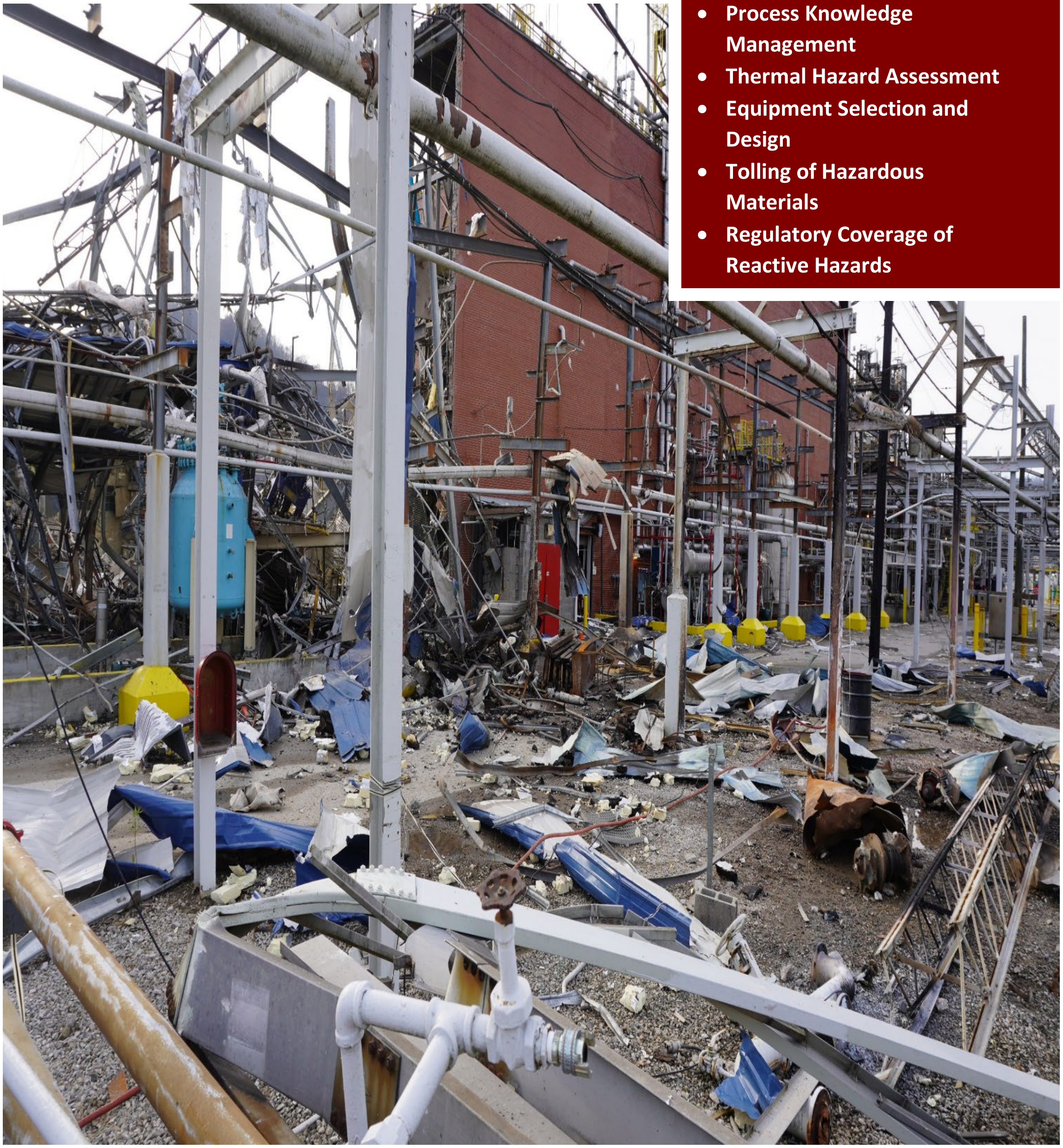
U.S. Chemical Safety and Hazard Investigation Board

Fatal Chemical Decomposition Reaction and Explosion at Optima Belle LLC

Belle, WV | *Incident Date: December 8, 2020* | **No. 2021-02-I-WV**

Investigation Report

Published: July 6, 2023



SAFETY ISSUES:

- Process Knowledge Management
- Thermal Hazard Assessment
- Equipment Selection and Design
- Tolling of Hazardous Materials
- Regulatory Coverage of Reactive Hazards

U.S. Chemical Safety and Hazard Investigation Board

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The December 8, 2020 chemical decomposition reaction and explosion at the Optima Belle LLC fatally injured John Mark Gillenwater II.

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Abbreviations

API	American Petroleum Institute
ARC	Accelerating Rate Calorimetry
ASME	American Society of Mechanical Engineers
ASTM	ASTM International (formerly American Society for Testing and Materials)
BPVC	ASME Boiler and Pressure Vessel Code
CAS	Chemical Abstracts Service
CCPS	Center for Chemical Process Safety
CDB	chlorinated dry bleach
CFR	Code of Federal Regulations
CRW	Chemical Reactivity Worksheet
CSB	U.S. Chemical Safety and Hazard Investigation Board
DCS	distributed control system
DSC	Differential Scanning Calorimetry
ECHA	European Chemicals Agency
EPA	U.S. Environmental Protection Agency
GHS	Globally Harmonized System
HWS	heat-wait-search
J/g	joules per gram
in. Hg	inches of mercury
ISO	International Organization for Standardization
kJ/g	kilojoule per gram
lbs.	pounds
MTSR	maximum temperature of synthesis reaction
MTT	maximum temperature for technical reasons
NAICS	North American Industry Classification System
NaDCC	sodium dichloroisocyanurate
NCBI	National Center for Biotechnology Information
NFPA	National Fire Protection Association
NOAA	National Oceanic and Atmospheric Administration
OSHA	Occupational Safety and Health Administration
PHA	process hazard analysis
psig	pounds per square inch gauge
PSI	process safety information
PSM	process safety management
PSV	pressure safety valve
RBPS	Risk-Based Process Safety
RCI	Richman Chemical Inc.
RAGAGEP	recognized and generally accepted good engineering practices
REACH	Registration, Evaluation, and Authorization of Chemicals
RMP	Risk Management Program (sometimes referenced as Risk Management Plan)
SADT	self-accelerating decomposition temperature
SDS	safety data sheet
TMR	Time to Maximum Rate

Executive Summary

At approximately 10:00 p.m. on December 8, 2020, a pressure-rated rotary double cone dryer containing a chlorinated isocyanurate compound (sodium dichloroisocyanurate dihydrate, or NaDCC dihydrate, trade named *CDB-56*®) exploded, causing a subsequent fire and toxic chlorine release at Optima Belle LLC (Optima Belle) in Belle, West Virginia. The explosion prompted local authorities to issue a shelter-in-place order for the region within two miles of the Optima Belle site for over four hours. The facility experienced significant property damage, and debris was found almost a half mile from the site. One Optima Belle employee was fatally injured, two others were evaluated for respiratory irritation, and one Kanawha County resident reported a minor leg injury.

The explosion occurred while Optima Belle, a toll manufacturer, was dehydrating CDB-56® to remove water from the compound to make anhydrous sodium dichloroisocyanurate on behalf of Clearon Corporation (Clearon) through a contractual agreement with tolling outsourcing partner Richman Chemical Inc. (RCI).[a] While dehydrating CDB-56® inside the dryer unit, the chlorinated isocyanurate compound underwent an unexpected decomposition reaction, releasing gases that increased the dryer internal pressure above its design pressure, and the dryer exploded. Metal debris and dryer fragments propelled off-site and within the facility, striking a methanol pipe that subsequently caught fire. Optima Belle's estimated property damage from the incident is $33.1 million.

