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Runaway chemical reaction exposes community to highly toxic chemicals ☆

Mark Kaszniak *, John Vorderbrueggen

U.S. Chemical Safety and Hazard Investigation Board, 2175 K Street NW, Washington, DC 20037-1809, United States

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Abstract

The U.S. Chemical Safety and Hazard Investigation Board (CSB) conducted a comprehensive investigation of a runaway chemical reaction at MFG Chemical (MFG) in Dalton, Georgia on April 12, 2004 that resulted in the uncontrolled release of a large quantity of highly toxic and flammable allyl alcohol and allyl chloride into the community. Five people were hospitalized and 154 people required decontamination and treatment for exposure to the chemicals. This included police officers attempting to evacuate the community and ambulance personnel who responded to 911 calls from residents exposed to the chemicals.

This paper presents the findings of the CSB report (U.S. Chemical Safety and Hazard Investigation Board (CSB), *Investigation Report: Toxic Chemical Vapor Cloud Release*, Report No. 2004-09-I-GA, Washington DC, April 2006) including a discussion on tolling practices; scale-up of batch reaction processes; Process Safety Management (PSM) and Risk Management Plan (RMP) implementation; emergency planning by the company, county and the city; and emergency response and mitigation actions taken during the incident. The reactive chemical testing and atmospheric dispersion modeling conducted by CSB after the incident and recommendations adopted by the Board are also discussed.
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Keywords: Toxic chemical release; Runaway reaction; Emergency response; Process Safety Management; Risk Management Planning

1. Introduction

On the evening of April 12, 2004, MFG Chemical (MFG) was attempting to make the first production batch of triallyl cyanurate (TAC) at their facility in Dalton, Georgia. At approximately 9:30 PM, the reaction went out of control and over-pressurized a 4000-gallon (15,142 l) reactor. The runaway reaction released highly toxic and flammable allyl alcohol and allyl chloride vapors from the reactor into the community. The dense vapors continued to escape from the reactor for more than 8 h. Neither the Dalton Fire Department emergency responders nor MFG personnel had the appropriate personnel protective equipment 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 vapors and required treatment at the hospital for respiratory distress, and eye and skin irritation. One MFG employee received 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 9 h 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 a previously released CSB report, *Improving Reactive Hazard Management* [2]. Therefore, the CSB launched an investigation to determine

☆ Disclaimer: This paper is based on a U.S. Chemical Safety and Hazard Investigation Board report [1]. This paper has not been independently approved by the Board and is published for general informational purposes only. Every effort has been made to accurately represent the contents of the Board-approved reports referenced in this paper. Any material in the paper that did not originate in a Board-approved report is solely the responsibility of the authors and does not represent an official finding, conclusion or position of the Board.

* Corresponding author. Tel. +1 202 261 7654; fax +1 202 974 7654.
E-mail address: mark.kaszniak@Csb.gov (M. Kaszniak).

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the root and contributing causes and make recommendations to prevent similar occurrences.

Small and large businesses that 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.

2. A tolling agreement to manufacture TAC

A company interested in a multi-year contract to purchase large quantities of TAC, a chemical used in the manufacture of rubber and other polymers, from a U.S.-based manufacturer contacted GP Chemical (GPC), a company that specializes in marketing and selling chemicals. GPC identified an expired American Cyanamid patent that provided a straightforward method to manufacture TAC and produced one laboratory-scale test batch in a 3-l flask to confirm that the basic recipe would produce a product that met the quality standards established by their customer. Then, because GPC did not have suitable facilities to manufacture the TAC, they searched for another firm that could make it for them.

MFG began operations in 1979. The company manufactures a number of chemical products, including emulsified mineral oils, phosphate esters, surfactants and wetting agents, and various polymers. MFG produces many of these products in tolling arrangements[1] with other companies.

GPC began negotiations with MFG in late 2002 to manufacture TAC at their Dalton, GA facility. They discussed the details of the manufacturing process, which included selecting raw material suppliers, handling production quantities, and delivery schedules. The two companies also 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. MFG did not arrange for GPC to observe or otherwise participate in the first TAC production batch.

