrived on scene. The IC consulted with the Lyondell manager throughout the incident response. Lyondell recommended that the fire department spray foam on the liquid pool beneath the reactor to help suppress the vapor cloud. Lyondell also suggested that MFG attempt to place a container of water under the rupture-disc vent pipe since it vented directly to the atmosphere rather than safely venting into a hazardous material containment device, such as a scrubber. They hoped that by discharging the vapor directly into the water, any allyl alcohol in the vapor would dissolve in the water (Section 2.3.6).

2.3.3 Community Evacuation

Thirteen minutes after the MFG call to 911 (9:47 PM Monday night) the police department began evacuating residents. Having no emergency sirens or other community-wide emergency alert system, the police officers proceeded into the vapor-contaminated neighborhoods and used their PA system or went door-to-door as necessary, to instruct the residents to evacuate their homes. All responding police officers reported to the dispatcher that they experienced severe eye, nose, and throat discomfort as they approached the communities near the MFG facility.

The police sergeant requested the fire department to provide personnel with self-contained-breathing-apparatus (SCBA) to take over the evacuation. The unprotected police officers reported extreme difficulty breathing. Twenty minutes into the evacuation, and after notification of the continuing police officers distress, the fire department lieutenant directed the police officers to leave the area and the SCBA-equipped fire crews took over. Five police officers required transport to the hospital for decontamination and treatment for exposure to allyl alcohol vapor.

At 11:15 PM, the IC directed the fire crews to make one more pass through the neighborhoods using their PA system to announce the evacuation. Three hours later, the IC extended the evacuation to the businesses and residents south and west of the MFG facility because of changing wind direction. The IC finally cancelled the evacuation order just before 7:00 AM.

2.3.4 Triage of Injured Individuals

The fire department established a triage station at Fire Station 2, three miles north of the MFG facility. There, paramedics and emergency medical technicians (EMT) from the Hamilton Medical Center evaluated the injured. Police and fire crews directed individuals having significant difficulty breathing or complaining of burning sensations in their eyes, nose, and throat to the triage station.

Over the next two hours, an EMS ambulance crew made seven trips to the hospital, three miles north of the triage station. They transported 35 patients, including two EMS employees and the five injured police officers.

2.3.5 Toxic Chemical Decontamination and Treatment

The EMC dispatcher alerted the Hamilton Medical Center emergency room to prepare for people exposed to allyl alcohol. Emergency room personnel investigated the potential health impacts as well as the appropriate decontamination and treatment, and prepared a fact sheet for use by their personnel. The on-call emergency room physician consulted with the Georgia Poison Control Center, and reviewed the allyl alcohol MSDS. The Hamilton Medical Center declared a "Code Yellow" event at 10:29 PM, activating the Mass Casualty Plan.[21]

Emergency room personnel set up a decontamination station outside the hospital. Decontamination consisted of disrobing then rinsing the entire body with a cool water spray.

[21] The hospital declares a Code Yellow event if more than ten casualties are expected to be received and treated and calls off-duty doctors, nurses, and other personnel, to assist with treating the casualties.

Although hospital personnel did not collect and handle the potentially contaminated water, there was no reported environmental damage at the hospital. Hospital personnel placed personal belongings in sealed plastic bags and returned them to the owners with instructions for cleaning to remove residual allyl alcohol.

Only one patient, an MFG employee, required treatment for minor chemical burns from the toxic vapor. Five of the 154 individuals treated at the hospital required overnight treatment that included oxygen and albuterol.[22] The hospital treated thirteen police officers and four ambulance personnel for toxic chemical exposure.

2.3.6 Mitigation and Containment of the Toxic Vapor Cloud

The fire department operated in an "awareness level" response mode, performing defensive measures while remaining safely upwind of the toxic vapor because they did not have appropriate toxic chemical monitoring devices, protective clothing, or a trained and equipped hazmat response team. They used a four-gas detector device to monitor the air for the following chemicals: hydrogen sulfide, carbon monoxide, flammable vapor, and oxygen. Firefighters set up unmanned water cannons and directed the water flow on the top of, and around the reactor to in an attempt to absorb the releasing vapor[23] and to cool the reactor. The fire department decided not to use any vapor containment foam because the significant water volume spraying on the reactor would disrupt a foam cover and render it ineffective. Cooling the reactor was their first priority.

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[22] Albuterol is an inhaled preparation used in the relief and prevention of airway constriction caused by asthma and other conditions with reversible airway obstruction.

[23] Allyl alcohol is highly soluble in water so a water fog spray is an effective method to contain the vapor.

With the concurrence of the deputy fire chief, the IC permitted three MFG personnel to reenter the building to check the reactor temperature, quickly observe the reactor equipment, check on the status of the reactor cooling system, and retrieve their respirators from the building. The IC made it clear to the MFG personnel that they would enter at their own risk. Furthermore, the fire department would not attempt a rescue in the event that an employee was overcome by the vapor, or sustained serious injury during the entry since the fire department personnel did not have the protective equipment required for allyl alcohol exposure. Nevertheless, the inadequately protected MFG employees entered the facility without monitoring the allyl alcohol vapor concentration in the air. After the first entry into the building, one MFG employee returned to the building to retrieve the MSDS for the fire department.

Two Dalton Utilities employees arrived at 11:18 PM and informed the IC that firewater runoff was entering the storm-water drainage canal that flowed into the nearby Stacey Branch creek (See Figure 10). The IC decided that it was more important to minimize the airborne concentration of the chemical so they continued applying water to the reactor to knock down the vapor, acknowledging that contaminated water would enter the creek. The Georgia Department of Natural Resources subsequently conducted a survey of the creeks after the incident and determined that a significant aquatic kill occurred as far as seven miles downstream from the facility.

Shortly after 2:00 AM, the IC again permitted MFG personnel wearing only Tyvek/Tychem® suits, boots, gloves and full-face cartridge respirators,[24] to return to the process equipment to place a 5-gallon bucket filled with water under the rupture disc vent-pipe. The Lyondell Emergency Response Manager recommended this makeshift vapor scrubber to reduce the

[24] The Emergency Response Guidebook specifies fully encapsulating, vapor protective clothing when entering an allyl alcohol spill area. (U.S. DOT, 2004)

quantity of toxic vapor being released. However, the bucket had no effect on the continuing vapor release through the manway. The fire department did not monitor the air for toxic vapor concentration in the area during this activity.

At 5:30 AM, more than seven hours after the release had started, the fire department concluded based on visual observations and the four-gas detector device readings that the vapor release had subsided sufficiently to permit them to stop the water spray. MFG personnel reentered the building and began monitoring the reactor temperature. They forwarded the temperature data to the IC every 15 minutes.

Tuesday afternoon at 1:00 PM, more than 15 hours after the incident began, the reactor had cooled to 70°F and the reaction appeared to have ended. MFG personnel installed a new rupture disk, replaced the manway gasket, and tightened the clamps. The IC terminated the fire department response activities now that the reactor was resealed.

3.0 Incident Analysis

3.1 Process Chemistry Analyses

The CSB could not investigate the actual chemical reactions occurring during the incident because MFG did not document the actual conditions inside the reactor at the time of the incident. The CSB conducted a series of analytical chemical and thermal reactivity tests on the chemicals involved in the TAC process to determine if chemical contaminants might have contributed to or caused the runaway reaction, quantify the reactive chemistry characteristics of the process, and identify and quantify the chemicals that were likely released into the environment. The test results are summarized below. A detailed discussion of the methods and results are in Appendix A.

3.1.1 Raw Materials Purity Testing

The CSB analyzed samples of cyanuric chloride and allyl alcohol from the manufacturing lot numbers used by MFG in the production batch using combined gas chromatography and mass spectroscopy (GC/MS). The results were compared to high purity samples of the same materials. The chromatograms from the production batch were indistinguishable from chromatograms of the pure materials. These tests confirmed that the raw materials used in the batch recipe did not contain any contaminants that might have caused the runaway reaction.

3.1.2 Thermal Stability Studies

Thermo-chemical testing evaluated the desired and undesired chemical reactions that might have occurred in the reactor during the incident. Bench-top, adiabatic, and reaction calorimetry experiments provided data that assisted in understanding the allyl alcohol/cyanuric chloride runaway reaction. The test results indicated that if all of the powdered cyanuric chloride in the reactor had thoroughly mixed with the allyl alcohol and catalyst as planned, the reactor would most likely have violently ruptured.

3.1.2.1 Qualitative Analyses

Bench-top experiments qualitatively assessed the nature and extent of the reaction resulting from mixing the two reactants under different conditions. Experiments examined the effects of reactant order-of-addition, the catalyst, and mixture agitation on the reaction. The experiments did not use active cooling. A calorimeter recorded the reaction mass temperature as a function of time. The results of these experiments demonstrated that the reaction between the allyl alcohol and cyanuric chloride is spontaneously exothermic at room temperature regardless of the order of addition of reactants, the presence or absence of the catalyst, or whether agitated or not. In the absence of adequate cooling and/or control of the rate of chemical addition, the reactants will readily generate a runaway reaction.

3.1.2.2 Reactive Chemistry Analyses

Adiabatic calorimetry provided data to characterize the temperature and pressure behavior of the runaway reaction as a function of time under near-adiabatic conditions[25] exhibited in a production reactor. The test data permitted calculation of the size of the emergency relief device required to protect the reactor vessel from overpressure in the event of a runaway reaction.

The adiabatic calorimetry testing of the TAC recipe demonstrated the extremely energetic nature of the reaction. The tests showed that the reaction progressed very slowly for about 90 minutes, after which the temperature rapidly increased at a rate exceeding 500 °F/minute (260 °C/minute) with a pressure rise rate approaching 2260 psi/min (155 bar/minute) (Figure 11). Testing

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[25] Adiabatic refers to any change in which there is no gain or loss of heat.

confirmed that the decomposition reaction is highly energetic and capable of causing severe damage to equipment. Appendix A, Table 1 summarizes the test results.

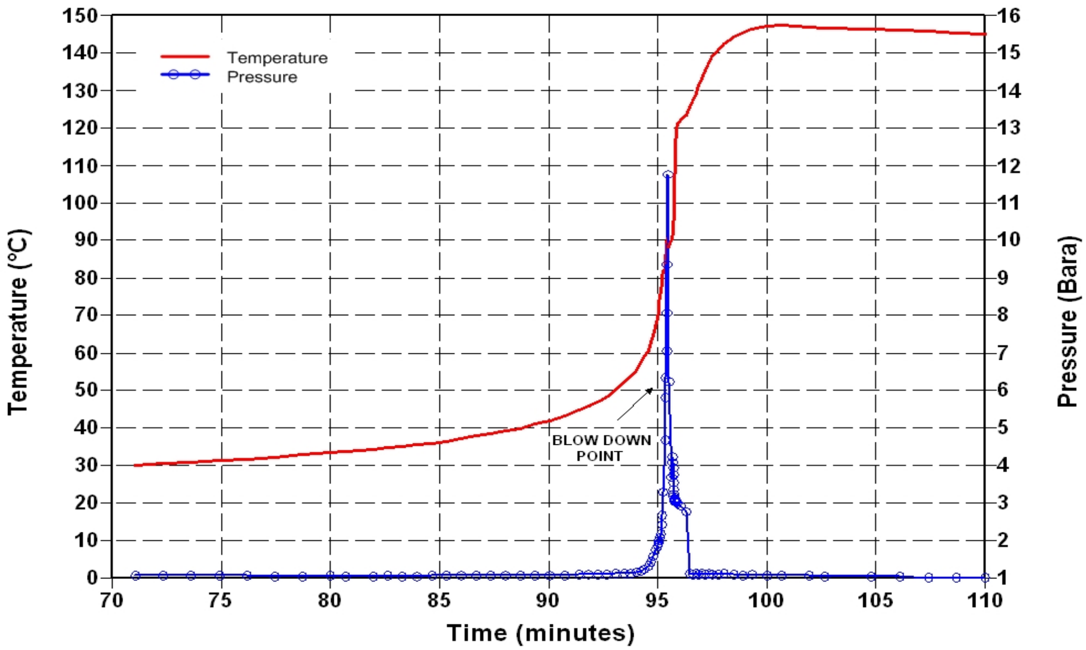

Figure 11. Test cell reaction mass temperature and pressure as a function of time. The blowdown vent opened at six bara (75 psig).

The incident at the MFG facility involved two reactions: (1) the intended synthesis reaction to form the TAC product; and (2) an unintended decomposition reaction.[26] The reactor was first loaded with all of the dry powdered cyanuric chloride, followed by the liquid catalyst, and finally the allyl alcohol, filling the reactor to approximately 60 percent of capacity. It is likely that a highly non-homogeneous mixture resulted, even after starting the agitator, with much of the solid

[26] Decomposition is a chemical reaction that leads to chemicals containing smaller molecules or elements, often with the liberation of heat energy and product gasses.

and the catalyst remaining on the bottom, tied up in a "sludge" layer. Even with only a portion of reagents available for the reaction, the heat produced quickly exceeded the heat removal capacity of the reactor cooling system. The increase in temperature then caused the un-reacted allyl alcohol to boil,[27] pressurizing the reactor. The temperature continued to increase above the decomposition temperature. This caused a rapid increase in gas production, further increasing reactor pressure until the incorrectly installed manway gasket blew out. The vent rate through the manway was not sufficient to keep the reactor pressure below the rupture disc setpoint, and the pressure in the reactor increased until the disc ruptured a few seconds later. The maximum reactor pressure reached was thus at least 75 psig (five barg), the set point of the rupture disk. The peak reactor pressure during the runaway reaction could not be determined.[28, 29]

3.1.2.3 Reactor Emergency Vent Analysis

Applying the data obtained from the calorimetry testing showed that the 4-inch diameter rupture disc installed on the reactor was undersized. The CSB determined the minimum vent size for the reactor using the American Institute of Chemical Engineers (AIChE) Design Institute of Emergency Relief Systems (DIERS) methodology. DIERS is widely accepted in industry as the best technology available to determine the pressure relief system requirements for highly reactive chemical processes. These usually involve a two-phase flow (i.e., vapor with entrained liquid) through the emergency relief device and discharge piping. To vent the reactor properly required an opening with 16-inch-diameter rupture disc (See Appendix A). The CSB concluded that the reactor vessel did not rupture because the non-homogeneous mixture, discussed above, prevented

[27] Allyl alcohol has a normal boiling point of 97 °C (206 °F).

[28] The only pressure instrument on the reactor was a pressure gauge on the reactor head. There was no recording device used.

[29] The ASME Boiler and Pressure Vessel Code, Section VIII, Division 1 allows a maximum overpressure equal to 110% of the maximum allowable working pressure during emergency venting due to a process upset.

the reaction from progressing at the rate predicted by the calorimetry testing. In addition, the manway gasket leak provided some additional relieving capacity.

3.1.2.4 Reactor Cooling Analysis

Reaction calorimetry tests evaluated the reaction heat generated at a predetermined, controlled temperature. It measured the instantaneous heat output (power), and the total energy output of the reacting chemicals in a laboratory test apparatus. From the results, one can estimate the cooling requirements for a full size production reactor. A discussion of the reaction calorimetry testing performed is in Appendix A.

The rate of temperature rise inside the reactor depends on the balance between the rate of heat generation due to the reaction, the heat capacity of the chemicals, and the heat removal through the cooling jacket. The quantity of heat removed is directly proportional to the difference between the temperature of the reactants and the reactor cooling jacket temperature. However, the reaction rate increases exponentially with reaction temperature, as shown in Figure 12. If the reaction temperature increases beyond a critical point (Figure 12, Point A), the heat generation rate will exceed the heat removal rate provided by the reactor cooling jacket—the reaction will run away.