The Chemours Belle site fire brigade, Belle Volunteer Fire Department, Kanawha County Emergency Management, West Virginia Emergency Management, and others responded to the incident.

Safety Issues

The CSB's investigation identified the safety issues below.

- **Process Knowledge Management.** Effective risk management hinges upon thorough understanding and documentation of the hazards of a process and the chemicals being processed. Clearon lacked effective process knowledge management systems, and as a result the Technology Package that Clearon delivered to Optima Belle as part of the tolling arrangement did not adequately communicate the circumstances and temperatures that could lead to the hazardous decomposition of CDB-56®. (Section 4.1)

- **Thermal Hazard Assessment.** None of the parties involved in the tolling operation effectively assessed the hazards of the NaDCC dihydrate or operation. The deficiencies included:
  1. failure to identify the initiation of a NaDCC dihydrate decomposition as a credible scenario, except as a result of a decomposition temperature greater than 240°C, water intrusion, or contamination of the product with other contaminants. During the incident, a runaway decomposition reaction had begun in the dryer by the time the dryer temperature reached 83°C—a temperature significantly lower than the identified decomposition temperature of 240°C—indicating that the thermal hazards of the material were not adequately understood or assessed by the parties involved in the tolling operation;

[a] Sodium dichloroisocyanurate (anhydrous), trade named CDB-63®, is a white free-flowing crystalline isocyanurate that has the potential to be used as a disinfectant.

2. inadequate literature searches for publicly available or internal Clearon-owned NaDCC dihydrate data; and
3. failure to utilize available reactive hazard screening methods to assess the potential reactivity or explosivity of heated NaDCC dihydrate inside a metal pressure vessel.

The effective use of publicly available or Clearon-owned data and thermal hazards evaluation methods could have resulted in a more robust and effective assessment of the hazards of the dehydration operation, which could have prevented the incident. (Section 4.2)

- **Equipment Selection and Design.** Optima Belle used its existing production equipment for the CDB-56® dehydration, but this equipment was not designed, sized, or re-engineered for CDB-56® dehydration. As a result, the equipment was not designed to quickly cool the dryer contents or to relieve the excess pressure generated during the decomposition reaction. In addition, Clearon and Optima Belle essentially conducted an experiment on a new method to remove water of hydration[a] from the CDB-56® at full production scale (involving over 8,000 pounds) without first experimenting at the laboratory and pilot scales. The end result of this production-scale experiment was a catastrophic explosion. Had scaled studies been conducted, Optima Belle, Clearon, and RCI likely would have gained additional NaDCC dihydrate thermal stability data, reactivity information, and process knowledge before running the first production-scale batch, which might have led to changes in the process and potentially prevented the decomposition reaction and the explosion. (Section 4.3)

- **Tolling of Hazardous Materials.** Companies often augment in-house production by outsourcing chemical processes and other operations. These agreements are called tolling contracts. Clearon established a tolling contract with RCI, a tolling broker, who in turn contracted with Optima Belle. The Center for Chemical Process Safety (CCPS) provides industry guidance for safe and effective tolling arrangements. The dryer explosion might have been prevented had Clearon and Optima Belle applied the suggested industry guidance. (Section 4.4)

- **Regulatory Coverage of Reactive Hazards.** NaDCC dihydrate and NaDCC are chlorinated isocyanurate compounds that can undergo self-accelerating decomposition when heated. These reactions may lead to explosions, fires, and toxic emissions with severe impacts to people, property, and the environment. Yet, many such reactive chemicals are not regulated under the Occupational Safety and Health Administration's (OSHA's) Process Safety Management (PSM) standard or the U.S. Environmental Protection Agency's Risk Management Program (RMP) rule. Had NaDCC dihydrate been covered under the PSM standard or RMP rule, Optima Belle would have been required to implement risk mitigation and management systems that could have prevented this incident. (Section 4.5)

Cause

The CSB determined that the cause of the Optima Belle rotary dryer's over-pressurization and its ultimate explosion was a self-accelerating decomposition of heated sodium dichloroisocyanurate dihydrate inside the dryer unit. Optima Belle did not adequately understand the potential for, analyze the hazards of, or detect and mitigate the self-accelerating thermal decomposition reaction. Contributing to the incident was Clearon

[a] "Ionic compounds called hydrates have a specific number of water molecules associated with each formula unit. [...] The water molecules, referred to as 'waters of hydration,' are part of the hydrate's structure. Heating can remove some or all of them, leading to a different substance" [108].

Corporation's failure to transmit sufficient process safety information to Optima Belle. Also contributing to the incident were Clearon's and Optima Belle's ineffective process safety management systems, poor knowledge management, failure to follow existing industry guidance for toll manufacturing, and insufficient regulatory coverage of reactive hazards.

Recommendations

<u>Previously Issued Recommendations Superseded in This Report</u>

To Occupational Safety and Health Administration (OSHA)

2001-01-H-R1 (from the 2002 CSB Reactive Hazard Study)

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

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

Superseded by **2021-02-I-WV-R13** *to OSHA below.*

<u>Previously Issued Recommendations Reiterated in This Report</u>

To U.S. Environmental Protection Agency (EPA)

2001-01-H-R3 (from the 2002 CSB Reactive Hazard Study)

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

<u>New Recommendations</u>

To Optima Belle LLC (Optima Belle)

2021-02-I-WV-R1

Develop and implement a written thermal and reactive hazards evaluation and management program. The program should adhere to industry guidance provided in publications such as the Center for Chemical Process Safety's *Essential Practices for Managing Chemical Reactivity Hazards*. At a minimum, the program should identify the process that Optima Belle will use to manage chemical reactivity hazards, resources for collecting and assessing reactivity hazards, steps for determining how and when to test for chemical reactivity, documentation requirements, and training.

2021-02-I-WV-R2

Develop and implement a written program for tolling process design and equipment selection using guidance from the Center for Chemical Process Safety's *Guidelines for Risk Based Process Safety* and *Guidelines for Process Safety in Outsourced Manufacturing Operations* to ensure that:

a) equipment design basis is adequate for any new tolling process or product;

b) safeguards and ancillary equipment are considered and adequately designed, installed, and function as designed and required; and

c) new processes are evaluated for potential process hazards at the laboratory and/or pilot scale before production scale.

This written program should incorporate the information developed in Optima Belle's thermal and reactive hazards evaluation program (see CSB recommendation 2021-02-I-WV-R1) to ensure that chemical hazards are fully understood and controlled.

2021-02-I-WV-R3

Develop and implement a formalized program for the development of toll manufacturing agreements using resources such as the Center for Chemical Process Safety's *Guidelines for Process Safety in Outsourced Manufacturing Operations* and *Guidelines for Risk Based Process Safety*. Ensure that the program provides for the following:

a) Identification of roles and responsibilities of all parties, including the client, toller, and any third-party technical service providers, for all phases of a proposed arrangement;

b) Evaluation of equipment requirements/specifications to ensure that they are adequate for intended operation; and

c) Participation by all parties in the tolling process development, including process hazards analysis and emergency planning, and appropriate stages of the pre-planning, pre-startup, and production phases.

2021-02-I-WV-R4

Develop and implement a process safety management system consistent with industry guidance publications such as is contained in the Center for Chemical Process Safety's *Guidelines for Risk Based Process Safety*. At a minimum, the process safety management system should address hazard identification, risk analysis, and management of risk.