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 chemical 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 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. GPC indicated that their customer was anxious for the delivery of large quantities of TAC.

3. TAC process scale-up

3.1. TAC synthesis

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

$$\text{AllylAlcohol} + \text{CyanuricChloride} + \text{Catalyst}$$
$$\rightarrow \text{TAC} + \text{HydrogenChloride} + \text{Catalyst}$$

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. MFG planned to synthesize fixed-volume batches of TAC using a 4000-gallon (15,142 l) glass-lined reactor equipped with an external cooling jacket. 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 the cyanuric chloride was also highly exothermic and the newly formed TAC if excessively heated can also decompose.

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.

3.2. Patent literature search

MFG began the scale-up process by conducting a literature search to discover any patent restrictions that would adversely affect their TAC production. However, MFG did not conduct a detailed literature search pertaining to the reactive chemistry hazards involved in the process; if had they done so, the CSB believes 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. An earlier CSB Report, *Hazard Investigation: Improving Reactive Hazard Management* [2], noted that more than 90% of incidents involving reactive haz-

[1] “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.

ards are documented in publicly available literature accessible to the chemical processing and handling industry. For example, a standard reference used in researching reactive chemistry hazards, *Bretherick's Handbook of Reactive Chemical Hazards* [4], lists two incidents involving mixtures of cyanuric chloride and allyl alcohol from reports originally published in the Institution of Chemical Engineers (UK) *Loss Prevention Bulletin*. Both incidents have strikingly similarities to what occurred at MFG; namely, a runaway chemical reaction due to inadequate cooling of reactor contents causing rapid increases in both temperature and pressure resulting in venting of the contents of the reactor into the surrounding atmosphere.

Furthermore, the UK Health and Safety Executive (HSE) publication, *Designing and Operating Safe Chemical Reaction Processes* [5] discusses the importance of proper scale-up in designing production equipment. This publication points out that one factor not fully understood is that as reactor scale increases from laboratory size to plant production, batch cooling requirements may be underestimated because reaction rate increases exponentially with temperature while heat removal capacity is limited by the temperature difference between the reactants and the available surface area of the reactor cooling jacket.

3.3. Laboratory testing

Next, 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.

3.4. Pilot plant testing

MFG performed three batch tests in the 30-gallon (114-l) reactor, but the final production batch procedure was different from the test batch procedures. The first two batches did not use a catalyst. Both used an incremental chemical addition sequence that included neutralizing the mixture with caustic soda at each increment. Small increments of cyanuric chloride, followed by caustic soda, were added to the reactor while maintaining the batch temperature below 95 °F (35 °C). The third test batch loaded the reactor with the entire quantity of allyl alcohol, cyanuric chloride, and the catalyst with batch temperature controlled below 50 °F (10 °C), which was easy to accomplish in the 30-gallon (114-l) reactor. The second and third test batches used recycled allyl alcohol from the first test batch, not fresh allyl alcohol.

3.5. First production batch

The procedure used to attempt the first full-scale TAC production in the 4000-gallon (15,142-l) reactor was similar to the third 30-gallon (114-l) reactor test, but used only fresh allyl alcohol and did not limit the batch temperature. The production procedure also did not specify the incremental addition and neutralization steps used in the first two test batches. MFG and GPC management personnel had only briefly discussed this important reaction-rate control technique, and that was more than 1 year before MFG finalized the TAC procedure.

Consequently, during the first production batch, MFG personnel did not attempt to control the reaction rate by using closely controlled, slow additions of the chemicals. Instead, the operators added the total quantity of each chemical all at once, sequentially. This highly dangerous "all-in" approach maximized the potential for rapid energy release in the reactor. The CCPS book, *Inherently Safer Chemical Processes* [6], notes that the safety of batch processes increases with the gradual addition of one or more reactants, especially when the reaction is exothermic.