MFG personnel underestimated the heat removal rate required for TAC production because they did not consider either the TAC synthesis reaction or the decomposition reaction when they evaluated reactor cooling requirements. MFG only evaluated the cooling system requirements based on the acid neutralization step that was to occur later in the batch process. Since the procedure did not restrict the chemical addition rates, operators charged the reactor with the entire quantity of each reactant and the catalyst. The cooling system was unable to control the reactor temperature and, as the temperature rose, the decomposition reaction began to dominate, resulting in a runaway reaction. The increasing pressure blew out the manway gasket, and then the rupture disk. The vapor continued venting for many hours, until the reaction consumed all the reactants.

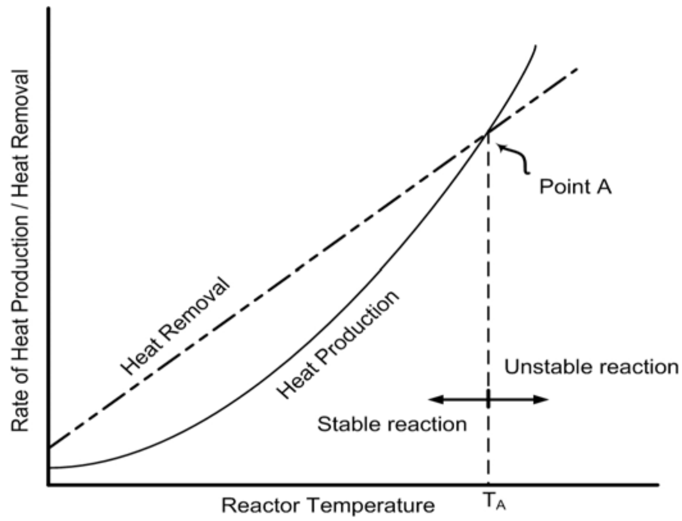

Figure 12. Typical reaction heat production and cooling system heat removal vs. reactor temperature.

3.1.3 Reaction Decomposition Products Analyses

The CSB team used reaction decomposition product analyses to identify the toxic chemicals that were likely released into the atmosphere during the runaway reaction. MFG and Lyondell expressed concern about the possible release of hydrogen chloride into the environment because it was a known byproduct of the normal TAC reaction chemistry. Gas and vapor sample GC/MS analyses collected during the adiabatic calorimeter testing showed that the major compounds vented during these tests were allyl alcohol, allyl chloride, carbon monoxide, and a C_{12} unsaturated compound[30] derived from allyl alcohol and/or allyl chloride. The chromatograms and the GC/MS data of the runaway reaction products showed no evidence of hydrogen chloride.

[30] A C_{12} unsaturated compound consists of twelve carbon atoms connected by at least one double covalent bond. A C_{12} compound can be a straight chain, branched, or cyclic.

Furthermore, the test did not detect cyanuric chloride, or its degradation products, such as cyanogen chloride.

3.2 Vapor Cloud Plume Model

A vapor cloud plume model was developed as part of the CSB investigation to predict the endpoint distance[31] for the spread of allyl alcohol vapor using the criteria contained in the EPA Risk Management Program (Section 4.2.2). The model incorporated the actual weather conditions recorded at a nearby meteorological tower. The model assumed that the reactor released 6,300 pounds of allyl alcohol, as determined from the reactive chemistry analytical results. The calculated endpoint distance of the cloud extended more than three miles downwind from the facility.

The results of the model are comparable to the actual exposure in the community based on the symptoms described by the exposed individuals. The CSB could not compare the actual conditions to the model because allyl alcohol air concentration measurements were never performed in the community and the measurements made at the facility used the wrong test apparatus (Section 3.7.2.3). A detailed discussion of the model is in Appendix B.

3.3 Process Design and Scale-up

The CSB investigation determined that MFG management did not conduct a comprehensive evaluation of the reactive chemistry hazards involved in the TAC production. The process development work failed to examine exothermic reactions, so MFG did not learn of the runaway potential of their process system. They conducted basic laboratory and pilot plant scale testing to

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[31] The toxic endpoint is a specific lower concentration of the toxic chemical in air. The EPA toxic endpoint for allyl alcohol is 0.036 milligrams per liter (40 CFR 68.22).

improve the quality, yield, and reduce costs. Their literature search consisted only of a review of patents for the manufacture of TAC, none of which contained any information about the potential reactive hazards associated with the process. Had they conducted a thorough literature search,[32] they would most likely have identified the thermal and runaway reaction hazards in the TAC process as well as important information addressing reactive chemistry scale-up from laboratory to production. For example, *Designing and Operating Safe Chemical Reaction Processes* (HSE, 2000) discusses the importance of proper scale-up design of process equipment:

> One particular factor…between the heat generated and the heat lost is the effect of scale-up from laboratory…to full commercial size…is not always appreciated…As reactor scale increases cooling may become inadequate. Incidents have occurred when processes are carried out on a plant scale that were uneventful in the laboratory.

MFG did not have a hazardous chemical collection system on the emergency vent, such as a toxic vapor scrubber or liquid collection tank on the reactor. Lacking these devices, operators were unable to mitigate or stop the toxic vapor release.

3.4 Chemical Addition Rate Control

MFG personnel did not control the reaction rate using closely controlled, slow addition of the chemicals during the batch process. MFG and GPC management personnel had only briefly discussed this important reaction-rate control technique, and that was more than one year before finalizing the TAC procedure. The final recipe contained no fill rate limitations or warnings. *Inherently Safer Chemical Processes*, (CCPS, 1996) notes:

[32] The CSB report *Improving Reactive Hazard Management* (CSB, 2002) discusses the importance of comprehensive literature research as part of the reactive chemistry planning.

> Semi-batch or gradual addition batch processes limit the supply of one or more reactants, and increase safety when compared to batch processes in which all reactants are included in the initial batch. For an exothermic reaction, the total energy of reaction available in the reactor at any time is minimized.

During the process development phase of the project, MFG and GPC management discussed the hazards associated with the rapid chemical addition into the reactor and acknowledged that it could result in significant heat generation (See Section 1.6). However, the final batch procedure did not include any limits on the chemical addition rate. During the first production batch on the day of the incident, the operators added the total quantity of each chemical all at once, a highly dangerous "all-in" approach that maximized the potential for rapid energy release in the reactor.

3.5 MFG Emergency Management

The CSB determined that MFG was required to comply with the reporting, emergency planning, response, and notification requirements of the EPA Emergency Planning and Community Right to Know Act (EPCRA) and Risk Management Program regulations, and the OSHA Hazardous Waste Operations and Emergency Response (HAZWOPER) standard. Below is a discussion of specific deficiencies identified by the CSB investigation.

3.5.1 Reporting and Notifications

In late March 2004, the facility manager informed the Dalton Fire Department that they planned to introduce allyl alcohol into the facility for a new chemical trial, as required by EPCRA (Section 4.2.1). MFG provided the fire department with a copy of the MSDS and the Lyondell *Allyl Alcohol Product Safety Bulletin.* During that telephone conversation, the deputy fire chief informed the plant manager that the fire department was not equipped to respond to a large allyl alcohol release because they did not have a fully trained and equipped hazardous materials response team. He informed the manager that MFG would remain responsible for emergency response and mitigation in the event of an allyl alcohol release and arranging to have a qualified contractor available for both emergency response and spill mitigation. MFG did not implement either emergency action plan item.

3.5.2 Risk Management Program

MFG management reported that they were aware of the EPA Risk Management Program regulation (40 CFR 68) but none of their staff, including the safety and health manager had any detailed knowledge or direct experience with it. They simply "overlooked" it and did not check the list of covered chemicals, which included allyl alcohol (Section 4.2.2). Had they applied this regulation as required, including conducting a comprehensive review of the process and process hazard analysis, they would most likely have identified the deficiencies in the TAC procedure, process equipment, and emergency shutdown and mitigation equipment. Furthermore, MFG would have provided comprehensive information to the local emergency response agencies, including the worst case and alternative accident scenarios required by the regulation. That information most likely would have better prepared them for the emergency response.

3.5.3 Emergency Response Plan

The existing MFG emergency response plan as required by OSHA (Section 4.0) contained a general description of the site and liquid containment features beneath the process equipment; a discussion of emergency equipment; a list of emergency response actions, including notifications and emergency evacuation; and spill prevention and control procedures. However, the CSB identified the following deficiencies in the plan:

- It was not updated to address the TAC production activities,
- There were no provisions for pre-emergency planning and coordination with outside parties,
- It did not contain information concerning personnel roles, lines of authority, training and communication,
- Emergency recognition and prevention information was incomplete,
- There were no personnel decontamination procedures,
- There was no discussion of personal protective equipment and emergency response equipment.

The CSB concluded that these deficiencies most likely resulted in the exposure of the employees to the toxic vapor and the chemical burns sustained by one employee during emergency response activities.

3.6 Product Tolling

The TAC manufacturing plan was the first tolling arrangement between the two companies and the first time MFG handled allyl alcohol. The American Institute of Chemical Engineers Center for Chemical Process Safety, *Guidelines for Process Safety in Outsourced Manufacturing Operations* (CCPS, 2000) is an industry recognized "best practice" that provides comprehensive guidance for safe tolling operations.[33] Had GPC and MFG applied these guidelines, they might have prevented or significantly reduced the allyl alcohol release. Although, neither MFG nor

[33] As a member of SOCMA, MFG had access through the SOCMA website to the American Chemistry Council's Responsible Care Toolkit. Element 4.5 of the Technical Specification Guidance Document discusses toll manufacturing best practices.

GPC were members, this and other relevant CCPS publications are readily available to industry. Furthermore SOCMA (MFG is a member) frequently refers their members to the CCPS guidelines.

3.6.1 Client Responsibilities

CCPS recommends that the client (GPC) become familiar with the toller's (MFG) planned operation and audit the health, safety, and environmental practices as part of the client's product stewardship responsibilities. GPC did not ensure that MFG specifically addressed the hazards of production-scale manufacturing of TAC, even though they pointed them out in early discussions.

The CCPS best practice guidelines recommend that the client ensure that the training program at the toller's facility meets process safety, and environmental risk management training recommendations and requirements. GPC did not review the MFG employee-training program, nor did it request any proof of adequate training addressing the hazardous chemicals involved in the TAC production.

The guidelines further recommend that the client audit the toller during ongoing operations in order to assure that "operations are going as planned and obligations are being met." GPC did not visit the MFG facility, or actively participate in the verification runs or the attempt to make the first full-scale production batch.

Finally, the guidelines list actions to take if the raw materials are not regulated by the Risk Management Program or PSM. The guidelines recommend evaluating good process safety practices even "when a candidate toller is not currently regulated by a governmental process safety requirement and the proposed toll project will not trigger regulation." Despite MFG management's assumption that the TAC process was exempt from PSM compliance and that they overlooked the EPA Risk Management Program regulation, GPC should have ensured that MFG had applied good process safety practices.

3.6.2 Toller Responsibilities

The CCPS best practice guidelines recommend that the toller share any techniques, information, or experience learned as part of the contractual agreement with the client. Additionally, the guidelines recommend that the toller discuss and agree on any changes made to the equipment, chemicals, technology, or procedure of the tolling arrangement with the client.

> An agreement should be made between client and toller on how change is to be managed for a toll….Any change requires the toller and client address the hazards and risks associated with the production process.

MFG did not share all process information with GPC, at least in part for proprietary reasons. They only provided a copy of the "final" production-scale procedure to GPC, who assumed that MFG knew of the risk of a runaway reaction, and that they would adhere to the procedure, as well as slowly add the raw materials into the reactor. However, the procedure used on the day of the incident did not match the procedure provided to GPC.[34] Furthermore, operators added the full production quantity of each raw material to the reactor without considering how that action might increase the probability of a runaway reaction.

Although MFG made specific changes to the original recipe provided by GPC, and GPC was aware of those changes, neither company completed and documented the risk assessments. The CCPS guidelines recommend that the toller discuss and agree on any changes made to the

[34] Only after the accident did GPC become aware that MFG changed the sequence of addition of the raw chemicals and that the entire quantity of each was loaded without consideration for controlling the reaction.

equipment, chemicals, technology, or procedure of the tolling arrangement with the client. “An agreement should be made between client and toller on how change is to be managed for a toll.” “If covered under U.S. PSM or RMP regulations, any deviation from the original design specifications is considered a change." Any change requires the toller and client to address the hazards and risks associated with the production process.

The guidelines also contain specific recommendations for the tolling parties to conduct process hazard analyses (PHA) of the tolling project: “For every new tolling situation a process hazard analysis should be conducted." The tolling parties should consider all aspects of the toll while performing the PHA to identify potential problems caused by the scale-up:

> Simple mixing of raw materials and intermediates may present special problems when processing significantly larger quantities in comparison to the pilot process or laboratory bench amounts.

Furthermore, the guidelines recommend augmented observation during scale-up of the critical process characteristics that were designed in pilot testing to take into account the order-of-magnitude changes in vessel size and quantity of materials that may have been engineered into the new process:

> When scaling up exothermic or high temperature processes, heat removal capability must be considered. The pilot or bench process design may be compromised by a lower surface-to-volume ratio. This may be a key factor during equipment selection for the scale-up.

MFG did not adequately evaluate the hazards associated with the scale-up of the process, such as evaluation of the heat removal capability of the production reactor compared to the bench-scale testing.

The following deficiencies were less likely to have occurred had GPC and MFG adequately applied the CCPS best practice tolling guidance:

- MFG did not consider a major toxic release scenario and did not conduct any formal hazard assessment. Interviews with plant supervisors revealed that their (and Lyondell's) main areas of concern were the allyl alcohol transfer process and the potential fire hazard associated with a small spill.

- MFG did not anticipate a runaway reaction and make provisions to mitigate a large spill or vapor release. The emergency vent on the reactor released the contents directly to the atmosphere; it did not safely capture the toxic vapor.

- MFG did not verify the adequacy of the reactor overpressure relief system. The CSB analyses concluded that the required size for the TAC process was as much as 27 times larger than the installed relief device.

- MFG did not prepare an adequate emergency response plan. MFG did not train or properly equip employees with appropriate personal protective gear, yet they entered the toxic vapor exposure area on multiple occasions.

3.7 City and County Emergency Management

The Emergency Planning and Community Right to Know Act (SARA Title III) requires the establishment of both state and local emergency planning committees (Section 4.2.1). Local emergency planning committees (LEPCs) are responsible for developing comprehensive emergency response plans that address hazardous facility identification, emergency notification and response procedures, and evacuation plans. The state reviews the completed plan, which should be publicized throughout the community. The LEPC is required to review, test, and update the plan each year.

Whitfield County did not have an established LEPC.[35] However, it did have a county Emergency Management Agency (Section 4.3.3) as required by the Emergency Management Act of 1981. The Whitfield County Emergency Management Agency (EMA) established an Emergency Operations Plan (EOP) for managing all emergency response activities.

3.7.1 Whitfield County Emergency Operations Plan

The CSB found that the county EOP did not address all of the EPCRA requirements for emergency planning and response. Significant shortcomings identified were:

- Whitfield County developed the emergency plan with minimal involvement of the companies who handle hazardous chemicals within the county, and had not updated the plan to address changes in company hazardous material usage,
- The agency assigned to perform the emergency activity did not develop all of the standard operating procedures (SOP) cited in the EOP, such as community evacuation.

The EOP contains 17 emergency support functions (ESF) for emergency management planning and response. The EOP relies on close coordination among the county Emergency Management Center, the county fire department, county sheriff's office, Dalton city fire and police departments, the hospital and ambulance service, the American Red Cross, and mutual aid, as available, from other county or state agencies.

Each ESF assigns primary and secondary support responsibilities, requires the development and maintenance of standard operating practices, and lists key concepts that the ESF must address.

[35] In the mid 1990's Whitfield County emergency response agencies and a few chemical companies, including MFG, discussed creating an LEPC. However, interest waned due to lack of funding.

The MFG incident primarily involved eight ESFs, of which four had significant shortcomings that hindered the evacuation effort.