To Clearon Corporation

2021-02-I-WV-R5

Develop and implement a comprehensive process knowledge management program or evaluate and revise existing process safety management procedures to ensure consistency with industry guidance publications such as the Center for Chemical Process Safety's *Guidelines for Risk Based Process Safety*. The program should:

a) assign specific responsibilities for compiling content and maintaining robust process technology and safety information packages that incorporate relevant knowledge for all hazardous processes and substances operated, manufactured, and/or handled by Clearon Corporation;

b) ensure that key process personnel are aware of critical reactive chemistry information, including thermal stability and calorimetry data, chemical compatibility information, and descriptions of any past reactive incidents and safety studies involving the materials; and

c) define procedures for the transmittal of such information to toll manufacturers.

2021-02-I-WV-R6

Update the sodium dichloroisocyanurate dihydrate (CDB-56®) safety data sheet. At a minimum, the document should:

a) provide the underlying reasoning for the storage temperature maximum and the consequences of exceeding that temperature;

b) provide the underlying reasoning for the decomposition temperature and the consequences of exceeding that temperature;

c) explain or make clear the reason(s) for and/or the circumstance(s) resulting in the differences between the decomposition temperature and the lowest temperature at which self-accelerating decomposition may occur; and

d) provide the exothermic decomposition energy in the Physical Properties section.

2021-02-I-WV-R7

Develop and implement a written program for tolling process design and equipment selection using resources such as the Center for Chemical Process Safety's *Guidelines for Process Safety in Outsourced Manufacturing Operations* and *Guidelines for Risk Based Process Safety* to ensure that:

a) equipment design basis is adequate for any new tolling process or product; and

b) safeguards and ancillary equipment are considered and adequately designed, installed, and function as designed and required.

2021-02-I-WV-R8

Develop and implement a formalized program for the development of toll manufacturing agreements using resources such as the Center for Chemical Process Safety's *Guidelines for Process Safety in Outsourced Manufacturing Operations* and *Guidelines for Risk Based Process Safety*. Ensure that the program provides for the following:

a) Identification of roles and responsibilities of all parties, including the client, toller, and any third-party technical service providers, for all phases of a proposed arrangement;

b) Evaluation of equipment requirements/specifications to ensure that they are adequate for the intended operation; and

c) Participation by all parties in tolling process development, including process hazards analysis and emergency planning, and appropriate stages of the pre-planning, pre-startup, and production phases.

2021-02-I-WV-R9

Develop and implement a process safety management system consistent with industry guidance publications such as is contained in the Center for Chemical Process Safety's *Guidelines for Risk Based Process Safety*. At a minimum, the process safety management system should address hazard identification, risk analysis, and management of risk.

To Richman Chemical Inc. (RCI)

2021-02-I-WV-R10

Develop and implement a formalized program for the development of toll manufacturing agreements using resources such as the Center for Chemical Process Safety's *Guidelines for Process Safety in Outsourced Manufacturing Operations* and *Guidelines for Risk Based Process Safety*. Ensure that the program provides for the following:

a) Identification of roles and responsibilities of all parties, including the client, toller, and any third-party technical service providers, for all phases of a proposed arrangement; and

b) Participation by all parties in tolling process development, including process hazards analysis and emergency planning, and appropriate stages of the pre-planning, pre-startup, and production phases.

To Occupational Safety and Health Administration (OSHA)

2021-02-I-WV-R11

Update the Chemical Reactivity Hazards website (https://www.osha.gov/chemical-reactivity) to include various reactivity assessment tools developed since the 2002 Index-Based Method for Assessing Exothermic Runaway Risk and the 2004 Preliminary Screening Method. Mathematical methods, thermal analysis methods (e.g., Accelerating Rate Calorimeter (ARC) testing), ASTM E1231-19 *Standard Practice for Calculation of Hazard Potential Figures of Merit for Thermally Unstable Materials*, Stoessel Criticality, and the O.R.E.O.S. Method (an assessment that combines Oxygen balance calculations, the Rule of 6, and the Explosive functional group list with Onset decomposition and scale) are tools that could be considered for the update. The "Additional Resources" section of the website should also be evaluated for necessary changes and updates.

2021-02-I-WV-R12

Following the implementation of CSB recommendation 2021-02-I-WV-R11, ensure that the chemical industry is aware of the Chemical Reactivity Hazards website (https://www.osha.gov/chemical-reactivity) by developing and implementing a comprehensive outreach plan that actively targets the chemical industry and related trade associations. The outreach plan may include such means as a national news release and OSHA's "*QuickTakes*" newsletter and/or *Safety and Health Information Bulletins*. This outreach plan should be coordinated with OSHA's On-Site Consultation Program partners.

2021-02-I-WV-R13

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

- Broaden the application to cover reactive hazards resulting from process-specific conditions and combinations of chemicals. Additionally, broaden coverage of hazards from self-reactive chemicals. In expanding PSM coverage, use objective criteria. Consider criteria such as the North American Industry Classification System (NAICS), a reactive hazard classification system (e.g., based on heat of reaction or hazardous gas evolution), incident history, or catastrophic potential.
- In the compilation of process safety information, require that multiple sources of information be sufficiently consulted to understand and control potential reactive hazards. Useful sources include but are not limited to:
    - Literature surveys (e.g., Bretherick's Handbook of Reactive Chemical Hazards, Sax's Dangerous Properties of Industrial Materials, CAS SciFinder).
    - Information developed from computerized tools (e.g., ASTM's CHETAH, CCPS's Chemical Reactivity Worksheet).
    - Chemical property data compiled in PubChem and the REACH (Registration, Evaluation, and Authorization of Chemicals) dossiers maintained by the European Chemicals Agency (ECHA).
    - Chemical reactivity test data produced by employers or obtained from other sources following established standards such as:
        - ASTM E537-20, Standard Test Method for Chemicals by Differential Scanning Calorimetry;
        - ASTM E1981-22, Standard Guide for Assessing Thermal Stability of Materials by Methods of Accelerating Rate Calorimetry;
        - ASTM E2550-21, Standard Test Method for Thermal Stability by Thermogravity; and
        - ASTM E1231-19, Standard Practice for Calculation of Hazard Potential Figures of Merit for Thermally Unstable Materials.
    - Relevant incident data from the plant, the corporation, industry, and government.
- Augment the process hazard analysis (PHA) element to explicitly require an evaluation of reactive hazards. In revising this element, evaluate the need to consider relevant factors, such as:
        - Rate and quantity of heat or gas generated.
        - Maximum operating temperature to avoid a runaway reaction from decomposition.
        - Time to Maximum Rate under Adiabatic Conditions (TMR_{ad}).
        - Thermal stability of reactants, reaction mixtures, byproducts, waste streams, and products.

- Effect of variables such as charging rates, catalyst addition, and possible contaminants.
- Understanding the consequences of runaway reactions or hazardous gas evolution.

To the National Center for Biotechnology Information (NCBI)

2021-02-I-WV-R14

Update the safety information in PubChem for sodium dichloroisocyanurate (NaDCC) dihydrate, to include publicly available reactivity and decomposition information including but not limited to the Self Accelerating Decomposition Temperature (SADT), the explosion hazard when heating metal containers containing NaDCC dihydrate, and the Differential Scanning Calorimetry (DSC) and Accelerating Rate Calorimetry (ARC) results presented in this report. When compiling this information, review sources including the Registration, Evaluation, Authorization, and Restriction of Chemicals Regulation (REACH) dossier and other publications.

To the Center for Chemical Process Safety (CCPS)

2021-02-I-WV-R15

Update *Guidelines for Process Safety in Outsourced Manufacturing Operations* or develop a new tolling guidance document to supplement existing guidelines. The publication should include current best practices, introduce guidance specific to tolling brokers and/or project managing companies such as Richman Chemical Inc., and cross-reference and align with the comprehensive management systems framework and terminology contained in *Guidelines for Risk Based Process Safety* and other contemporary industry good practice guidance.