Also, controlling the temperature of the reacting chemicals was significantly more difficult in the 4000-gallon (15,142-l) reactor than in the 30-gallon (114-l) reactor. The heat removal capacity of a glass-lined reactor equipped with an external cooling 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,[2] thus the ability to remove excess heat may be significantly less in a large production reactor compared to the bench-scale reactor.

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

4. Tolling agreement flaws

During the investigation, CSB discovered that TAC manufacturing plan was the first tolling arrangement between the two companies and the first time MFG handled allyl alcohol. The CCPS book, *Guidelines for Process Safety in Outsourced Manufacturing Operations* [3] is an industry recognized "best practice" that provides comprehensive guidance for safe tolling operations. Had GPC and MFG applied these guidelines, the CSB believes they might have prevented or significantly reduced the release. Although, neither MFG nor GPC were members, this and other relevant CCPS publications are readily available to industry.[3]

[2] 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.

[3] As a member of Synthetic Organic Chemical Manufacturers Association (SOCMA), MFG had access through the association's website to the American Chemistry Council's Responsible Care Toolkit. Element 4.5 of the Technical Specification Guidance Document discusses toll manufacturing best practices.

4.1. 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 recommend employing good process safety practices even if the chemicals are not governed by OSHA PSM or EPA RPM regulations. Despite MFG management's assumption that the TAC process was exempt from PSM compliance and that they overlooked the EPA Risk Management Plan regulation, GPC should have ensured that MFG had applied good process safety practices.

4.2. 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. 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.[4] 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 equipment, chemicals, technology, or procedure of the tolling arrangement with the client. The guidelines also remind the toller and client to address the hazards and risks associated with the production process using management of change (MOC) procedures if it is subject to OSHA PSM and/or EPA RMP regulations.

The guidelines also contain specific recommendations for the tolling parties to conduct a process hazard analyses (PHA) of the tolling project. The tolling parties should consider all aspects of the toll while performing the PHA to identify potential problems caused by the scale-up. The guidelines even warn about special problems that may develop when mixing raw materials and intermediates in larger quantities than those used in a pilot plant or in the laboratory.

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, especially concerning heat removal capacity. 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 CSB concluded that 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 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.

5. PSM/RMP implementation

5.1. Process Safety Management

The CSB concluded that MFG should have applied the OSHA PSM standard to the allyl alcohol 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,

[4] 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.

in quantities of 10,000 pounds (4536 kg) or more. Although the standard contains certain exemptions, none applied to the MFG TAC process.

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 9900 pounds (4491 kg) of allyl alcohol, 1% below the 10,000-pound (4536 kg) 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 [7]. 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.

Moreover, MFG incorrectly concluded that the allyl alcohol in the isotainer was exempt from the PSM standard based on the flammable liquid exemption criteria [§1910.119 (a)(ii)(B)]: "Flammable liquids stored in atmospheric tanks or transferred which are kept below their normal boiling point without the benefit of chilling or refrigeration". The CSB concluded that this exemption did not apply because isotainers[5] with a design pressure exceeding 0.5 psig (3.44 kPa) do not meet the PSM definition of an "atmospheric tank" [§1910.119 (b)]. In addition, the isotainer remained parked less than 20 feet (6.1 m) away from the process equipment, and the transfer hose remained connected to the (otherwise non-PSM covered) reactor. Consequently, the 25,100 pounds (11,385 kg) of allyl alcohol remaining inside the isotainer needed to be added to the 9900 (4491 kg) pounds inside the reactor when determining whether or not this process was covered under PSM because OSHA's definition of a "process" includes interconnected vessels even if they are only being used for storage [29 CFR 1910.119(b)].

5.2. Risk Management Planning

MFG management reported that they were aware of the EPA Risk Management Plan 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. The total quantity of allyl alcohol present at the MFG facility (e.g., the stationary source) was 35,000 pounds (15,876 kg), which clearly exceeded the RMP listed threshold quantity of 15,000 pounds (6084 kg). Had they applied this regulation, including conducting a comprehensive review of the process and process hazard analysis, the CSB believes 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 MFG and the fire department for the emergency response.