- ESF 2: Procedures needed to alert the public in the event of an emergency were not developed. There was no automated system, such as emergency sirens or "reverse-911" callout equipment to inform the public in the event of an emergency. Police had to go door-to-door to alert residents to evacuate.

- ESF 10: Facility profiles were too general:

  - Offsite toxic exposure distance was not established (other than a half-mile radius circle at all but two facilities) and prevailing wind direction was not shown.

  - Community vulnerability studies were not conducted.

  - Only transportation related emergencies were addressed even though hazardous substance(s) releases were listed for 38 fixed facilities.

- ESF 17: Communication resources were only in English. Many of the evacuees impacted by the MFG incident only spoke Spanish.

City, county, state, and federal agencies rely on facility-specific hazard data in the event of a release. Incomplete, conflicting, or out-of-date information addressing toxic hazards in a community can significantly degrade the ability to respond safely to an incident. The CSB identified the following shortcoming:

- The company-specific hazardous chemical information contained in the Whitfield County Emergency Response Plan on file in the county EMA office and on file at the Georgia Department of Natural Resources, Environmental Protection Division (EPD) was not up-to-date. The MFG updated information addressing the chemicals used in the TAC process was never provided to the EPD.

3.7.2 City and County Emergency Response

Lack of LEPC participation in developing a comprehensive county Emergency Response Plan may have contributed to the significant number of individuals that required decontamination and treatment for exposure to toxic chemicals released from the MFG facility. The Dalton fire and police departments, the ambulance staff, and the hospital staff were not aware of the potential of a major toxic chemical release and were not fully prepared to respond. The fire and police departments lacked the special equipment and training necessary to respond safely to a highly toxic liquid or vapor release. The triage and decontamination procedures performed by the ambulance crews and the hospital staff did not effectively control the potential spread of toxic chemicals. Contaminated individuals had to travel five miles beyond the evacuation zone to be decontaminated; personnel did not collect and handle the water used to rinse off the contaminated individuals as hazardous waste.

3.7.2.1 Toxic Chemical Exposure Hazard

The CSB determined that the fire department incident command should have directed all emergency response personnel to remain a safe distance away from the advancing toxic vapor cloud. This would have significantly reduced the toxic chemical exposure received by the emergency responders. The IC advised police officers to enter the neighborhoods to begin notifying the residents of a precautionary evacuation. However, even though informed by the dispatcher that strong noxious vapor was severely hindering police evacuation activities in the neighborhoods, the IC did not advise them to leave the exposure area for many minutes. More than 15 police and ambulance personnel responding to the scene were directly exposed to the allyl alcohol vapor when they drove into the vapor cloud while attempting to evacuate the residents (See Section 2.3.3). None of the exposed individuals had the necessary personnel protective equipment to prevent contamination when they entered the rapidly expanding toxic cloud. A properly trained and equipped hazmat response team should be the only personnel allowed to enter a contaminated area, not police and ambulance crews.

3.7.2.2 Evacuation Notification

The CSB investigation found that the city and county lacked effective methods to promptly alert the public and keep them informed during the emergency evacuation. Having no automated notification systems such as automatic telephone dialing systems, siren systems, or radio and TV announcement procedures delayed the evacuation.[36] The notification and verification process took approximately two hours, which extended the period of public exposure.

Emergency evacuation instructions were only in English, yet many of the residents primarily spoke Spanish.[37] The evacuation notification process also failed to provide any specific instructions to the evacuees concerning the evacuation routes, or for obtaining updated information on the status of the evacuation. Additionally, many residents claimed that they were never notified when the evacuation order was lifted, causing confusion among the residents and delaying their return to their homes.[38] Residents also complained that they did not receive guidelines for decontaminating their personal belongings, including any food potentially exposed to the toxic vapor that entered their houses.

3.7.2.3 Air and Water Toxic Chemical Monitoring

The Dalton Fire Department four-gas monitor used throughout their response activities at the facility was not suitable for detecting hazardous concentrations of the toxic allyl alcohol (see

[36] Oak Ridge National Laboratory has conducted studies that show that evacuations using the door-to-door method take 2.5 to 3 hours, but only take 20 to 35 minutes using combined sirens and an Emergency Broadcast System (Sorensen, 1988).

[37] Families that primarily spoke Spanish reported to CSB investigators that they had to rely on young multi-lingual children to translate the evacuation information for their parents.

[38] At least one local radio station broadcast announcements that the evacuation order was lifted.

Section 1.5.1). Fire department personnel would be exposed to many thousands of parts per million of the toxic gas before the oxygen depletion alarm would have sounded.

The CSB found that the air and water monitoring for allyl alcohol performed by MFG was inadequate. Monitoring did not begin until several hours after the release had started. When finally initiated, this monitoring was ineffective because the lower detection limit of the test device was too high for the chemicals released.[39] In addition, the only air sampling performed was near the MFG facility; there was no air sampling in the affected community.

MFG employees suffered exposure to unknown concentrations of the toxic vapor. One employee sustained chemical burns from his exposure (See Section 2.3.6). The National Response Team[40] considers that it is "crucial" to monitor the release and to assess its impact as soon as possible. Decisions about response personnel safety, citizen protection (whether to be sheltered or evacuated), and the use of food and water in the area are dependent on an accurate assessment of spill or plume movement and concentration. Decisions about containment and clean up also depend on air and water exposure monitoring (NRT, 2001). Furthermore, OSHA requires emergency response personnel to use positive-pressure SCBA for emergency response activities involving hazardous substances that present an inhalation hazard, until the IC determines through the use of air monitoring that a decreased level of respiratory protection will not result in hazardous exposures [29 CFR 1910.120(q)(3)(iv)].

[39] Air sampling was performed with generic alcohol sensitive "Drager Tubes". They had a minimum detection threshold limit of 20 ppm, ten times greater than the OSHA PEL and the same value as the IDLH concentration (see Section 1.5).

[40] The U.S. National Response Team is an organization of 16 Federal departments and agencies responsible for coordinating emergency preparedness and response to oil and hazardous substance pollution incidents. The Environment Protection Agency (EPA) and the U.S. Coast Guard (USCG) serve as Chair and Vice Chair respectively. (See 49 CFR 300).

3.7.2.4 Toxic Chemical Contamination Beyond the Evacuation Zone

The CSB concluded that the decontamination area should have been established as close to the incident scene as possible to minimize the exposure and contamination from the toxic chemical. The National Response Team recommends establishing standard operating and decontamination procedures for protecting the safety of emergency response personnel from the risks posed by hazardous materials, and minimizing the spread of the toxic material (NRT, 2001). The only decontamination area was set up at the hospital, more than five miles away from the evacuation zone. Responders transported exposed individuals in ambulances from the triage station to the hospital, leading to EMT and paramedic exposure to the toxic chemical, as well as contamination of the triage area and the ambulances.

4.0 Regulatory Analysis

4.1 OSHA

Federal OSHA administers and enforces worker safety and health standards in Georgia. Prior to the April 2004 incident, OSHA had never conducted an inspection at MFG. The post-incident inspection conducted by OSHA did not address PSM program elements.

4.1.1 Process Safety Management

The CSB concluded that MFG should have applied the OSHA Process Safety Management (PSM) standard to isotainer and the TAC process equipment. The PSM standard requires employers to prevent or minimize the consequences of catastrophic releases of highly hazardous chemicals. PSM applies to processes that involve listed toxic chemicals at, or above threshold quantities and processes with flammable liquids or gases onsite, in one location, in quantities of 10,000 pounds or more. Although the standard contains certain exemptions, none applied to the MFG TAC process or isotainer.

4.1.1.1 Threshold Quantity in the TAC Reactor

The MFG decision to limit the allyl alcohol quantity in the TAC reactor to avoid PSM compliance was technically correct. The MFG TAC fixed process equipment contained 9,900 pounds of allyl alcohol, one percent below the 10,000-pound regulatory threshold limit. OSHA suggests in the preamble to the PSM standard that reducing the quantity of a hazardous material below the threshold quantity might be an acceptable approach to reducing the potential hazard and avoiding application of the PSM standard (57 FR 6356, pg 16, 1992). The listed threshold quantity of a flammable liquid or listed toxic chemical is used to determine only if PSM compliance is required. The threshold quantity does not establish whether a process involving a specific quantity of a covered chemical is safe or unsafe. The CSB concluded that the insignificant reduction applied by MFG did not reduce the potential process hazards as envisioned when OSHA published the guidance.

4.1.1.2 Flammable Liquid Exemption

MFG incorrectly concluded that the allyl alcohol in the isotainer was exempt from the PSM standard as provided in the flammable liquid exemption criteria: "Flammable liquids stored in atmospheric tanks or transferred which are kept below their normal boiling point without the benefit of chilling or refrigeration" [§1910.119 (a)(ii)(B)]. The CSB concluded that the exemption did not apply because isotainers[41] with a design pressure exceeding 0.5 psig do not meet the PSM definition of an "atmospheric tank" [§1910.119 (b)]. Furthermore, since the isotainer remained parked less than 20 feet away from the process equipment, and the transfer hose remained attached to the (otherwise non-covered) reactor and process equipment, the process equipment was subject to the PSM standard. [42]

4.1.2 Hazardous Waste Operations and Emergency Response

The Hazardous Waste Operations and Emergency Response standard (HAZWOPER) §1910.120 requires that if employees are expected to perform emergency response activities, the employer must prepare and implement an emergency response plan. The plan is required to address emergency response procedures, training, and personnel decontamination for each functional performance level defined in the standard. The MFG emergency response plan did not address

[41] The isotainer was a DOT Specification IM101 cargo tanker. The design pressure was approximately 90 psig.

[42] OSHA intends that "boundaries of a process extend to quantities in storage, use, manufacturing, handling,…which are interconnected…" (57 FR 6356, Preamble to the PSM Standard, pg 36, 1992).

the HAZWOPER "Hazardous Materials Technician" tasks,[43] which enable trained and equipped individuals to respond to releases or potential releases. During the incident, employees without training or proper personnel protective equipment attempted to mitigate the release. Consequently, one MFG employee sustained chemical burns while performing hazardous material technician emergency response activities.

4.2 EPA

4.2.1 Emergency Planning and Community Right to Know Act

In 1986, Congress passed the Superfund Amendments and Reauthorization Act (SARA). SARA established a national baseline for planning, response, management, and training for chemical emergencies. Title III of SARA, the Emergency Planning and Community Right-to-Know Act (EPCRA), is intended to promote state and local government hazardous chemical emergency preparedness and response capabilities through better coordination, planning, and access to chemical information. EPCRA Section 302 requires the governor of each state to establish a State Emergency Response Commission (SERC), which is responsible for implementing EPCRA provisions. The SERC designates emergency planning districts and appoints local emergency planning committees (LEPC) for each district. Each LEPC is responsible for developing an Emergency Response Plan as set forth in EPCRA Section 303.

LEPCs use chemical inventory information from facilities handling hazardous chemicals to participate in the development of comprehensive local emergency response plans. The EPA

[43] Hazardous Materials Technician - trained individuals who are equipped to respond to releases or potential releases. They assume a more aggressive role than a first responder at the "Operations Level" in that the hazardous materials technician will approach the point of release in order to plug, patch, or otherwise stop the release of a hazardous substance.

requires that participants in the LEPC include not only emergency response authorities and representatives of facilities that use covered chemicals, but also community representatives such as local hospital personnel, the media, environmental groups, and residents. Broad participation in the LEPC ensures that emergency response planning takes into account all of the community issues in the event of an actual chemical emergency. The LEPC may also participate in natural disaster emergency response planning.

The SERC supervises and coordinates the LEPC activities, establishes procedures for receiving and processing public requests for information collected under EPCRA, and reviews local emergency response plans. Although the EPA has no mandatory oversight authority, their regional response teams may review and comment on an emergency response plan or other issues related to preparation, implementation, or exercise of the plan when requested to do so by an LEPC.

Section 303 of EPCRA requires each LEPC to prepare an emergency response plan (ERP) and submit a copy to the SERC for review and comment. The ERP must:

- Document the name and location of each business in the community that has more than specified quantities of “extremely hazardous substances”,
- Develop procedures for the business and local emergency and medical personnel to use when responding to a hazardous chemical release,
- Assign emergency coordinators for both the business establishment and the community,
- Develop procedures for notifying the community that there has been a hazardous chemical release, and
- Develop evacuation plans that include effective notification methods and evacuation routes.

Facilities covered under EPCRA, such as the MFG facility, are required to submit emergency and hazardous chemical information to the LEPC, the SERC, and the local fire department. LEPCs are to have access to the facility Risk Management Plans (Section 4.2.2) and to work with industry and local officials to improve local emergency response plans and to inform the public about chemical accident hazards and risks.

Whitfield County has not established an LEPC. The county's Emergency Management Agency is responsible for the emergency response plan (the Whitfield County EOP). The CSB investigation identified a number of deficiencies in the county emergency response as discussed in Section 3.7. It is possible that if Whitfield County had an LEPC with active participation by the community and companies that use covered chemicals, it may have prevented many of the problems involving community notification, evacuation procedures, and coordination among responding agencies that were encountered during the MFG incident.

4.2.2 Risk Management Program

The EPA Risk Management Program regulation (40 CFR 68), mandated by Section 112(r) of the Clean Air Act Amendments of 1990, regulates the use of highly hazardous chemicals at facilities (stationary sources[44]). The purpose is to prevent accidental releases of these substances and to ensure that the company and community are able to respond effectively in the case of a release. The regulation applies to facilities that use or store regulated substances that exceed the threshold quantity defined in the EPA regulations.

The TAC process fell under the Risk Management Program regulation because MFG took delivery of 35,000 pounds of allyl alcohol, more than twice the 15,000-pound threshold

[44] Stationary sources include transportation containers (e.g. the isotainer) no longer in transit.

quantity.[45] Covered facilities are required to develop a Risk Management Program and submit the Risk Management Plan (RMP), a summary of the facility's Risk Management Program, to the EPA before receiving the covered chemical on site. The EPA then delivers each RMP to the responsible state agency. Each state agency is required to make the RMP information available to the affected LEPC or county emergency management agency. The EPA may enforce the Risk Management Program regulation directly or may delegate the authority to a state agency, as is the case in Georgia.

The Risk Management Program consists of three parts:

- Hazard assessment that details the potential effects of an accidental release, an accident history for the last five years, and an evaluation of worst-case and alternative accidental releases;
- Prevention program that includes safety precautions and maintenance, monitoring, and employee training measures; and
- Emergency response program, detailing emergency health care, employee training measures, and procedures for informing the public and response agencies (e.g., the fire department) in the event of a release.

The facility-specific hazard information contained in the Risk Management Plans enables local governments and the public to understand what each company is doing to minimize the likelihood of a release. Furthermore, the information helps fire, police, and emergency response personnel, with assistance from the LEPC to develop a comprehensive emergency response plan to minimize the impact of a chemical release on the community.

[45] The TAC process would most likely have been covered as "Program 3" because the process was covered by the PSM standard and the worst case scenario would have identified off-site receptors (Appendix B).

MFG management should have implemented the Risk Management program for the TAC process. Under the program, they should have prepared and communicated a comprehensive written emergency plan to local authorities as well as training their own personnel in the appropriate emergency response. By not implementing the program before receiving the allyl alcohol, MFG contributed to the city and county emergency planning and response shortcomings (see Section 3.5.2).

4.3 Georgia Regulations

4.3.1 Georgia Department of Natural Resources, Environmental Protection Division

The Georgia Department of Natural Resources (GDNR), Environmental Protection Division (EPD**)** is responsible for administering the EPCRA requirements in the state and serves as staff to the State Emergency Response Commission. The EPD has access to and reviews chemical inventory data, and identifies facilities that have not filed documents required by EPCRA. The EPD is also responsible for receiving reports of chemical releases and enforcing the requirements of the EPA Risk Management Program regulation. This includes processing written requests for a copy of the nearly 400 facility RMP submittals, an important data source for emergency planning at the local level as discussed in Section 4.2.2. It makes RMPs available to LEPCs (and county emergency response agencies) upon request. However, the Georgia EPD reported that neither Whitfield County nor the City of Dalton had requested RMP submittal data for the covered facilities in the county or city.