1 Background

1.1 Optima Belle LLC

Optima Belle LLC (Optima Belle) operates in Belle, West Virginia, and was formed in 2014.[a] Optima Belle offers its equipment for chemical toll manufacturing services[b] and is a tenant at The Chemours Company Belle site in Kanawha County, West Virginia. In December 2020, Optima Belle had 29 employees, including full-time employees, interns, and contractors.[c]

1.2 Richman Chemical Inc.

Richman Chemical Inc. (RCI) provides custom manufacturing, product sourcing, and project management services to life science, specialty chemical, and emerging technology companies.

1.3 Clearon Corporation

Clearon Corporation (Clearon) produces chlorinated isocyanuric compounds—including trichloroisocyanuric acid, dichloroisocyanuric acid, and sodium dichloroisocyanurate (NaDCC) dihydrate—at its South Charleston, West Virginia, facility and converts these compounds into an array of finished good products [1]. These products include sanitizers and disinfectants for household and industrial applications, recreational water treatment, and other applications. The Clearon facility ownership has changed over time. Former owners include FMC Corporation, Olin Corporation, and Israel Chemicals Limited.[d] At the time of the incident, Clearon was a subsidiary of Hui Yu Xin American Corp. In September 2022, Solenis acquired Clearon [2].

1.4 Chemicals Involved in the Incident

This incident occurred during an operation in which water molecules of hydration[e] were being removed from NaDCC dihydrate,[f] a chlorinated isocyanurate compound, to produce NaDCC,[g] as depicted in **Figure 1**. Clearon referred to this process as "drying." Clearon's trade names for NaDCC dihydrate and NaDCC are CDB-56®[h] and

[a] Optima Belle is a separate entity from Optima Chemical Group LLC; both entities are owned by the same members. In June 2015, Optima Belle executed an Asset Purchase Agreement with Chemours FC, LLC. The parties also entered a Ground Lease and Site Services Agreement. The Chemours Company owns the land at the Belle plant, and Optima Belle owns specific buildings and equipment with a long-term lease for the land.

[b] Toll manufacturing is a mode of manufacturing in which a third-party company is outsourced or contracted to provide processing services to a customer [35, pp. 4-5]. The customer often provides the raw materials and product specifications to the third-party company or details the suppliers that must be used [35, p. 106].

[c] Five of the 29 Optima Belle employees were on-site during the incident.

[d] In early 1985, Olin entered an agreement with FMC that included FMC's plant at South Charleston. Olin Corporation transferred ownership to Clearon in 1995. Israel Chemicals Limited acquired Clearon in 1995 and sold it to Hui Yu Xin American Corp. in 2016.

[e] "Ionic compounds called hydrates have a specific number of water molecules associated with each formula unit. [...] The water molecules, referred to as 'waters of hydration,' are part of the hydrate's structure. Heating can remove some or all of them, leading to a different substance" [108].

[f] Clearon's NaDCC dihydrate (CDB-56®) contains 11.0–13.9% moisture.

[g] Clearon's NaDCC (CDB-63®) contains less than 1% moisture.

[h] In addition to CDB-56®, sodium dichloroisocyanurate dihydrate (CAS# 51580-86-0) is referred to by several other names, including troclosene sodium dihydrate and sodium dichloro-s-triazinetrione dihydrate [62].

CDB-63®,[a] respectively, based on the percent by weight of available chlorine in the compounds.[b] CDB-56® is approximately 56% available chlorine by weight [3], and CDB-63® is approximately 63% available chlorine by weight.

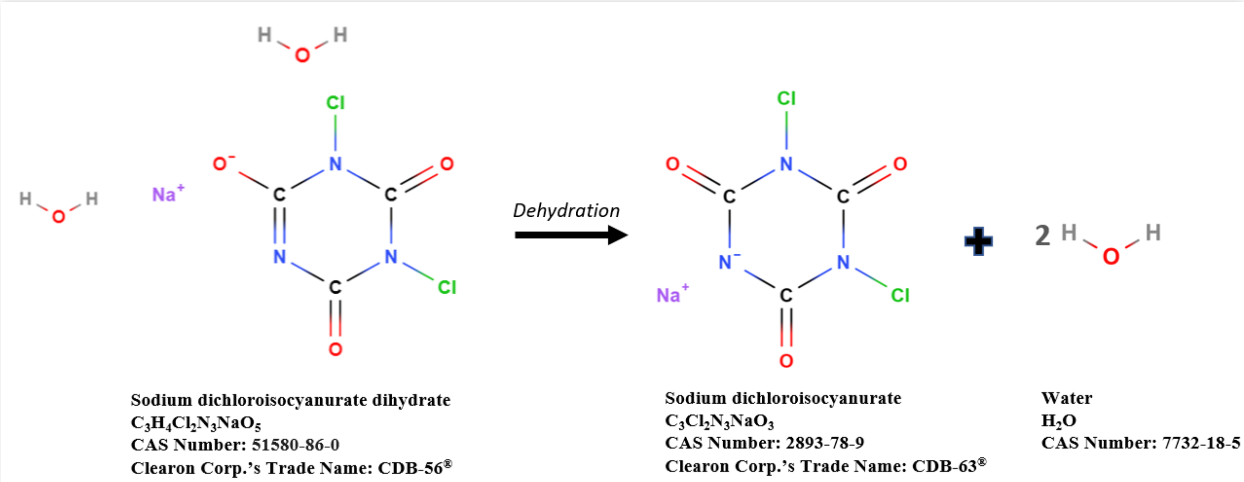

Figure 1. Depiction of NaDCC dihydrate converted to NaDCC. (Credit: CSB)

NaDCC dihydrate is a dry, white, free-flowing crystalline powder or granular solid with a chlorine odor used as a source of available chlorine for cleaning, bleaching, disinfecting, and sanitizing applications. It is an oxidizing agent that,[c] when heated to its decomposition temperature,[d] can undergo a decomposition reaction that releases chlorine gas, nitrogen trichloride (NCl_3),[e] and other byproducts.[f] The National Fire Protection Association (NFPA) classifies NaDCC dihydrate as a Class 1 oxidizer [4, pp. 400-202 and 400-203]. NaDCC dihydrate is highly corrosive, and processing NaDCC dihydrate typically requires the use of equipment constructed of corrosion-resistant materials such as Inconel® Alloys[g] or Hastelloy®.[h] Significantly, NaDCC dihydrate is not covered by either the Occupational Safety and Health Administration (OSHA) Process Safety Management (PSM) standard or the U.S. Environmental Protection Agency (EPA) Risk Management Program (RMP) rule (see Section 4.5).

NaDCC is a white granular material with a bleach-like or chlorine-like odor. When heated, it can decompose and emit toxic fumes, including chlorine, nitrogen oxides, and sodium oxide [5]. It is sold as a source of active

[a] Sodium dichloroisocyanurate (CAS#: 2893-78-9) is also known as sodium dichloro-s-triazinetrione ("dichlor") [5], among other names.

[b] Available chlorine is a measure of the oxidizing power expressed in terms of elemental chlorine (Cl_2).

[c] Clearon's *CDB®56, Clearon ® Stabilized Dry Chlorinated Compound* Technical Product Bulletin describes the compound as "a strong oxidizing agent."

[d] Decomposition temperature is the "temperature at which spontaneous decomposition occurs" [100]. Decomposition is the "[b]reakdown of a material or substance (by heat, chemical reaction, electrolysis, decay, or other processes) into parts or element or simpler compounds" [100]. When a material decomposes, it may release toxic substances such as chlorine gas or other dangerous byproducts, creating excess pressure that could over-pressurize a vessel, as happened in the Optima Belle incident.