6. Pre-incident emergency planning

6.1. MFG Chemical

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. MFG purchased a 125-pound (57-kg) portable foam fire extinguisher and provided training to the employees who would be conducting the TAC production activities. They also contacted the Dalton City Fire Department and confirmed that the nearest fire station had foam fire suppression equipment useable in the event of a spill or fire involving allyl alcohol.

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. MFG management provided a copy of the Lyondell Chemical Company allyl alcohol product safety bulletin to the fire department and verbally informed them of their intent to handle allyl alcohol by telephone. They also agreed to notify the fire department after the allyl alcohol isotainer arrived on site, but before connecting it to the reactor.

6.2. Dalton fire department

The Dalton fire department told CSB investigators that in their telephonic discussions with MFG management they clearly explained that the fire department was not qualified or equipped to respond to a toxic chemical release[6] and that the company would have to make provisions for such an event. The fire department acknowledged receiving the Lyondell materials from MFG. The fire department also agreed that they would send a representative to the facility, but only to become familiar with the placement of the equipment and to discuss emergency response activities with operators and supervisors before MFG started their production run. However, MFG never notified the fire department when the allyl alcohol arrived, so the fire department site visit did not occur.

[5] The isotainer was a DOT Specification IM101 cargo tanker. The design pressure was approximately 90 psig (619 kPa).

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

6.3. Whitfield County

The Emergency Planning and Community Right to Know Act (SARA Title III) requires the establishment of both state and local emergency planning committees. 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.[7] However, it did have a county Emergency Management Agency as required by the Georgia Emergency Management Act of 1981. The Whitfield County Emergency Management Agency (EMA) established an Emergency Operations Plan (EOP) for managing all emergency response activities.

7. Emergency response to the incident

7.1. MFG Chemical

MFG procedures 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[8] if the vapor concentration level necessitated its use.

The existing MFG emergency response plan as required by OSHA (see 29 CFR 1910.120) 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.

During the company's attempts at mitigating the release, MFG employees suffered exposure to unknown concentrations of the toxic vapor. One employee sustained chemical burns from his exposure. The U.S. National Response Team[9] (NRT) 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 [8]. 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 Incident Commander (IC) determines through the use of air monitoring that a decreased level of respiratory protection will not result in hazardous exposures [see 29 CFR 1910.120(q)(3)(iv)].

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.[10] In addition, the only air sampling performed was near the MFG facility; there was no air sampling in the affected community.

7.2. Dalton fire department

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. 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 determined that the fire department incident commander 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

[7] 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.

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

[9] 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).

[10] Air sampling was performed with generic alcohol sensitive "Drager Tubes". They had a minimum detection threshold limit of 20 ppm, 10 times greater than the OSHA PEL and the same value as the IDLH concentration.

responding to the scene were directly exposed to the allyl alcohol/allyl chloride vapors when they drove into the vapor cloud while attempting to evacuate the residents. 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.

7.3. Whitfield County

CSB believes that 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 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. Studies conducted by Oak Ridge National Laboratory [9] show that evacuations using the door-to-door method take 2.5–3 h, but only take 20–35 min using combined sirens and an Emergency Broadcast System. 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.[11] 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.[12] 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.

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 only decontamination area was set up at the hospital, more than 5 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. The triage and decontamination procedures performed by the ambulance crews and the hospital staff did not effectively control the potential spread of toxic chemicals. In addition, hospital personnel did not collect and handle the water used to rinse off the contaminated individuals as hazardous waste. The NRT recommends establishing standard operating and decontamination procedures [8] for protecting the safety of emergency response personnel from the risks posed by hazardous materials, and minimizing the spread of the toxic material.

8. Post incident materials testing conducted by CSB

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.

8.1. 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.

8.2. 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.

8.2.1. 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

[11] 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.