The Georgia EPD has the authority, as provided through the Clean Air Act, to conduct compliance inspections at any facility that is required to conform to the EPA Risk Management Program regulation. Shortly after the MFG incident, EPD personnel acknowledged that inspections had been infrequent, and the facility management usually received advance notification of planned inspections.[46]

4.3.2 Georgia Emergency Response Commission

The governor of Georgia created the Georgia (State) Emergency Response Commission (SERC) within the EPD in 1987 in response to the requirements of SARA Title III. Instead of establishing an LEPC in each county that contained facilities that handled large quantities of hazardous chemicals, as envisioned (but not required) by the federal regulations, the governor initially established a single statewide LEPC to cover all 159 counties. The state now encourages each county to establish an LEPC. The CSB found that as of June 2005, Georgia reported 21 LEPCs were in place. Ten additional LEPCs were in the process of formation.[47]

Where LEPCs exist, companies covered by EPCRA send their Tier II[48] information to the LEPCs, fire departments, and the SERC. Counties lacking an LEPC send the required information to the fire department and the SERC. The SERC by-laws state that they review the local emergency response plans. However, staff stated that the emergency response plan oversight required by EPCRA is the responsibility of Georgia Emergency Management Agency (Section 4.3.3).

The CSB found that even though the SERC had been in place for more than 18 years, the commission had not developed any written procedures or guidelines for conducting the plan reviews. Furthermore, it had conducted no formal meetings between 2001 and April 12, 2004, the date of the MFG incident.

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[46] EPD reported to the CSB that as of the end of 2005, they had conducted initial compliance inspections at all of the "more than 350 facilities in the state that have filed an RMP." EPD further claimed that staff had completed second inspections at approximately 20% of the facilities.

[47] As of June 2005, the U.S. EPA website listed only 16 LEPCs in Georgia.

[48] Companies must report to the local emergency response organization the total on-site quantity of each chemical listed in the Tier II extremely hazardous chemical list.

4.3.3 Georgia Emergency Management Agency

The Georgia Emergency Management Agency (GEMA), created under the Georgia Emergency Management Act of 1981, has the authority to exercise overall direction and control of emergency or disaster operations in the Georgia as required by the Federal Emergency Management Agency (FEMA). The GEMA director is responsible for the statewide emergency management program elements mandated by FEMA regulations and is responsible for overseeing each county's development of an "All Hazards Plan" required by FEMA. All Hazards Plans are required to address chemical releases, transportation incidents, natural disasters, and terrorist actions, and comply with the EPCRA and FEMA requirements.

Each county in Georgia must include any information required by EPCRA emergency response plan requirements, as an attachment to their All Hazards Plan (Emergency Operations Plan), although GEMA does not review the content of the submissions for compliance with EPCRA requirements. In addition, each county is required to develop Standard Operating Procedures that accompany the hazard plan. GEMA does not review the SOPs.

GEMA shares responsibility with the EPD for encouraging counties to establish LEPCs and monitoring their activity. Because of the overlapping emergency planning responsibilities between SERC and GEMA, GEMA was to serve as the planning unit for the SERC.

The Georgia Emergency Management Act of 1981 requires all counties to create an Emergency Management Agency (EMA). Each EMA is required to develop and submit an Emergency Operations Plan to GEMA. The plan identifies the responsibilities of the county officials during an emergency but contains limited details about individual facilities. The EMA also has the responsibility to develop the All Hazards Plan and submit it to the EPD. Although the CSB identified deficiencies in the Whitfield County emergency operations plan (See Section 3.7.1), the county had never received any plan review comments from GEMA or EPD.

5.0 Similar Incidents

A joint OSHA/EPA report and two recent CSB reports discuss industrial incidents with many similarities to the MFG incident. Two incidents discussed in *Bretherick's Handbook of Reactive Chemical Hazards* [Urben, et al., 1999] directly involved TAC manufacturing. The CSB investigation concluded that had MFG been aware of these incidents, they would have had a better understanding of the reactive chemistry hazards involved in manufacturing TAC.

5.1 Napp Technologies

In April 1995, an explosion and fire at Napp Technologies, in Lodi, New Jersey, killed five employees and injured several others, destroyed much of the facility, and significantly damaged nearby businesses. More than 300 residents and a nearby school required evacuation for almost 24 hours. Additionally, water used to suppress the fire mixed with chemicals at the facility and flowed into the Saddle River, causing a fish kill.

Napp had contracted with another company to provide toll manufacturing of a special chemical mixture using aluminum powder, sodium hydrosulfite, potassium carbonate, and benzaldehyde. A runaway reaction resulted following the inadvertent introduction of water into a mixer containing aluminum powder and sodium hydrosulfite, both of which are water reactive, combustible solids.

The EPA and OSHA joint accident investigation team identified the following contributing factors (U.S. EPA/OSHA, 1997):

- Inadequate communications between Napp and the tolling contractor,
- Inadequate process hazard analysis,
- Less than adequate operating procedures and personnel training,
- Inadequate training of Napp employees who were emergency responders.

5.2 Reactive Hazard Management

The CSB report *Hazard Investigation: Improving Reactive Hazard Management* (USCSB, 2002b), examined chemical process safety in the United States—specifically hazardous chemical reactivity. The data analyzed included 167 serious incidents in the United States involving uncontrolled chemical reactivity from January 1980 to June 2001. Forty-eight of these incidents resulted in 108 fatalities. Approximately 30 percent of the incidents directly affected the public i.e., documented injury, community evacuation, or shelter-in-place.

Key findings in the CSB reactive chemical report closely parallel the MFG incident findings:

- More than 60 percent of the incidents for which some causal information was available involved inadequate practices for identifying hazards or conducting process hazard evaluations,
- More than 90 percent of the incidents involved reactive hazards that are documented in publicly available literature accessible to the chemical processing and handling industry.

5.3 Incidents Directly Involving TAC Manufacturing

Bretherick's Handbook of Reactive Chemical Hazards list two incidents involving mixtures of cyanuric chloride and allyl alcohol from reports originally published in the Institution of Chemical Engineers *Loss Prevention Bulletin*. The incidents are similar to the MFG incident even though there was no ignition of the flammable vapors at MFG.

5.3.1 Early 1970s Overpressure and Fire Incident

A company was attempting to make TAC in a 2000-liter (528 gallon) reactor charged with cyanuric chloride, allyl alcohol, and water. A runaway chemical reaction occurred due to inadequate cooling of the contents in the reactor. The rapidly rising temperature and pressure caused the reactor rupture disc to burst and the manway gasket to dislodge. Allyl alcohol vapors escaped and subsequent ignition caused an explosion and flash fire. Four people sustained minor injuries.

5.3.2 1979 Attempt to Manufacture TAC

A runaway chemical reaction occurred when operators were charging cyanuric chloride into an allyl alcohol/water mixture in an attempt to manufacture TAC. Operators failed to provide adequate cooling to the contents of the reactor. Pressure generated in the reactor caused the manway gasket to fail. Approximately 400 kilograms (880 pounds) of allyl alcohol vapor escaped and ignited, causing a severe explosion.

6.0 Industry Associations

6.1 Synthetic Organic Chemical Manufacturers Association

6.1.1 Responsible Care

In 1989, the American Chemistry Council (ACC) developed the Responsible Care Process Safety Code for use by the member companies. The Code includes management system elements designed to prevent fires, explosions, and accidental chemical releases. The Synthetic Organic Chemical Manufacturers Association (SOCMA) adopted the Responsible Care Process Safety Code in 1990 for use by their member companies.[49]

As an active member in SOCMA, MFG management implemented the Responsible Care Code at their two facilities and conducted self-assessments as required by the program. The CSB reviewed the Responsible Care self-assessments performed by MFG prior to the incident. The self-assessments were conducted for the Process Safety program, the Environmental Health & Safety (EH&S) program, the Product Stewardship program, and the Community Awareness and Emergency Response (CAER) program. Each MFG self-assessment concluded that the programs were adequate. However, the CSB investigation identified significant deficiencies, as previously discussed in Section 1.7.2

6.1.2 Reactive Chemicals Hazards Awareness

The CSB report *Hazard Investigation: Improving Reactive Hazard Management* (USCSB, 2002b) published more than two years before the MFG incident recommended SOCMA

[49] In September 2005, SOCMA replaced the Responsible Care Code with a new program named ChemStewards. SOCMA believes that broad participation from its members in the new program "will lead to a safer, more secure chemical manufacturing sector."

"communicate the findings and recommendations of the report to their membership." SOCMA formally responded to the CSB report recommendation by highlighting the report findings in two editions of their membership newsletter (September 20 and 27, 2002) and by posting a web link to the CSB online version of the report on their member web page. However, MFG management stated that they were not aware of the CSB report and they did not see the newsletter articles or the web link provided through SOCMA.

Had MFG reviewed the CSB report, they likely would have had a better awareness of the hazards associated with reactive chemicals. A more rigorous process safety review and control of the reaction rate by MFG could have prevented the incident or, at least minimized the toxic chemical release.

6.2 AIChE/CCPS Tolling Guidance

The American Institute of Chemical Engineers (AIChE) is a professional organization that provides chemical process safety guidance to individuals in the chemical industry through education, training, and outreach. The AIChE Center for Chemical Process Safety (CCPS) is a major source of chemical process information. CCPS works with industry to develop engineering and management practices to prevent or mitigate catastrophic releases of hazardous materials.

CCPS publishes guidelines for a variety of chemical safety issues. The intent of the tolling process safety guidelines in *Guidelines for Process Safety in Outsourced Manufacturing Operations (CCPS 2000)* is to help minimize risk and improve safety for the companies involved, the public, and the environment. These guidelines are available to SOCMA member companies.

Had MFG (a SOCMA member) and GPC applied the tolling process safety guidelines discussed in Section 3.6, many of the deficiencies identified by the CSB that led to the incident could have been avoided.

7.0 Root and Contributing Causes

The Logic Tree (Appendix C) graphically displays the progression from the top event, personnel injury from exposure to a toxic chemical, to the management systems root and contributing causes.

7.1 Root Causes

1. MFG did not understand or anticipate the reactive chemistry hazards. They did not make use of readily available literature on the hazards of reactive chemistry, or conduct a comprehensive literature search of the reactive chemistry hazards involved in TAC production, which would have alerted them to the hazards involved in manufacturing TAC. For example, *Bretherick's Handbook of Reactive Chemical Hazards*, (Urben, et al ., 1999), a well-known reference publication on reactive chemical process design, includes TAC production hazards and previous TAC incidents.

2. MFG did not perform a comprehensive process design and hazard review of the laboratory scale-up to full production before attempting the first TAC batch:

   - They did not evaluate or control the rate of chemical addition into the reactor.
   - They did not evaluate the primary TAC reaction chemistry, heat generation and process cooling requirements for the production batch.
   - They did not consider or provide critical process controls or alarms, such as high pressure or high temperature alarms.
   - They did not install and use toxic material containment devices, such as an emergency vent vapor-collection system to control or mitigate a toxic release.
   - They did not evaluate the reactor overpressure relief system.

3. The MFG emergency response plan was inadequate. MFG did not train or equip employees to conduct emergency mitigation actions.

4. MFG did not implement the EPA Risk Management Program or the OSHA Process Safety Management program prior to receiving the allyl alcohol. The regulations require comprehensive engineering analyses of the process, emergency planning, a pre-startup safety review, and coordination with the local community before receiving the covered chemical at the site and introducing the covered chemical into the process.

7.2 Contributing Causes

1. MFG and GPC did not apply industry best practices for toll manufacturing, such as those provided in Guidelines for Process Safety in Outsourced Manufacturing Operations (CCPS, 2000).

2. The City of Dalton emergency response planning did not adequately address a toxic release at a fixed facility.

    - City Fire Department procedures did not adequately address incident scene hot zone access control.

    - City Police Department procedures did not adequately address measures to protect emergency response personnel against toxic exposure during entry into a known, or suspected hazardous area.

3. The Whitfield County Emergency Operations Plan did not adequately anticipate or address the specific problems associated with this incident.

   - The plan did not adequately address important emergency response activities such as shelter-in-place, evacuation planning, and notification. During the MFG incident evacuation, the notification process relied only on door-to-door notification.

   - The emergency planning process did not involve community and business participation to ensure adequate preparation for responding to emergencies involving hazardous chemicals.

4. The Georgia EPD did not review the Whitfield County Emergency Operations Plan. The Georgia EMA review did not address the EPCRA elements. A more comprehensive review by these two state agencies may have identified the deficiencies in the emergency planning and response procedures.

8.0 Recommendations

8.1 MFG Chemical, Inc.

2004-09-I-GA-R1 Develop written procedures that require a comprehensive hazard analysis of new processes, especially those involving reactive chemistry. Ensure the hazard evaluations address critical process controls, overpressure protection, alarms, and other equipment such as vent collection/containment devices to minimize the possibility and consequences of a toxic or flammable release.

2004-09-I-GA-R2 Provide EPA Risk Management Program regulation and OSHA Process Safety Management program training to affected personnel to ensure that the facility understands the scope and application of each regulation, and implements all requirements prior to receiving and using covered chemicals.

2004-09-I-GA-R3 Create a comprehensive emergency response plan and provide equipment and training that is appropriate to the duties assigned to employees in the event of an emergency.

2004-09-I-GA-R4 Implement written tolling procedures using resources such as the CCPS book *Process Safety in Outsourced Manufacturing Operations*. Ensure effective communication between the toller (MFG) and client throughout the process development, completion of a detailed process hazard analysis, creation of emergency procedures, and dissemination to all parties who would be involved in emergency response situations.

8.2 GP Chemical

2004-09-I-GA-R5 Implement written procedures for tolling agreements using resources such as the CCPS book *Process Safety in Outsourced Manufacturing Operations*. Ensure that tolling agreements provide for:

- Direct GPC involvement in new process development, including the detailed process hazard analysis and emergency planning,
- Active participation in the first production run, as appropriate.

8.3 Lyondell Chemical Company

2004-09-I-GA-R6 Revise the applicable sections of the Allyl Alcohol Product Safety Bulletin, appendices, and web page, to emphasize the applicability of the EPA Risk Management Program regulation and OSHA Process Safety Management standard. Clearly identify the threshold quantity of allyl alcohol applicable to each regulation.

2004-09-I-GA-R7 Revise the customer site safety assessment process, clearly addressing both PSM and Risk Management Program applicability before shipping allyl alcohol to a new customer. Include a requirement to review the customer's program documents, including the (draft) RMP, and internal and external safety audit or assessment records. Require that appropriate Lyondell health, safety, and environmental personnel review the written customer safety assessment before approving the shipment of allyl alcohol.

8.4 City of Dalton

2004-09-I-GA-R8 Establish, equip, and train a hazardous materials response team. Work with the Whitfield County Emergency Management Agency to update the Emergency Operations Plan, clearly defining the roles and responsibilities of the response team.

2004-09-I-GA-R9 Revise fire department and police department procedures and training to clearly define facility and evacuation zone access control responsibilities when hazardous chemicals are involved or suspected in an emergency.

8.5 Whitfield County

2004-09-I-GA-R10 Establish a Local Emergency Planning Committee to assist the Whitfield County Emergency Management Agency to:

- Develop site-specific agency emergency response plans and standard operating procedures,
- Develop training programs and conduct drills for emergencies at fixed facilities,
- Educate the community regarding proper protective actions, such as shelter-in-place and evacuation procedures.

2004-09-I-GA-R11 Work with the City of Dalton, representatives from local facilities, and relevant community representatives to review and revise the Emergency Operations Plan to:

- Update the list of facilities handling hazardous chemicals, including those covered by the EPA Risk Management Program regulation,
- Develop standard operating procedures addressing communication of emergency information, evacuation, and shelter-in-place,
- Conduct community training and drills that involve operation of the emergency notification system and potential actions in the event of an emergency,
- Implement an automated community emergency notification system.