[e] NCl_3 is explosive, and upon decomposition it emits toxic fumes [91].

[f] Clearon's *CDB®56, Clearon® Stabilized Dry Chlorinated Compound* Technical Product Bulletin states that contamination with moisture may start a chemical reaction.

[g] Inconel® is "a type of nickel-chromium-iron alloy used for process plant equipment, noted for its strength at high temperature and corrosion resistance" [72, p. 194, 97].

[h] Hastelloy® is "a widely used alloy of nickel, molybdenum, and chromium used for process equipment. It provides good resistance to wet chlorine, hypochlorite bleach, ferric chloride, and nitric acid" [72, p. 175, 96].

chlorine for water chlorination, especially in swimming pools, as well as in detergents and bleaching agents.[a] As with NaDCC dihydrate, NaDCC is not covered under the PSM standard or RMP rule.

Post-incident testing results found that NaDCC dihydrate begins a runaway exotherm[b] at approximately 81°C when heated in a closed container. This exotherm is a result of the NaDCC dihydrate undergoing a runaway decomposition. Olin, a Clearon predecessor, performed similar testing on the decomposition of NaDCC dihydrate in the 1970s and 1980s.[c] In the 1990s, further industry studies estimated a self-accelerating decomposition temperature (SADT) for NaDCC dihydrate between 45°C to 65°C [6, p. 601 and 604].[d] The Center for Chemical Process Safety (CCPS) defines SADT as:

> The lowest temperature that a mass of material, capable of an exothermic decomposition reaction, must be held such that the heat of decomposition exceeds the amount of energy lost to the surroundings. This will result in an increase in the mass temperature and acceleration of the decomposition reaction rate [7].

The United Nations *Manual of Tests and Criteria* defines the SADT as "the lowest temperature at which self-accelerating decomposition may occur with a substance in the packaging" [8, p. 311]. The SADT is a measure of "the combined effect of the ambient temperature, reaction kinetics, package size and the heat transfer properties of the substance and its packaging" [8, p. 311].

At the time of the incident, Clearon's NaDCC dihydrate (CDB-56®) safety data sheet (SDS) listed a NaDCC decomposition temperature[e] of 240°C to 250°C.

1.5 Similar Chlorinated Isocyanurate Handling Facilities in the U.S.

Multiple facilities in the U.S. manufacture, formulate, package, or distribute similar chlorinated isocyanurates, including facilities operated by Bio-Lab (in Conyers, Georgia, and Westlake, Louisiana),[f] Occidental Chemical Corporation (in Sauget, Illinois, and Luling, Louisiana),[g] Clearon Corporation (now Solenis, in South Charleston, West Virginia), and Haviland (in Grand Rapids, Michigan).[h]

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[a] NaDCC is desirable for these uses because it remains relatively stable under ambient storage conditions and in the absence of substantial amounts of moisture [75].

[b] The onset temperature of the exotherm was 81.90°C [10, p. 5]. An exotherm is "the liberation or evolution of heat during the curing of a plastic product or during any chemical reaction" [104, p. 161].

[c] The CSB notes that this report provides temperatures in degrees Celsius because this is the temperature unit predominantly used by Clearon, Optima Belle, and NaDCC literature. **Appendix B** includes the temperature conversions to degrees Fahrenheit.

[d] The United Nations *Manual of Tests and Criteria* includes a series of test methods (Series H test) for determining the SADT. Test Code H.1 is the United States SADT test and "determines the minimum constant temperature air environment at which [self-accelerating decomposition] occurs for a substance in a specified package" [8, p. 315].

[e] When NaDCC dihydrate decomposes, it releases hazardous byproducts such as toxic chlorine gas and creates excess pressure that could over-pressurize a vessel, as happened during the Optima Belle incident.

[f] KIK Consumer Products acquired Bio-Lab in 2013. It manufactures and distributes trichloroisocyanuric acid, among other chemicals.

[g] Oxy Chemical Corporation manufactures chlorinated isocyanurates, including NaDCC dihydrate and NaDCC under the registered trademarks ACL®.

[h] Durachlor by Haviland is a brand of Haviland's Pool and Spa division [73]. NaDCC dihydrate is one of several pool chemicals Haviland manufactures.

1.6 CDB-56® Dehydration

1.6.1 Contractual Agreement Between Optima, Clearon, and RCI

Clearon contracted another company to manufacture NaDCC (CDB-63®), an arrangement known as "toll manufacturing." In August 2020, Clearon submitted a toll manufacturing inquiry to RCI for the dehydration of NaDCC dihydrate (CDB-56®) to manufacture NaDCC (CDB-63®), stating:[a]

> **Service Required:** Full-scale manufacturing
>
> **Technical Description:** Chlorinated Dry Granular Solid [CDB-56®] dried via fluid bed [dryer]. All metals in contact with the product or dust should be Inconel 600. Other materials may corrode – causing damage to the equipment and black speck issues in the product. Using hot air, preferably between 100°C and 135°C, uniformly dry the raw material to a moisture content of approximately 0.5-1.0%. Do not exceed an inlet air temperature of 140°C.
>
> **Timing:** Immediate

RCI asked Clearon if an alternate drying technology—such as a rotary double cone dryer—was acceptable.[b] Clearon responded, saying it "could be viable" and "maybe worth a conversation." The CSB does not have evidence that a comprehensive evaluation was conducted to identify the potential hazards of using an alternate dryer, excluding equipment material of construction. After communications regarding viable alternate dryer options, RCI identified to Clearon a possible service provider—Optima Belle[c]—who had multiple double cone dryers constructed of corrosion-resistant material, including Hastelloy® C-276. In September 2020, RCI, Clearon, and Optima Belle began holding meetings to discuss the toll manufacturing project. Clearon provided a "CDB-56 Drying to CDB-63" Toll Manufacturing Technology Package (Technology Package), as well as a "report related to CDB-63 decomposition studies" in October (see Section 4.1.2).

RCI submitted the following proposal to Clearon:[d]

> The following proposal covers four (4) trial drying runs involving the drying of Clearon supplied CDB-56 which when dried is designated CDB-63.
>
> **<u>Operation / Process:</u>**
> Clearon will be providing to Richman Chemical and our manufacturing partner Optima Chemical CDB-56, Clearon Materials #12000006, which will contain between 11.0%-13.9% moisture. Clearon is contracting with RCI/Optima to dry the CDB-56 down to a moisture content of <1% [to produce CDB-63].
>
> **<u>Timing:</u>**
> Once decomposition data has been reviewed and a [purchase order] is in place we will provide an estimated run date. We expect to be able to conduct the trial, 4 drying batches, two 24-hour run days, within 2020.

---

[a] The Clearon inquiry to RCI did not state an ISO or Good Manufacturing Practices certification requirement. Neither did it include an assessment or requirement to ensure compliance for such industry certifications.

[b] Section 4.3 discusses rotary dryers versus fluidized bed dryers.

[c] RCI proposed Optima Chemical for the service, which included dryers at Optima sites in both Belle, West Virginia and Douglas, Georgia. Clearon ultimately selected the Optima Belle location in Belle, West Virginia, to conduct the dehydration operation.

[d] The original proposal was submitted on October 27, 2020, with a revision on November 3, 2020.

In November 2020, after Optima Belle reviewed the CDB-63® decomposition report and responded, "it appears we can stay in the safe range with a few adjustments to our normal operating procedures," Clearon agreed to the proposal and continued working with RCI and Optima Belle to prepare for the conversion of four batches of its CDB-56® into CDB-63® at the Optima Belle facility.[a] Each batch was expected to start with approximately 8,820 pounds (lbs.) of CDB-56®.