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

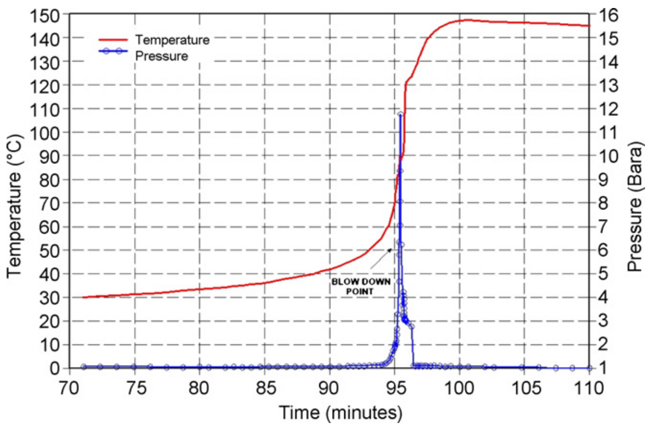

Fig. 1. Test cell reaction mass temperature and pressure as a function of time. The reactor rupture disc opened at six bara (75 psig).

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.

8.2.2. 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 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 min, after which the temperature rapidly increased at a rate exceeding 500 °F/min (260 °C/min) with a pressure rise rate approaching 2260 psi/min (155 bar/min) (Fig. 1). Testing confirmed that the decomposition reaction is highly energetic and capable of causing severe damage to equipment.

The incident at the MFG facility involved two reactions: (1) the intended synthesis reaction to form the TAC product; and (2) an unintended TAC decomposition reaction. 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% of capacity. It is likely that a highly non-homogeneous mixture resulted, even after starting the agitator, with much of the solid 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, pressurizing the reactor. The temperature continued to increase above the TAC decomposition temperature. This caused a rapid increase in gas production, further increasing reactor pressure until the incorrectly torqued 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 disc. The peak reactor pressure during the runaway reaction could not be determined.[13], [14]

8.2.3. Reactor emergency vent analysis

Applying the data obtained from the calorimetry testing showed that the 4-in. 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. The CSB determined that a 16-in. (40.6-cm) diameter opening fitted with a rupture disc would be required to vent the reactor properly in the event of a runaway reaction. The CSB concluded that the reactor vessel did not rupture because the non-homogeneous mixture, discussed above, prevented the reaction from progressing at the rate predicted by the calorimetry testing. In addition, the manway gasket leak provided some additional relieving capacity.

8.2.4. Reactor cooling analysis

Reaction calorimetry tests evaluated the reaction heat generated at a predetermined, controlled temperature. These tests measured the instantaneous heat output (power), and the total energy output of the reacting chemicals in a laboratory test apparatus. From the results, the cooling requirements for a full size production reactor can be estimated.

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 Fig. 2. If the reaction temperature increases beyond a critical point (Point A on Fig. 2), 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 the 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

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

[14] The ASME Boiler and Pressure Vessel Code, Section 8, Division 1 allows a maximum overpressure equal to 110% of the maximum allowable working pressure during emergency venting due to a process upset.

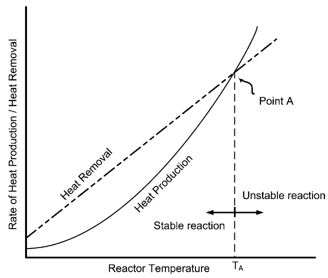

Fig. 2. Typical reaction heat production and cooling system heat removal versus reactor temperature.

control the reactor temperature and, as the temperature rose, the TAC decomposition reaction began to dominate, resulting in a runaway reaction. The increasing pressure blew out the manway gasket, and then the rupture disc. The vapor continued venting for many hours, until the reaction consumed all the reactants.

8.2.5. 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. During the incident, MFG and Lyondell expressed concern about the possible release of hydrogen chloride into the environment because it was a known by-product 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 an unidentified C_{12} unsaturated compound 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. Furthermore, the test did not detect cyanuric chloride, or its degradation products, such as cyanogen chloride.

8.3. Vapor cloud dispersion model

A vapor cloud dispersion model was developed as part of the CSB investigation to predict the toxic endpoint distance[15] for the spread of allyl alcohol vapor using the criteria contained in the EPA Risk Management Plan. The model incorporated the actual weather conditions on the day of the incident recorded at a nearby meteorological tower. The model assumed that the reactor released 6300 pounds (2858 kg) of allyl alcohol, as determined from the reactive chemistry analytical results. The calculated toxic endpoint distance of the cloud extended more than 3 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 at noted downwind locations. 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.