8.6 Governor of the State of Georgia

2004-09-I-GA-R12 Clearly designate and define the roles of the agencies responsible for ensuring compliance with all sections of the SARA Title III (Emergency Planning and Community Right-to-Know Act) including review of Local Emergency Response Plans and accompanying attachments, such as standard operating procedures.

2004-09-I-GA-R13 Designate a responsible agency and develop a system that will encourage and assist local authorities to obtain and use Risk Management Plans for those facilities that are required to develop this information to aid in the development of the site-specific emergency response plans.

8.7 Synthetic Organic Chemical Manufacturers Association

2004-09-I-GA-R14 Revise the SOCMA website to simplify locating the link to the CSB website www.csb.gov, such as adding a link in "More Resources" on the SOCMA home page. Ensure that the CSB website and the report *Hazard Investigation: Improving Reactive Hazard Management*, Report No. 2001-01-H can be easily located using the SOCMA website search engine.

2004-09-I-GA-R15 Develop a *ChemStewards* Management System Guidance Module that addresses tolling, including the best practices described in the CCPS book *Process Safety in Outsourced Manufacturing Operations*, and emergency planning involving new products.

2004-09-I-GA-R16 Develop a formal training module for the *ChemStewards* Management System Tolling Guidance Module and provide appropriate training to SOCMA member companies. Include in the training program a discussion on the tolling issues identified in the MFG report.

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Appendix A

MFG Triallyl Alcohol Process Chemistry Analyses

Appendix A

MFG Triallyl Alcohol Process Chemistry Analyses

Baker Engineering and Risk Consultants, Inc. of San Antonio, Texas was contracted by the CSB to conduct a battery of analytical chemical and thermal reactivity tests on the chemicals involved in the TAC process. The test program results follow.

1.0 Raw Materials Tests

Samples of the cyanuric chloride and allyl alcohol from the same lots used by MFG Chemical on the day of the incident were obtained by the CSB and analyzed by Baker using combined gas chromatography and mass spectroscopy (GC/MS) and then compared against pure materials obtained from Sigma-Aldrich. The chromatograms of the samples originating from MFG Chemicals were indistinguishable from chromatograms of the pure materials obtained from Sigma-Aldrich. These tests confirmed that the runaway reaction was not the result of any contamination present in the raw materials.

2.0 Thermal Stability Studies

Thermo-chemical testing focused on the desired and undesired reactions encountered during the incident. Bench top, adiabatic, and reaction calorimetry were used to obtain data to assist in understanding the nature and extent of the allyl alcohol / cyanuric chloride runaway reaction.

2.1 Bench Top Experiments

Bench-top experiments qualitatively assessed the nature and extent of the reaction that results, under varying conditions, from mixing the reactants. Three experiments were run to understand the effects of reactant order addition; the impact of the catalyst; and the need for agitation of the reaction mass. The mass ratios of allyl alcohol, cyanuric chloride, and catalyst corresponded to those used by MFG on April 12, 2004. Each experiment was performed without active cooling. A calorimeter recorded the temperature of the reaction mass as a function of time.

The results of these bench top experiments clearly show that the reaction between these two reactants—at room temperature—is spontaneously exothermic (e.g., heat producing), regardless of the order of addition of reactants; the presence or absence of the catalyst; or whether agitated or not. No action was required to initiate the reaction other than to allow the allyl alcohol and cyanuric chloride to come in contact with each other.

2.1.1 Adiabatic Calorimetry

Adiabatic calorimetry provides data that enable the characterization of a runaway reaction in terms of the temperatures and pressures as a function of time developed under the near adiabatic conditions normally found in a closed reactor. Transforming these data into temperature and pressure rise data permits the determination of the size of the emergency relief device needed to protect the vessel in the event of a runaway reaction. The results are summarized in Table 1.

The runaway chemical reaction incident in the TAC process involved two reactions: (1) the desired synthesis reaction to form the products; and (2) an undesired decomposition reaction. The heat produced by the undesired decomposition reaction, which began at the exotherm onset temperature, exceeded the heat removal capacity of the R4 reactor and rapidly raised the temperature of the batch (see maximum recorded rate of temperature rise). That heat generation caused the vapor pressure of the allyl alcohol to rise until it boiled and the reaction released additional gases, pressurizing the vessel (see maximum recorded rate of pressure rise). The heat release also raised the temperature inside the R4 reactor above the decomposition temperature (see maximum exotherm temperature), at which point gaseous products produced by the decomposition reaction resulted in even greater pressure (see maximum pressure during exotherm). This culminated in the blowout of the manway gasket, activation of the rupture disc, and final release of the material to the atmosphere.

Table 1. TAC Recipe Adiabatic Calorimetry Results

Property	**High Thermal Inertia** [b, f]	**Low Thermal Inertia Unvented**	**Low Thermal Inertia Vented** [e]	**Units**
Maximum exotherm temperature [a]	424	310	147	Degrees centigrade
Maximum recorded rate of temperature rise a	205	1050	2618	Degrees centigrade / minute
Maximum pressure during exotherm [a]	103	48	11	Bar-absolute
Maximum Recorded Rate of Pressure Rise [a]	198	409	155	Bar-absolute / minute
Total Heat of Decomposition a, c, d	> -388	> -252	> - 72	Calories / gram of reaction mass

Notes:

a: The calorimeter was shut down by the safety control system. The final temperature achieved during the runaway reaction would have been much higher than recorded.

b: Test cell ruptured during final stages of runaway reaction

c: Using heat capacities calculated to be 2.0 Joule / gram-°Kelvin for all reactants

d: The exothermic decomposition heat is greater than this value – see Notes a and b

e: Sample was vented to atmosphere at 75 psi (6 bar) so exotherm was not run to completion

f: Thermal inertia represents the ability of a material to conduct and store heat.

The adiabatic calorimetry testing of the TAC recipe demonstrated the extremely energetic nature of the reaction. The test that simulated the rupture disc opening (Table 1- Low Thermal Inertia, Vented) showed that the reaction progressed very slowly for about 90 minutes, after which the temperature rapidly increased at a rate exceeding 500 °F/minute (260 °C/minute) with a pressure rise rate approaching 2260 psi/min (155 bar/minute). The test data is presented in Figure 1.

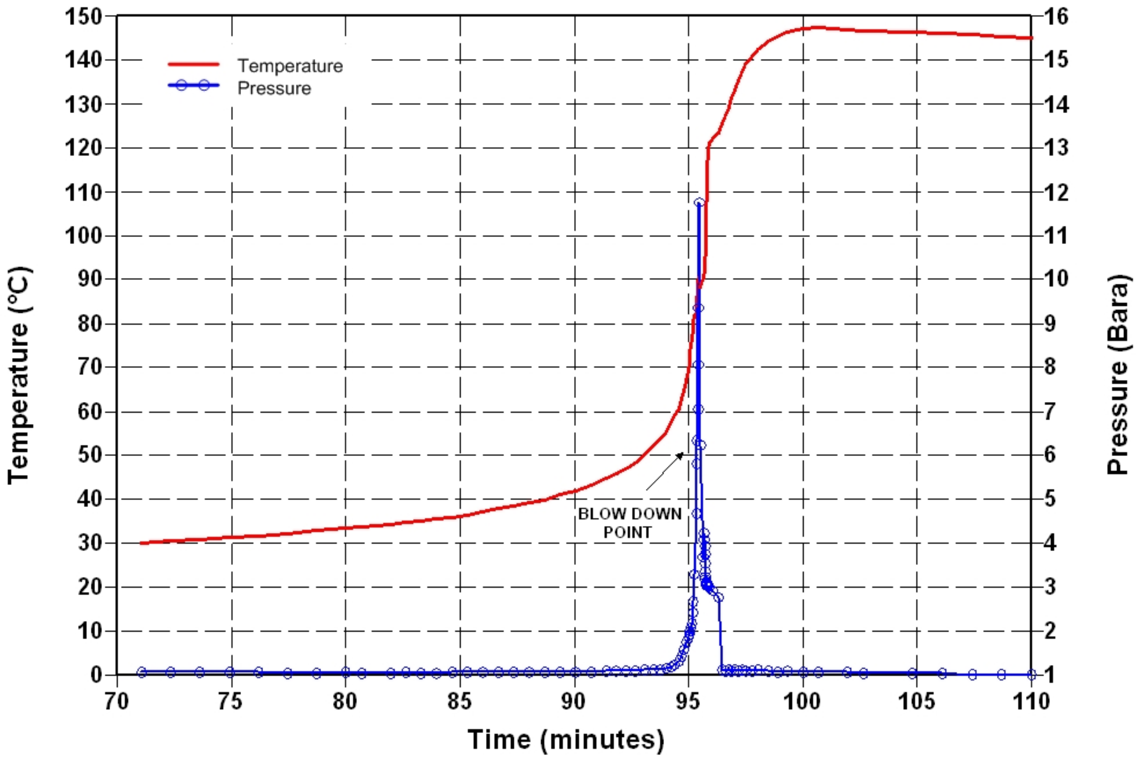

Figure 1. Test cell pressure and temperature for the low thermal inertia, vented at 6 barg (75psig) test.

2.1.2 Evaluation of Emergency Relief Size for Reactor R4

The test results from the low thermal inertia adiabatic calorimetry (see column 4, Table 1) were used to estimate the area of the emergency relief device required to protect the reactor against catastrophic failure in the event of a two-phase (e.g., vapor with entrained liquid) runaway reaction. The data generated by this type of calorimetry were used with the AIChE Design Institute of Emergency Relief Systems (DIERS) methodology to provide the required relief area.

The calculations show that an ideal vent diameter of 16.1 inches is needed, at a rupture disc burst pressure of 75 psig allowing for a 10% overpressure as stipulated in the ASME Boiler and Pressure Vessel Code, Section VIII, Division 1. The R4 relief device diameter, at the time of the incident, was 4 inches. Experimentally, the successful venting of the test cell contents at 75 psig, without rupturing the test cell, confirms that a 17-inch vent diameter of was needed to successfully vent the reactor. To account for friction losses in the vent system, a friction loss factor is included as a safety margin. Including this factor of 0.62 as recommended by API 520, increases the estimated vent diameter to 20.5 inches.

These experimental results lead to the following conclusions:

- The rupture disc on R4 at the time of the release was inadequate to relieve the pressure within the reactor without exceeding the ASME code limits for overpressure protection.

- The actual area of available venting on the reactor could not be accurately calculated because an additional vent paths developed before the rupture disc activated as the pressure rose inside the reactor. The pressure blew out the improperly installed manway gasket and material also vented up through the condenser and into another vessel. The rupture disc on that vessel also activated during the runaway reaction.

2.1.3 Reaction Calorimetry

Reaction calorimetry is used to study the desired reaction. Information obtained from this type of study includes the reaction heat at the study temperature, the instantaneous peak power, and the total energy output of the reactor. The latter quantity may be used to estimate the cooling requirements of the reactor. The results of these tests are shown in Table 2.

Table 2. Allyl Alcohol / Cyanuric Chloride Mixture Reaction Calorimetry Results

Property	Result
Total Energy	82 kJoule
Q_{max}	-121.3 calories / gram cyanuric chloride
Peak Power	6.5 watts

The test results show that the total energy liberated by the reaction was 82 kJ, which corresponds to 121.3 cal g-1 of cyanuric chloride (22.4 kcal mol-1). In the experiment the peak power output occurred about 125 minutes after mixing the reactants, it was about 6.5 watts for the total charge of cyanuric chloride.

2.1.4 Evaluation of Cooling Capacity for Reactor R4

The rate of temperature rise inside the R4 reactor depended on the balance between the reaction rate, the heat capacity of the chemicals, and the heat removal by the reactor cooling jacket. The following equation governs heat flow in the reactor:

$$Q = UA\,(T_J - T_R) \qquad \text{Equation 1}$$

Where:
Q = energy of the reaction (watts)
U = heat transfer coefficient of the system (watts/meter^2 ° Kelvin)
A = reactor wetted surface area (meter^2)
T_R = temperature of the reactants (° Kelvin)
T_J = temperature of the jacket (° Kelvin)

As shown in equation 1, the amount of heat removed is directly proportional to the difference between the temperature of the reactants and the temperature of the jacket.

However, the reaction rate is determined both by the volumetric concentrations of the two reactants and the temperature. The rate of reaction increases exponentially with temperature as shown in Equation 2.

$$R = f(C_1, C_2 \ldots C_n, e^{T_R}) \qquad \text{Equation 2}$$

Where:
R = reaction rate
C1, C2…Cn = volumetric concentration of reactants
T_R = temperature of the reactants (° Kelvin)

Equations 1 and 2 are shown graphically in Figure 2. If the reaction temperature exceeds the value at point A, the rate of heat production by the reaction exceeds the rate of heat removal provided by the reactor cooling jacket and the reaction will run away.

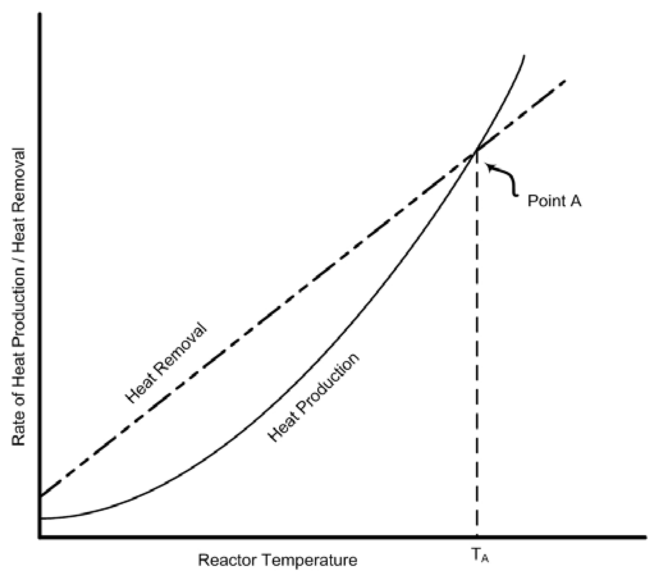

Figure 2. Heat Generation versus Heat Removal Rate

At the beginning of the reaction, the reactants are at their maximum concentrations. As the reaction proceeds to completion, the starting materials are depleted and the reaction slows down. Therefore, at the start of the batch with a high inventory of reactants, the influence of temperature on the heat generation rate is greatest and there is the most danger of exceeding the heat removal capacity of the reactor and cooling system.

After adding the full charge of allyl alcohol to the full charge of cyanuric chloride and catalyst inside the reactor, the only way to balance the heat removal rate with the heat generation rate was to manually adjust the flow of the cooling medium through the reactor's jacket. Even if the cooling system had been adjustable on the MFG reactor, the ultimate limit on cooling capacity is highly dependent on the surface-to-volume ratio of the reactor. If the heat generated inside the reacting chemical mass cannot be transferred to the reactor wall, where the cooling system is connected, the chemical mass will heat up above the critical temperature and the reaction will run away regardless how much cooling capacity the chiller can provide to the reactor cooling jacket.

Kriebitzsch and Klenk (2002) report that cyanuric chloride will decompose (e.g., undergo exothermal hydrolysis) during the manufacture of cyanurates from alcohols if the heat of reaction is not dissipated and the solution acidity is not neutralized. They also note that because this decomposition reaction liberates a large amount of heat [2164 KJ/kg (930 BTU/lb)], it can become uncontrollable and run away. The CSB calculated the required cooling capacity to be 6.45×10^6 BTU per batch based on the cyanuric chloride charge in the reactor. However, according to calculations performed by MFG, the required cooling capacity of the chiller was based on 56 kJ per mole of sodium hydroxide (612 BTU/lb of sodium hydroxide). This corresponded to a cooling capacity of only 2.88×10^6 Btu per batch.