The "Process" Section of the Technology Package provided to RCI and Optima Belle states:

> Toll manufacturer must develop the specific process for manufacturing at their facility.
>
> Clearon will review the process developed by the toll manufacturer to confirm it meets the requirements of this technology package.

Optima Belle used the technical information provided by Clearon to develop a dehydration process using its on-site equipment, as described below.

1.6.2 Dehydration Process Description

To dehydrate approximately 8,820 lbs. of CDB-56®, Optima Belle used its existing 165 cubic feet (working volume) Hastelloy® C-276 rotary double cone dryer (dryer) (**Figure 2**), utilities, and other process equipment (**Figure 3**). CDB-56® has a bulk density of 56–60 pounds per cubic foot; so 8,820 lbs. of the granular material would fill 89−95% of the dryer working volume.[b] The dryer, which could be rotated to tumble the contents, also had a jacket, which could be charged with process utilities, including cooling water, steam, and nitrogen. The CDB-56® was to be heated by steam in the jacket while tumbling the dryer. Optima Belle could remove evolved gases (such as water vapor from dehydration) using the dryer's vacuum system.[c] The vacuum system carried vapor discharge from the dryer to a tank with a level indicator[d] that served as a liquid collection and knockout tank,[e] where water could be collected and drained off. The vapor stream then flowed from the tank through a condenser (that condensed and removed additional liquid) and an eductor, which provided the driving force for the vacuum conditions in the dryer.[f] Ultimately, vapors from the dryer flowed into a scrubber, where they were mixed with a sodium hydroxide solution (caustic) to control the pH of the scrubber solution at greater than 7 and avoid an environmental permit deviation.[g] Liquid from the scrubber was transferred to waste totes, and vapors from the scrubber went into the atmosphere.

[a] The contractual agreement between RCI and Clearon did not include ISO or Good Manufacturing Practices certification-related assistance or services.

[b] 89−90% of the dryer working volume is between 147 to 157.5 cubic feet of granular material.

[c] The CSB calculated that approximately 125 gallons of water could be removed from 8,820 lbs. of CDB-56® during dehydration.

[d] The tank was equipped with a radar-level device calibrated at a span of 92 inches, limiting its capacity to indicate liquid level from an approximately 8,820-pound CDB-56® batch dehydration process capable of releasing approximately 125 gallons of water.

[e] A knockout tank is typically a vessel or drum used to separate liquids from a gas or vapor.

[f] The eductor is a device that pulls vapor from the dryer to decrease the dryer pressure below atmospheric pressure.

[g] If the eductor could not pull water vapor from the vessel, the water vapor could remain in the vessel, come into contact with the CDB-56®, and become a potential decomposition risk.

Figure 2. Optima Belle's rotary double cone jacketed dryer. (Credit: Optima Belle)

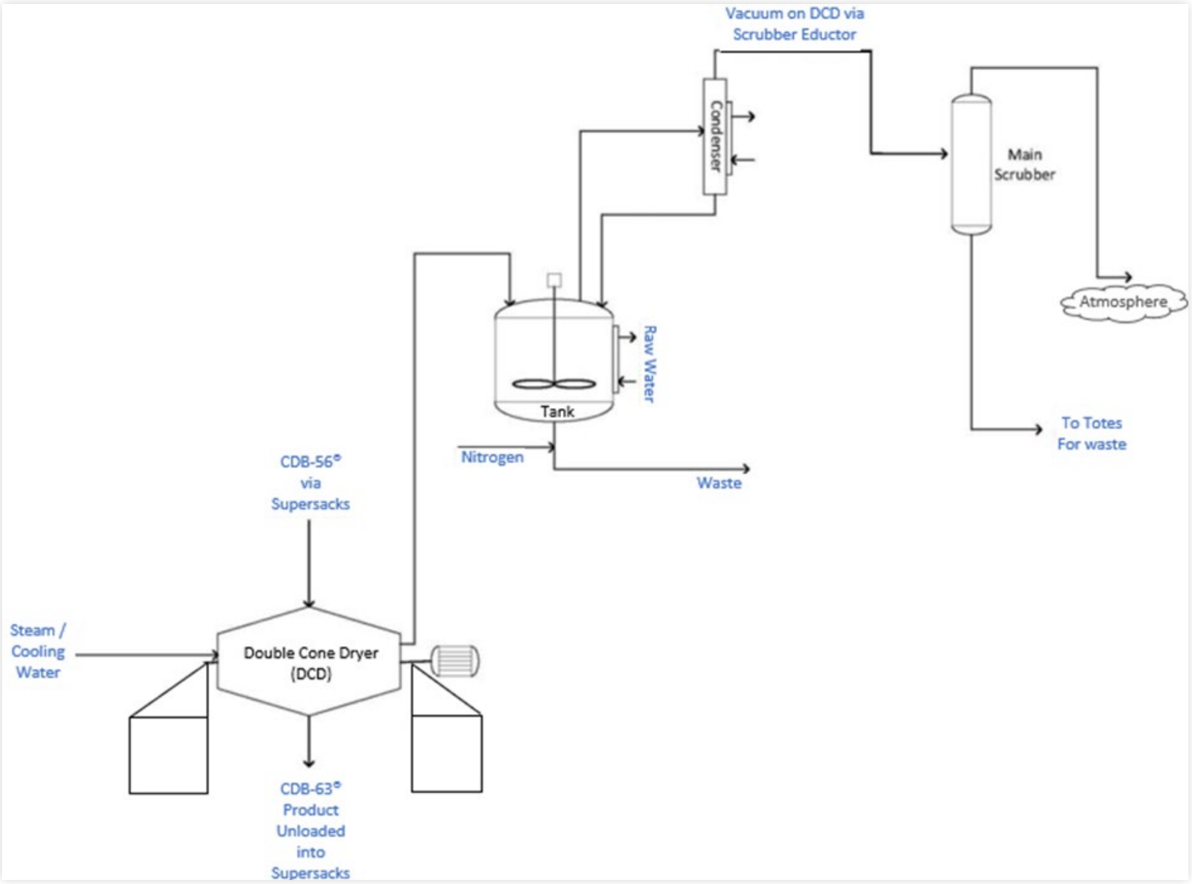


Figure 3. Optima Belle's CDB-56® dehydration flow diagram. (Credit: Optima Belle, annotations by CSB)

By design, the steam used to apply indirect heating to the dryer was regulated to 30 pounds per square inch gauge (psig). As a result, the maximum internal dryer temperature that could be achieved was approximately 130°C. Optima Belle's technical lead (a chemical engineer and process manager) for the dehydration process believed that this temperature would be sufficiently high for the release of the water of hydration from the CDB-56® but low enough to avoid the SDS listed decomposition temperature of 240°C to 250°C.

1.6.3 Dryer Equipment

Optima Belle's 165 cubic feet Hastelloy® C-276 rotary double cone dryer was designed and built as a pressure vessel in accordance with the American Society of Mechanical Engineers (ASME) *Boiler and Pressure Vessel Code* (BPVC).[a] Two valves constructed of stainless steel were attached to the dryer (**Figure 4**). The first was a 12-inch to 10-inch reducing manual ball valve installed on one end,[b] and the second was a 2-inch sample port valve installed on the manway on the opposite end.[c] Clearon expected some corrosion to occur in the stainless steel over long-term use with the CDB-56® dehydration process, but significant corrosion was not expected during the four batches.

[a] The rotary dryer's vessel/shell was designed for 30 psi and full vacuum (FV).
[b] The 12-inch to 10-inch reducing valve was used to charge material into the dryer.
[c] The 2-inch sample port valve is attached to the dryer's 18-inch manway.