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

9. Key findings of the CSB investigation

From its investigation, the CSB determined the following key findings [1]:

- There was a runaway reaction at the MFG facility during the TAC synthesis. The runaway reaction occurred when operators added the entire quantity of each reactant, as well as the catalyst, to the reactor at once, and they were then unable to control the reaction rate.
- MFG did not understand or anticipate the reactive chemistry hazards. The company did not conduct an adequate evaluation of the reactive chemistry hazards involved in manufacturing TAC before attempting the first production batch. The company 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 provide a hazardous vapor/liquid containment system on the reactor emergency vent. The runaway reaction released allyl alcohol and allyl chloride from the reactor into the atmosphere and into a nearby creek.
- MFG did not develop the comprehensive process hazards analysis, pre-startup safety review, and emergency response elements required by the OSHA Process Safety Management (PSM) standard and the EPA Risk Management Plan (RMP) regulation.
- MFG employees attempted emergency response and mitigation without the necessary procedures, training, or personnel protective equipment. One employee sustained chemical burns while engaged in these activities.
- The Dalton City and Whitfield County emergency response agencies did not have a hazmat team, appropriate personal protective equipment, or air monitoring devices needed to respond safely to the toxic chemical release.
- 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 to attempt mitigation efforts.
- 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 of the evacuation.
- The only decontamination station was more than 5 miles away from the perimeter of the evacuation zone, contributing to the spread of toxic material and exposure to additional personnel.
- 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 prior to the incident.

- MFG (the toller) and GP Chemicals (GPC – the client) did not apply industry best practices for toll manufacturing such as those provided in the Center for Chemical Process Safety (CCPS) *Guidelines for Process Safety in Outsourced Manufacturing Operations* [3]. 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 make the first production batch.
- 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 RMP regulation, including conducting appropriate design reviews and preparing comprehensive emergency plans, before receiving the allyl alcohol shipment at the MFG facility.

10. CSB recommendations

In its incident investigation report [1] released on April 11, 2006, the CSB listed a number of recommendations to MFG Chemical, GP Chemical, and other involved parties to prevent future incidents of this type:

10.1. MFG Chemical

- 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.
- Provide EPA Risk Management Plan 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.
- 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.
- Implement written tolling procedures using resources such as the CCPS book *Process Safety in Outsourced Manufacturing Operations* [3]. 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.

10.2. GP Chemical

Implement written procedures for tolling agreements using resources such as the CCPS book *Process Safety in Outsourced Manufacturing Operations* [3]. Ensure that tolling agreements provide for: (1) Direct GPC involvement in new process development, including the detailed process hazard analysis and emergency planning; (2) active participation in the first production run, as appropriate.

10.3. Lyondell Chemical Company

- 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.
- 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) Risk Management Plan, 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.

10.4. City of Dalton

- 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.
- 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.

10.5. Whitfield County

- Establish a Local Emergency Planning Committee to assist the Whitfield County Emergency Management Agency to: (1) Develop site-specific agency emergency response plans and standard operating procedures; (2) develop training programs and conduct drills for emergencies at fixed facilities; (3) educate the community regarding proper protective actions, such as shelter-in-place and evacuation procedures.
- Work with the City of Dalton, representatives from local facilities, and relevant community representatives to review and revise the Emergency Operations Plan to: (1) Update the list of facilities handling hazardous chemicals, including those covered by the EPA Risk Management Plan regulation; (2) develop standard operating procedures addressing communication of emergency information, evacuation, and shelter-in-place; (3) conduct community training and drills that involve operation of the emergency notification system and potential actions in the event of an emergency; (4) implement an automated community emergency notification system.

10.6. Governor of the State of Georgia

- 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.

- 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.

10.7. Synthetic organic chemical manufacturers association

- 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.
- 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.
- 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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