2.1.5 Condenser Cooling Capacity

In some batch operations, evaporation and condensation (refluxing) can be an effective heat removal technique. Heat generated by the reaction boils a solvent or other material in the reactor. A condenser cools the vaporized material and converts it back to liquid, thus transferring the heat to the water used to cool the condenser and removing it from the process. MFG did not consider the use of vaporization and condensation as a heat removal mechanism even though the reactor was fitted with a condenser. Some vaporization and condensation of the allyl alcohol did occur in the batch, but the rate of vaporization proceeded too fast for all the materials to condense in the condenser. Non-condensable gases (e.g., carbon monoxide) were also being generated which reduced the condenser cooling capacity.

3.0 Runaway Reaction Decomposition Products Analysis

Gas and vapor samples collected from two runaway reactions—carried out under conditions mimicking those of the incident in a calorimeter—were analyzed by GC/MS. The major compounds vented during these tests were allyl alcohol, allyl chloride, carbon monoxide, and a C_{12} unsaturated compound derived from allyl alcohol or allyl chloride that could not be positively identified. Neither the chromatograms, nor the mass spectrometer data of the runaway reaction products showed evidence of cyanuric chloride, or its degradation products, such as cyanogen chloride, or hydrogen chloride.

A sample taken from inside the R4 reactor was analyzed both visually and chemically. The material consisted mostly of a white solid interspersed with a small amount of granular black material (Figure 3). The black material could be elemental carbon arising from a high temperature event, such as a thermal runaway, or auto-ignition of allyl alcohol during the final stages of the runaway reaction. Auto-ignition of the allyl alcohol was possible because the maximum temperature reached during the lab experiments of the allyl alcohol/cyanuric chloride runaway reaction was 425 °C, which exceeds the reported auto-ignition temperature of allyl alcohol (375 – 378 °C). Chemical analysis of the sample, by GC/MS, was not successful due to insolubility of the material.

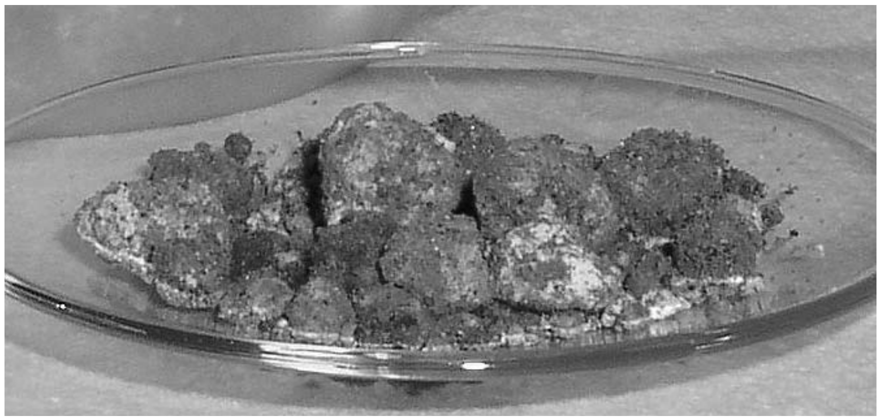

Figure 3. Residue removed from the reactor after the runaway reaction.

Appendix B

Plume Modeling Results

Appendix B

Plume Modeling Results

Air quality dispersion modeling is a tool used to predict potential offsite consequences of accidental chemicals releases. A dispersion model uses a set of mathematical equations to simulate the release and dispersion of a chemical into the atmosphere. The model is typically computer based and integrates information about chemical properties, atmospheric conditions, and terrain features to estimate the vulnerable population and sensitive environmental area(s) affected by the release.

The "hazard zone" is the geographical area affected by the release, which is typically displayed graphically on a local map. The "endpoint" is the outer boundary of the hazard zone. For flammable materials, the endpoint represents a blast wave capable of breaking glass (e.g., pressure equal to one psig), or radiant heat intense enough to blister human skin. If the material is toxic, the endpoint is based on a concentration -- referred to as a public exposure guideline -- considered hazardous to the affected community. Most people can be exposed to a toxic endpoint concentration for a certain duration (ranging from ten minutes to eight hours) without suffering irreversible health effects or other symptoms that would make it difficult to escape from the vapor cloud.

There are several possible sources of uncertainty in a dispersion model. For example, the toxic chemical mass released and the release duration are usually only rough estimates. Wind speed and direction might be based on measurements that are far from the vapor plume. In addition, the random variations in the plume concentration cannot be accurately modeled. Given these limitations, even the best dispersion model concentration estimates generally have uncertainties of a factor of two. Emergency management personnel need to consider this when using dispersion modeling information either for planning or during an actual emergency.

Baker Engineering and Risk Consulting was contracted by CSB to model the MFG incident time-dependent discharge rates (i.e., blow down) from the reactor and the reaction products dispersion to evaluate the likely impact on the surrounding community. The analyses used two validated computer dispersion models: SafeSite3G™ developed by BakerRisk and STRAPP developed by NIST.

1.0 Dispersion Model Input Parameters

Air dispersion models require input data from three main categories: land use and terrain information; meteorological conditions; and source/emission parameters. The MFG vapor cloud release model input data is summarized below.

1.1 Land Use and Terrain Information

The rate at which a vapor plume disperses and reaches ground level is affected by the degree of urbanization of the surrounding area. The MFG plant is located in a relatively flat, forested terrain in a semi-rural area southeast of downtown Dalton, GA. The surface roughness of this geographical area was judged to be 50 mm, using a rough correlation by Pasquill (1974) for the category "few trees in summer."

1.2 Meteorological Conditions

Wind direction and speed, ambient temperature, mixing (discharge) height, and atmospheric stability are typical inputs used to simulate vapor plume transport and dispersion. The model used weather data collected by the National Climatic Data Center of the National Oceanic and Atmospheric Administration at the Dalton regional airport on the day of the incident Because the release occurred after sunset at approximately 9:30 PM and with calm wind conditions, a slightly stable atmosphere (Pasquill-Gifford class E) was chosen.

1.3 Source/emission parameters

The source/emission parameters define how the hazardous materials were released to the atmosphere. The MFG Chemical, runaway reaction on April 12, 2004 resulted in a release of both allyl alcohol and allyl chloride vapors into the community (See Appendix A). There were two discharge points involved in the release: a leaking gasket on an 18-inch diameter reactor manway on top the reactor, followed about a minute later by discharge through a 4-inch diameter vent line after the reactor rupture disc blew. The manway leak area was estimated to be about 1/8-inch wide along half of the circumference, about 28 inches.

The calorimetry testing (see Appendix A) demonstrated that the actual reaction that occurred inside the reactor was substantially different from the expected reaction. Reaction mass, vapor, and enthalpy balances were calculated using the dominant molar stoichiometry from the calorimetric tests to find the fraction of cyanuric chloride reacted when the reactor pressure exceeded the rupture disc setpoint—this was computed to be 56%.

Next, the SafeSite3G™ and STRAPP models were used to develop a flash curve (Figure 1) for the initial conditions of the release. Two different models were required because the vapor liquid equilibrium properties of allyl alcohol and allyl chloride are distinctly non-ideal. The STRAPP model was used to determine the initial two-phase discharge rate using non-ideal vapor/liquid equilibrium correlations while the SafeSite3G™ model was used to predict the blowdown and dispersion.

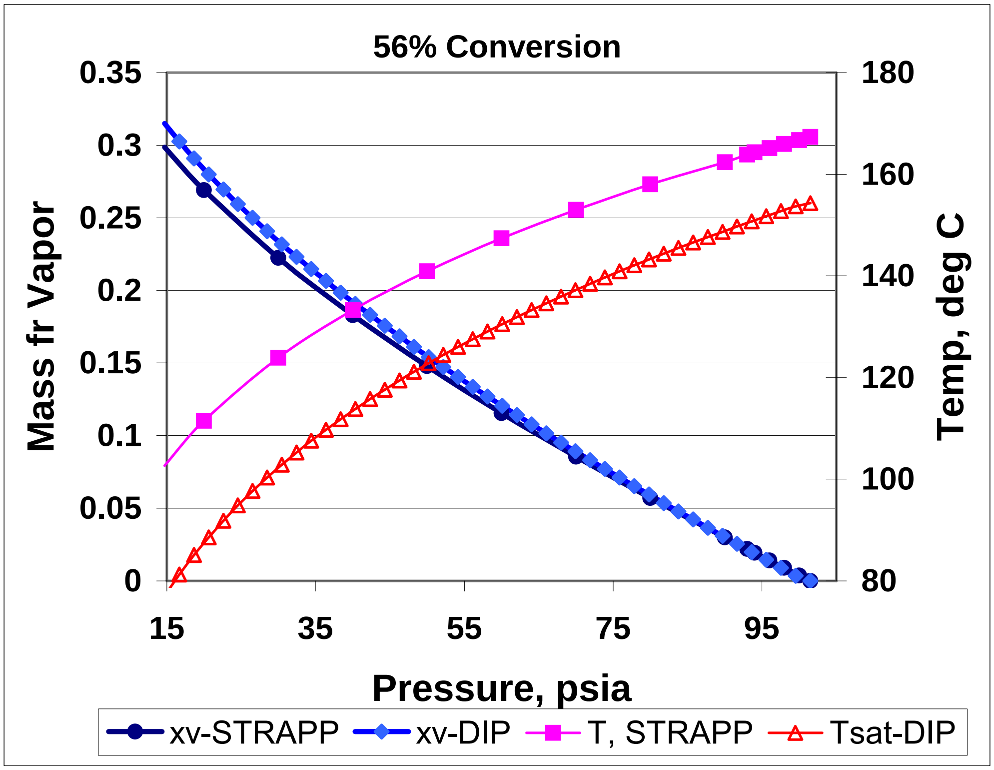

Figure 1. Flash Curves by STRAPP and DIPPR Properties

2.0 Air Dispersion Model Results

The models predict that the duration of two-phase flow (i.e., vapor and liquid discharge) was 70 seconds followed by a long vapor discharge (106 minutes before reactor pressure decayed to atmospheric. The manway gasket discharge was predicted to totally evaporate without rainout.[1] The tank conditions at the time of discharge were taken at a pressure just below the 75 psig rupture disc setpoint. The initial manway discharge was estimated to have occurred 133 seconds before the rupture disc blew. The manway discharge continued for the duration of the release.

[1] Rainout is fallout by liquid; in this case, the released vapors may condense in the atmosphere and form droplets that will then fall as liquid.

The rupture disc vent pipe discharge was directed downward, close to the ground. The model predicted the total duration of 208 minutes during which 58 mass percent will form a liquid pool in the diked concrete area.[2] This pool constantly expanded, but did not reach the dike walls before all of the liquid evaporated. Although the evaporation rate dropped off with time, the model predicted that 93% of the material discharged from the rupture disc either directly flashed, or evaporated from the pool into the atmosphere within the first 17 minutes of the release. In comparison, this was about the same elapsed time from the start of the release to the fire department arrival at the facility and initiation of the water fog spray to begin knocking down the vapors being released from the reactor and the liquid pool in the dike.

2.1 Dispersion Model Endpoint Concentrations

As both allyl alcohol and allyl chloride are flammable and toxic, the endpoint concentrations were determined for both cases.

2.2 Flammable Endpoint

The upper and lower flammable limits for the mixture released from the reactor were calculated using LeChatelier's rule. Figure B-2 is the side-view plot of the vapor cloud rupture disc release concentration limits. The flammable concentration profiles used a 15-second averaging time, essentially the instantaneous concentration in the plume. The model predicted that the flammable range occurred between 50 and 180 meters (164 and 591 feet) from the release (shaded area in Figure 2).

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[2] The model excluded the effects of the large volume of water added by the fire department.

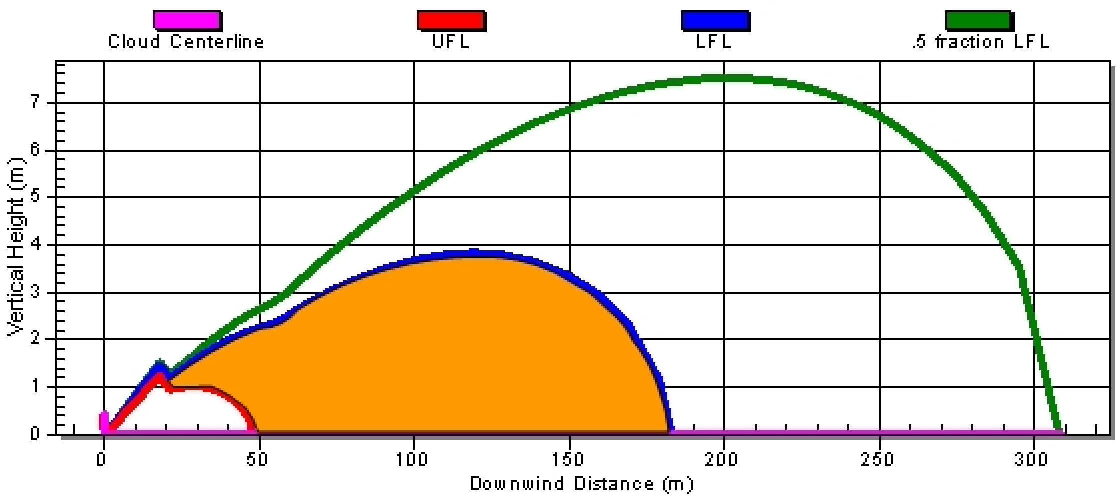

Figure 2. Plume Side View Plot of Rupture Disc Release

2.3 RMP Flammable Endpoint

The EPA Risk Management Program endpoint for a flammable liquid is the distance from the release where the explosion overpressure has attenuated to one psig. The overpressure is calculated using the TNT equivalence method with 10% explosion efficiency. The flammable endpoint was calculated to be 391 meters (1,283 feet) using the released mixture heat of combustion. Considering the location of the reactor in the MFG facility, if the released flammable material had ignited, explosion and/or fire damage would likely have been limited to the MFG facility with minor explosion overpressure damage (e.g., broken windows, damaged siding) to adjoining industrial properties on the east and west sides of the MFG property.

2.4 Toxic Endpoint

Public exposure guidelines are used as the basis for a toxic endpoint even though few have been developed. Public exposure guidelines are generally meant to protect all segments of the population, including the very young and the very old, pregnant women, and hypersensitive individuals.

2.4.1 Public Exposure Guidelines for the Released Materials

The American Industrial Hygiene Association (AIHA) has developed and published approximately 110 Emergency Response Planning Guidelines (ERPGs). They are used to anticipate human adverse effects caused by exposure to toxic chemicals. The ERPGs are three-tiered guidelines that use a one-hour contact duration:

ERPG-1 - general irritation or clearly defined objectionable odor,

ERPG-2 - experiencing or developing irreversible or other serious health effects or symptoms that could impair escape,

ERPG-3 - life-threatening health effects.

The ERPG guidelines do not protect everyone. Hypersensitive individuals are likely to suffer adverse reactions to concentrations far below those suggested in the guidelines.

ERPGs have been developed for allyl chloride (Table 1), one of the main components released from the reactor at MFG Chemical:

Table 1. Allyl Chloride ERPG Values

	ERPG-1	ERPG-2	ERPG-3
Allyl Chloride	3 ppm	40 ppm	300 ppm

The National Research Council's Committee on Toxicology is developing Acute Exposure Guideline Levels (AEGL) that include guidelines for sensitive individuals. The goal of the committee is to develop 400 to 500 high priority, acutely hazardous substance levels by the year 2010. As of late 2005, more than 160 substances have been evaluated. The AEGL guidelines consider five exposure durations: ten minutes, thirty minutes, one hour, four hours, and eight hours in each of three tiers. The AEGL tiers are the same as the EPRG tiers listed above. Interim AEGLs have been developed for allyl alcohol (Table 2), the primary component released during the MFG incident.