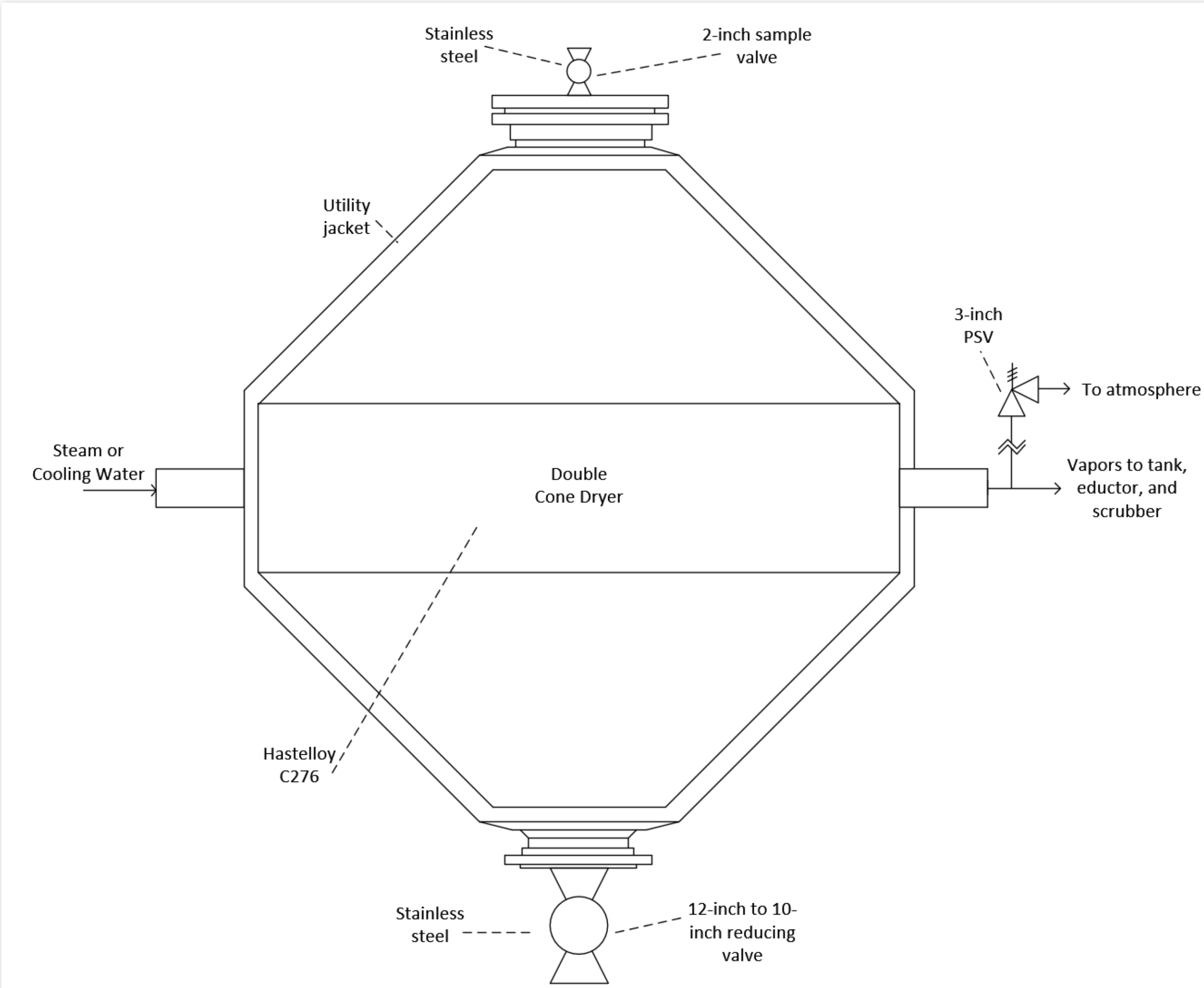


Figure 4. Conceptual diagram of Optima Belle's 3-inch PSV and rotary double cone dryer with a 12-inch to 10-inch charge valve and 2-inch sample port valve. Not to scale. (Credit: CSB)

A 3-inch pressure safety valve (PSV) and rupture disc in series, each set at 30 psig, were used to protect Optima Belle's dryer from over-pressurization (**Figure 4**). The PSV was located on the dryer's 3-inch vacuum line.

1.6.4 Dehydration Procedure

Clearon (and its predecessors) had previously dehydrated CDB-56® to CDB-63® using a fluidized bed dryer (see Section 4.3.1) at its South Charleston, West Virginia, facility. Neither Clearon, Optima Belle, nor RCI had ever conducted the CDB-56® dehydration using a pressure-rated rotary double cone dryer, and therefore, Optima Belle developed a new dehydration procedure utilizing the rotary dryer which was provided to Clearon for review.[a] The newly developed procedure included the following steps:

[a] Optima Belle only performs batch operations at its facility; there are no continuous operations.

1. Start the scrubber circulation.
2. Add the CDB-56® into the dryer and close the manual charge valve.
3. Ensure water is flowing through the tank's jacket and that the tank is connected to the correct vent header. [**Figure 2** shows the tank.][a]
4. Begin the rotation of the dryer.
5. Pull a vacuum using the main scrubber system. A nitrogen sweep may be applied inside the dryer at the discretion of Optima Belle Management or the Customer.
6. Apply steam to the dryer's jacket.[b,c] This step of the batch procedure also includes the following note:

   > If the rotation on the double cone stops, immediately shut off steam to remove heat from going to the vessel. Consult with management if cooling water needs to be applied to the jacket. If rotation stops, ensure a nitrogen sweep is going to the double cone until rotation resumes.

7. Allow the internal dryer temperature to reach 120°C.[d] **"Do not allow the internal temperature to increase beyond 130°C!"**[e]

The procedure also included physical data and reactivity information (**Figure 5**),[f] as well as an "Emergency Shutdown Procedure" section that directed personnel to turn off the steam and apply cold water to the dryer's jacket in the event the dryer's rotation stopped for any reason (**Figure 6**). The "Drying" section of the procedure, as quoted in Step #6 above, directs personnel to consult with management if cooling water needs to be applied to the jacket if rotation stops. The Emergency Shutdown Procedure (**Figure 6**) directs personnel to apply cold water to the dryer jacket if the rotation stops for any reason. Optima Belle's procedure did not specify whether Optima Belle would follow the instructions noted under the drying section or the instructions listed under the Emergency Shutdown Procedure if the dryer rotation stopped.

[a] Optima Belle's collection tank for its *Procedure for CDB-63 Drying (Clearon)* was Reactor 5.

[b] Optima Belle's saturated steam supply from its production building is not capable of heating the dryer above 200°C.

[c] Clearon had recommended that Optima Belle "[o]nly begin or maintain heating the dryer if it is rotating" to avoid localized hot spots when the material is not moving/mixing inside the dryer.

[d] Optima Belle management expected the CDB-56® water of hydration to release at 120°C

[e] The technology package is intended to provide safety, manufacturing, quality, and logistics information necessary to produce CDB-63®. It states: "Heat dryer to a temperature range of approximately 100–130°C, and no more than 140°C. Note: Somewhat lower temperature may achieve drying [dehydration] if the unit is under vacuum. Trials will be used to determine final steam/temperature settings and the resulting cycle times."

[f] The batch procedure also included personal protective equipment requirements.