Table 2. Allyl Alcohol Interim AEGL Values (ppm)

Guideline (Tier)	**Exposure time (minutes)**				
	10	30	60	240	480
AEGL-1	2.1	2.1	2.1	2.1	2.1
AEGL-2	4.2	4.2	4.2	4.2	4.2
AEGL-3	130	130	67	17	8.3

It is important to evaluate toxic endpoints using the proper exposure duration – preferably adjusting them to the actual exposure duration. The analysis applied the toxic endpoints to a common basis equal to 15-minute exposure as a molar average on a reciprocal basis. To obtain ERPG values for 15-minute exposures, the 60-minute ERPG exposure was multiplied by 2.0 as recommended by Brown, et al. , (2005). As the AEGL values are constant between 10 and 30-minute exposures, they were used for 15-minute exposures. Table 3 lists the toxic endpoint concentration values adjusted for a 15-minute exposure for each guideline group. The values in the last row represent weighted average contours using the ERPGs for allyl chloride and the AEGLs for allyl alcohol.

Table 3. Toxic Endpoint Values Adjusted For Dispersion Plumes (ppm)

Component	ERPG-1 (15 min.)	ERPG-2 (15 min.)	ERPG-3 (15 min)
Allyl Chloride	6	80	600
	AEGL-1 (15 min.)	AEGL-2 (15 min.)	AEGL-3 (15 min.)
Allyl Alcohol	2.1	4.2	130
Average Contour Value	3.4	9.3	238

2.4.2 Toxic Endpoint Results

Figure 3 shows the hazard zones for the weighted average contour values for the rupture disc vent release. The stars indicate locations where people exposed to the toxic vapor made calls to the Dalton 911 call center.

Figure 4 shows the hazard zones for the weighted average contour values for the manway gasket release. Although the manway discharge is a weaker source and the predicted dispersion is low, the small puff extends a considerable distance due to the low wind speed (approximately one meter/second) during the release. However, in dispersion prediction uncertainty increases as wind speeds decrease below about three meters/second.

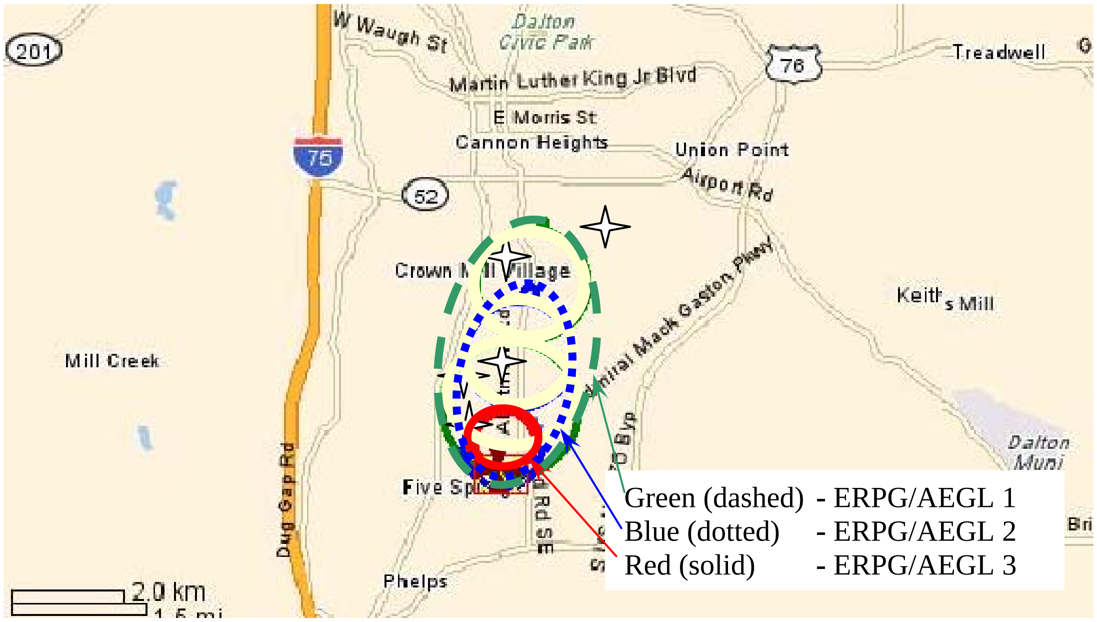

Figure 3. Predicted hazard zones for the rupture disc release.

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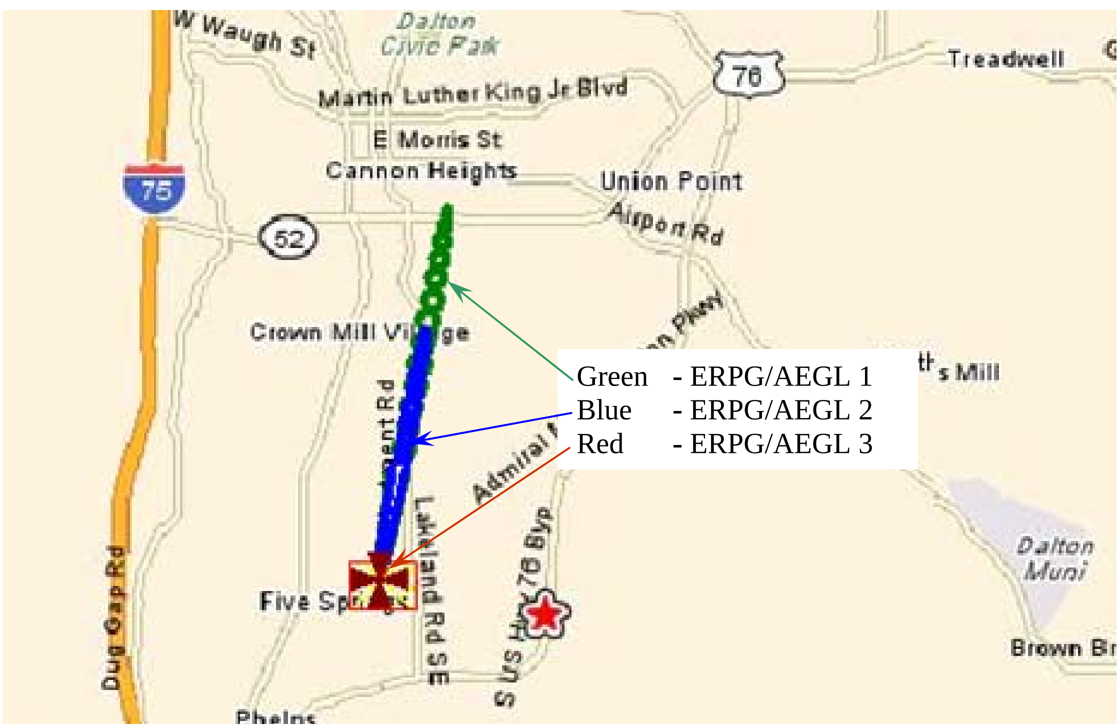


Figure 4. Predicted hazard zones for the manway gasket release.

2.4.3 Affected Population

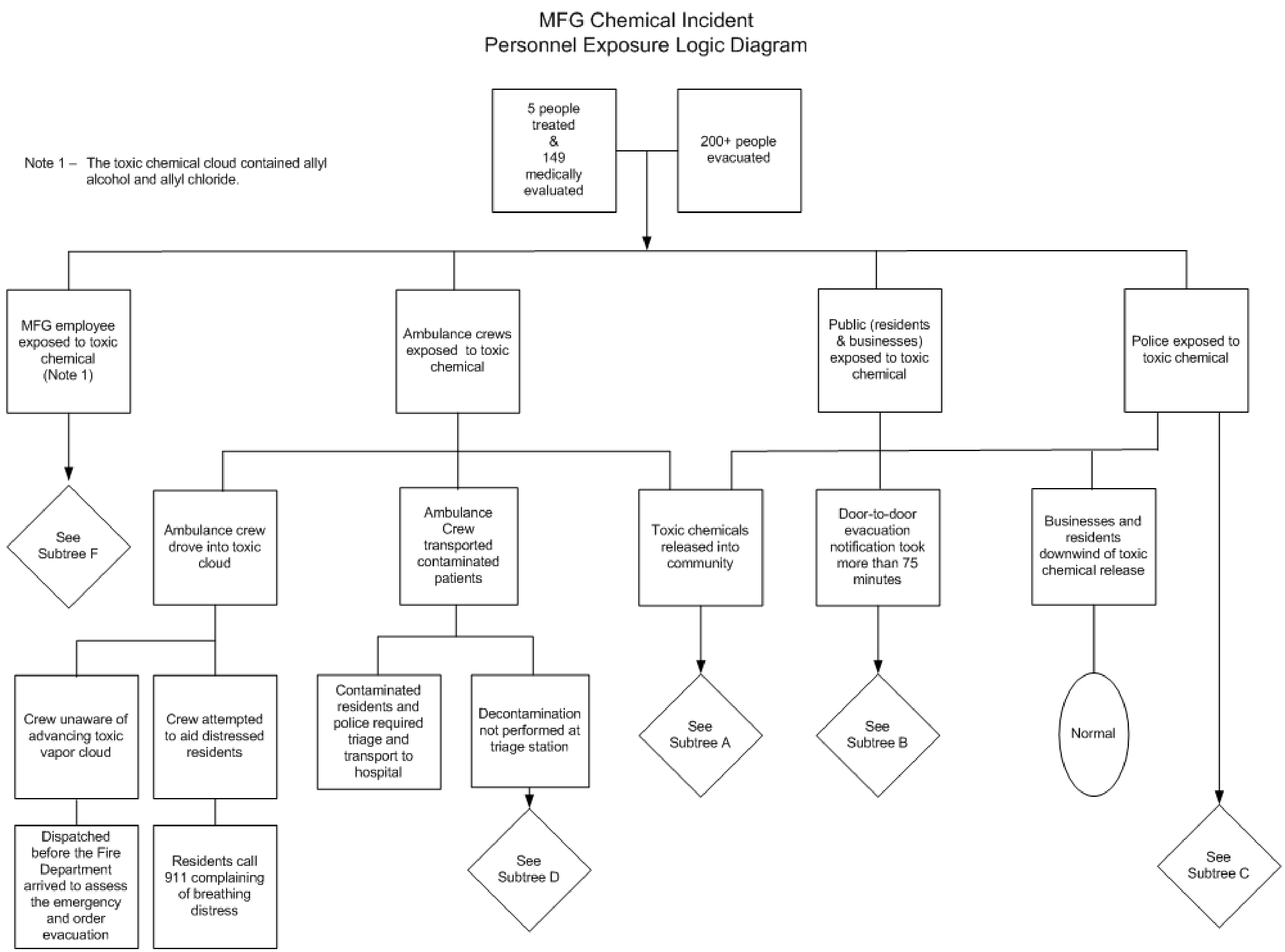
Information from the U.S. Census Bureau for Whitfield County, GA from the 2000 census was used to determine the population affected by these hazard zones. The estimated population affected by the rupture disc release was 1,533 people in the ERPG/AEGL 2 hazard zone, and 1,656 people in the ERPG/AEGL 1 hazard zone. The estimated population affected the manway gasket release was 305 people in the ERPG/AEGL 2 hazard zone, and 574 people in the ERPG/AEGL 1 hazard zone. The combined estimated population affected by both release points was 1059 - 1656 people in the ERPG/AEGL 1 hazard zone, and 687 - 1007 people in the ERPG/AEGL 2 hazard zone.

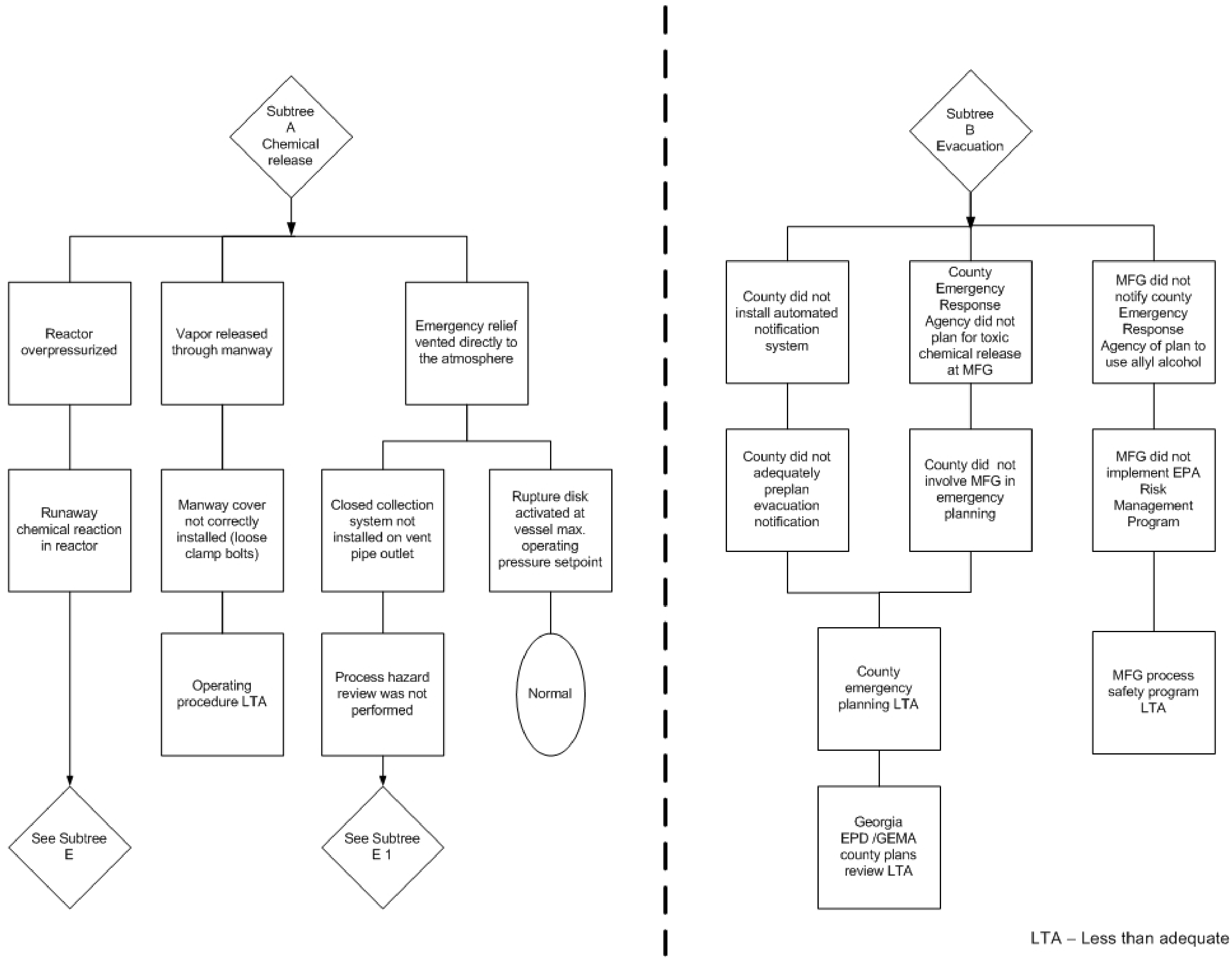
2.4.4 RMP Toxic Endpoint

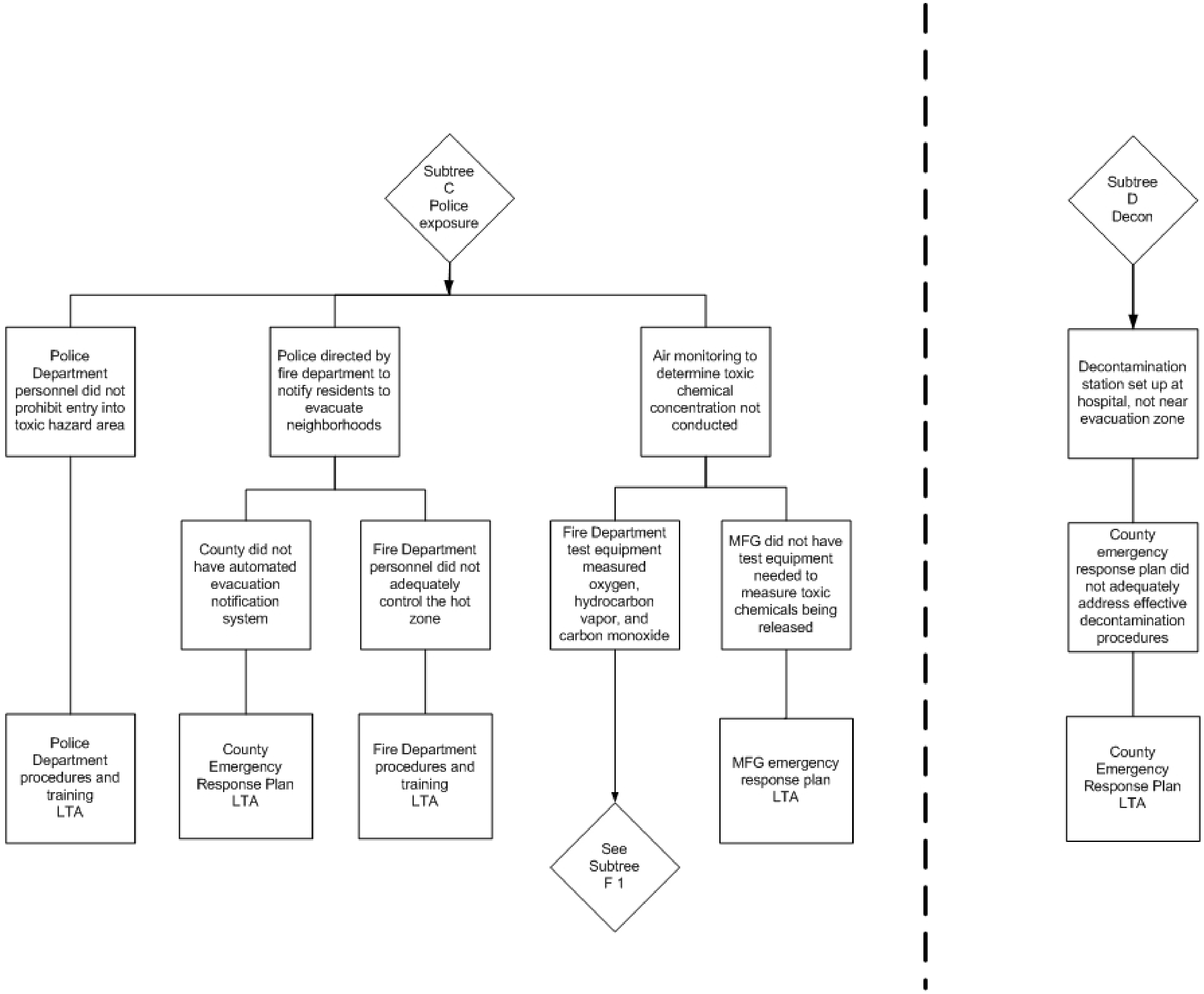
The EPA Risk Management Program regulates allyl alcohol as a toxic liquid, but does not regulate allyl chloride. The allyl alcohol toxic endpoint for a 60-minute exposure is 0.036 mg/l. The dispersion distance to the toxic endpoint is a function of the pool evaporation rate. The calculated evaporation rate was 85.4 pounds per minute based on the EPA formula for an undiked pool. The time required to evaporate all of the allyl alcohol in the pool was 74 minutes. The predicted distance to the toxic endpoint was 3.38 miles based on the EPA formula for a rural terrain. This is in good agreement with the maximum distances predicted by the dispersion model for the manway gasket leak plume (3.16 miles) and the rupture disc plume (2.84 miles) as shown in Figures 3 and 4.

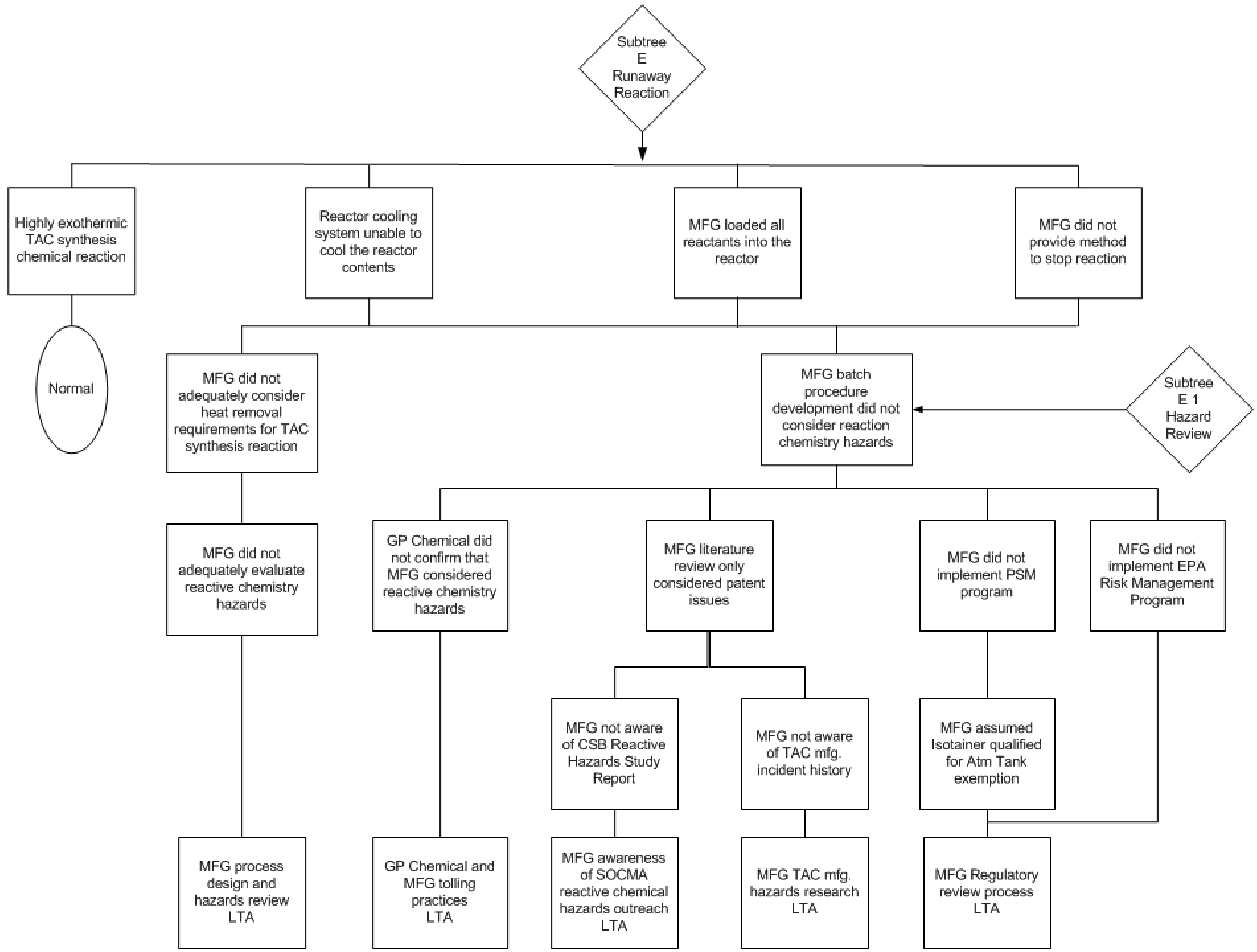
Appendix C

Logic Tree

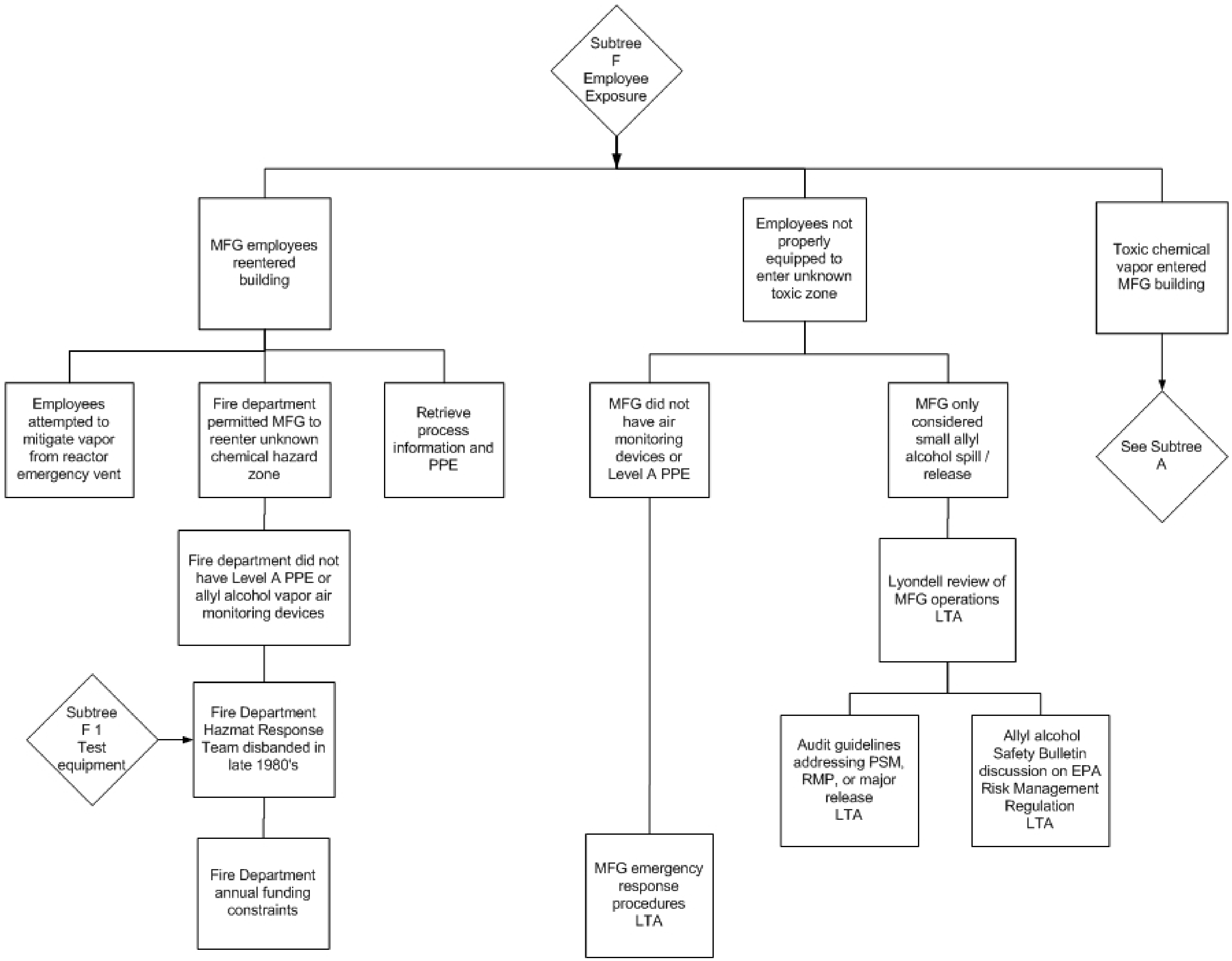

MFG Chemical Incident
Personnel Exposure Logic Diagram
5 people treated & 149 medically evaluated
200+ people evacuated
Note 1 – The toxic chemical cloud contained allyl alcohol and allyl chloride.
MFG employee exposed to toxic chemical (Note 1)
Ambulance crews exposed to toxic chemical
Public (residents & businesses) exposed to toxic chemical
Police exposed to toxic chemical
See Subtree F
Ambulance crew drove into toxic cloud
Ambulance Crew transported contaminated patients
Toxic chemicals released into community
Door-to-door evacuation notification took more than 75 minutes
Businesses and residents downwind of toxic chemical release
Crew unaware of advancing toxic vapor cloud
Crew attempted to aid distressed residents
Contaminated residents and police required triage and transport to hospital
Decontamination not performed at triage station
See Subtree A
See Subtree B
Normal
Dispatched before the Fire Department arrived to assess the emergency and order evacuation
Residents call 911 complaining of breathing distress
See Subtree D
See Subtree C


Subtree A Chemical release
Reactor overpressurized
Vapor released through manway
Emergency relief vented directly to the atmosphere
Runaway chemical reaction in reactor
Manway cover not correctly installed (loose clamp bolts)
Closed collection system not installed on vent pipe outlet
Rupture disk activated at vessel max. operating pressure setpoint
Operating procedure LTA
Process hazard review was not performed
Normal
See Subtree E
See Subtree E 1
Subtree B Evacuation
County did not install automated notification system
County Emergency Response Agency did not plan for toxic chemical release at MFG
MFG did not notify county Emergency Response Agency of plan to use allyl alcohol
County did not adequately preplan evacuation notification
County did not involve MFG in emergency planning
MFG did not implement EPA Risk Management Program
County emergency planning LTA
MFG process safety program LTA
Georgia EPD /GEMA county plans review LTA
LTA – Less than adequate


Subtree C Police exposure
Police Department personnel did not prohibit entry into toxic hazard area
Police directed by fire department to notify residents to evacuate neighborhoods
Air monitoring to determine toxic chemical concentration not conducted
County did not have automated evacuation notification system
Fire Department personnel did not adequately control the hot zone
Fire Department test equipment measured oxygen, hydrocarbon vapor, and carbon monoxide
MFG did not have test equipment needed to measure toxic chemicals being released
Police Department procedures and training LTA
County Emergency Response Plan LTA
Fire Department procedures and training LTA
See Subtree F 1
MFG emergency response plan LTA
Subtree D Decon
Decontamination station set up at hospital, not near evacuation zone
County emergency response plan did not adequately address effective decontamination procedures
County Emergency Response Plan LTA



Subtree E Runaway Reaction
Highly exothermic TAC synthesis chemical reaction
Normal
Reactor cooling system unable to cool the reactor contents
MFG loaded all reactants into the reactor
MFG did not provide method to stop reaction
MFG did not adequately consider heat removal requirements for TAC synthesis reaction
MFG batch procedure development did not consider reaction chemistry hazards
Subtree E 1 Hazard Review
MFG did not adequately evaluate reactive chemistry hazards
GP Chemical did not confirm that MFG considered reactive chemistry hazards
MFG literature review only considered patent issues
MFG did not implement PSM program
MFG did not implement EPA Risk Management Program
MFG not aware of CSB Reactive Hazards Study Report
MFG not aware of TAC mfg. incident history
MFG assumed Isotainer qualified for Atm Tank exemption
MFG process design and hazards review LTA
GP Chemical and MFG tolling practices LTA
MFG awareness of SOCMA reactive chemical hazards outreach LTA
MFG TAC mfg. hazards research LTA
MFG Regulatory review process LTA


Subtree
F
Employee
Exposure
MFG employees
reentered
building
Employees not
properly
equipped to
enter unknown
toxic zone
Toxic chemical
vapor entered
MFG building
Employees
attempted to
mitigate vapor
from reactor
emergency vent
Fire department
permitted MFG to
reenter unknown
chemical hazard
zone
Retrieve
process
information and
PPE
MFG did not
have air
monitoring
devices or
Level A PPE
MFG only
considered
small allyl
alcohol spill /
release
See Subtree
A
Fire department did not
have Level A PPE or
allyl alcohol vapor air
monitoring devices
Lyondell review of
MFG operations
LTA
Subtree
F 1
Test
equipment
Fire Department
Hazmat Response
Team disbanded in
late 1980's
Audit guidelines
addressing PSM,
RMP, or major
release
LTA
Allyl alcohol
Safety Bulletin
discussion on EPA
Risk Management
Regulation
LTA
Fire Department
annual funding
constraints
MFG emergency
response
procedures
LTA