Physical Data

CDB-56 (raw material)	Chemical Formula	$C_3N_3O_3Cl_2Na.2H_2O$
	Chemical Name	Sodium dichloro-s-triazinetrione dihydrate
	Appearance	White powder
CDB-63 (finished product)	Chemical Formula	$C_3N_3O_3Cl_2Na$
	Chemical Name	Sodium dichloro-s-triazinetrione
	Appearance	White powder

Reactivity

CDB-56 (raw material)	Autoignition temperature	N/A
	Extinguishing Agents	Copious amounts of Water
	Incompatibility	oil, fuels, solvents, reductants, small amounts of water, acids, strong oxidizing agents
CDB-63 (finished product)	Autoignition temperature	N/A
	Extinguishing Agents	Copious amounts of Water
	Incompatibility	oil, fuels, solvents, reductants, small amounts of water, acids, strong oxidizing agents

Refer to Material Safety Data Sheets for Further Information.

Figure 5. Excerpt from Optima Belle's *Procedure for CDB-63 Drying (Clearon)* listing physical data and reactivity information. (Credit: Optima Belle)

Emergency Shutdown Procedure

1. If the emergency occurs during a chemical transfer, stop the transfer immediately by closing the valves in the appropriate piping systems.
2. In the event the rotation of the double cone stops for any reason, turn off steam and apply cold water to the double cone dryer jacket. Continue vacuum, if possible. If vacuum cannot be maintained, apply a small nitrogen sweep to the double cone dryer for inertion.

Figure 6. Excerpt from Optima Belle's *Procedure for CDB-63 Drying (Clearon)*. (Credit: Optima Belle)

Product samples were to be taken every 30 minutes or as directed by management and given to the quality lab for moisture analysis, using gravimetric analysis, and visual inspection.[a] Once the product inside the dryer passed its moisture analysis, the steam was to be removed, the dryer's jacket was to be blown out with nitrogen, the vacuum released, the nitrogen purge turned off (if applicable), and the dryer cooled by flowing water through the jacket. Then the dryer was to be prepared for "Dryer Packout" once its internal temperature reached 50°C.[b]

1.7 Description of Surrounding Area

Figure 7 shows the Optima Belle facility and depicts the area within a 1-, 2-, and 3-mile radius of the facility boundary.

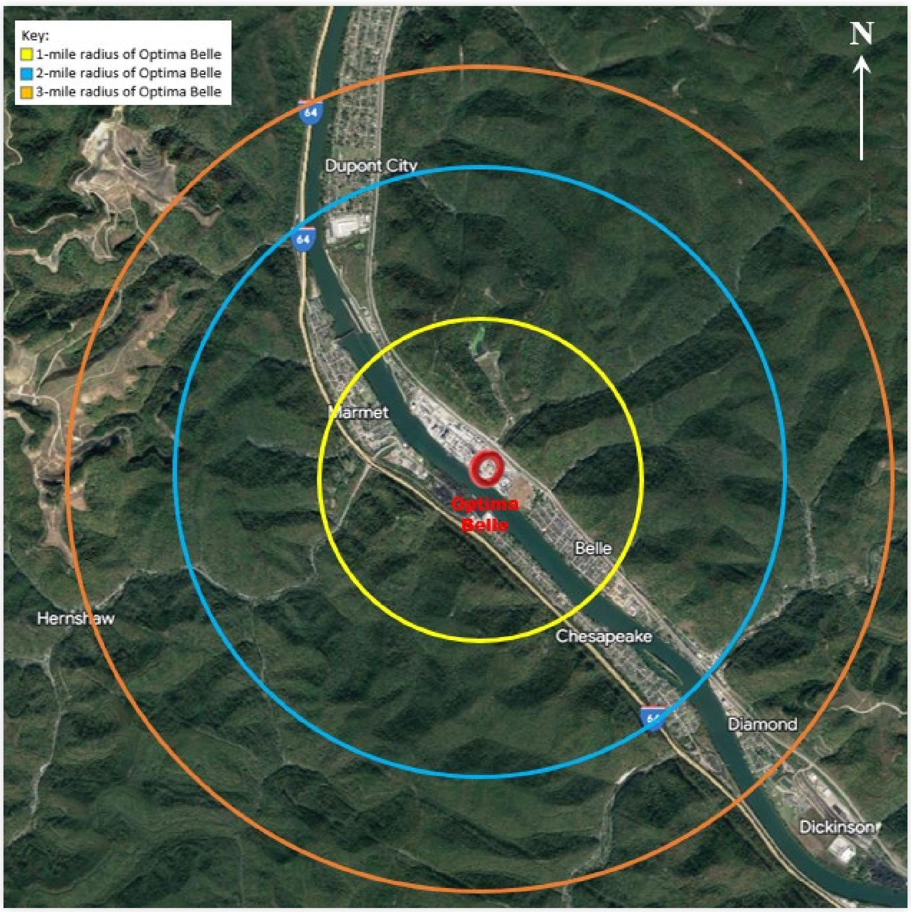


Figure 7. Optima Belle overhead imagery and surrounding vicinity. (Credit: Google Earth, annotations by CSB)

[a] The quality lab used a Mettler Toledo HG53 Halogen Moisture Analyzer to determine moisture content (mass percent after heating to a predetermined temperature) for the CDB-56®. The measured percentage was recorded on an Inspection Form. The results of the visual inspection were also recorded as pass or fail.

[b] The "Dryer Packout" is the process of unloading the dryer's contents (CDB-63®) into empty super sacks (flexible bulk bags) sitting on top of a pallet and scale. Once each super sack is filled, final preparation steps are taken before moving the material to the warehouse, including sealing the super sacks (inner liner and outer neck).

Summarized demographic data for the surrounding vicinity of the Optima Belle facility are shown below in **Table 1**. More detailed information, including data sources, can be found in **Appendix A**.

Table 1. Summarized demographic data of the Optima Belle facility and vicinity.

Population	Race and Ethnicity	Per Capita Income	% Persons Below Poverty Line	Number of Housing Units	Types of Housing Units
13,600	• 92% White • 4% Black • 3% Two+ • 1% Hispanic	$25,908[a]	16%	6,746	• Single Unit 73% • Multi-Unit 7% • Mobile Home 20%

[a] Census Reporter reports that Kanawha County's per capita income is $28,837 [90]. The Census Bureau reports that the 2021 per capita income for the United States is $41,285 [103].

2 Incident Description

2.1 Startup on December 8, 2020

On December 8, 2020, at approximately 10:00 a.m., Optima Belle employees started the first of four planned batch operations. They added approximately 8,820 lbs.[a] of CDB-56® to the dryer via the manual 10-inch charge ball valve.[b] After adding the CDB-56®, Optima Belle closed the valve, started the dryer's rotation, reduced the dryer's internal pressure to vacuum conditions, applied a slight nitrogen purge inside the dryer, and slowly added saturated 30 psig steam (approximately 130°C) to the dryer's jacket. Clearon representatives were present during the start of this first CDB-56® batch operation. RCI, the third party to the tolling agreement, was not present during the operations on December 8, 2020.

2.2 Process Monitoring and Troubleshooting

Throughout the day on December 8, 2020, Optima Belle and Clearon monitored the dehydration progress. As prescribed in the CDB-56® dehydration procedure (see Section 1.6.4), Optima Belle operators stopped the dryer's rotation and heating approximately every 30 minutes to take a sample of the material, which was then visually inspected and examined for moisture content to monitor the dehydration progress.[c] Later in the day, site personnel decided to extend the time between samples to one hour.

By late afternoon, personnel observed that the dryer internal temperature was increasing slower than anticipated and that the product moisture content was not decreasing as expected. An Optima Belle supervisor observed excessive condensation and water in the dryer's jacket through the sight glass and asked that the dryer be stopped to drain the jacket. At approximately 5:04 p.m., Optima Belle employees stopped the dryer rotation,[d] closed the steam supply, and manually drained the dryer's jacket.[e] At approximately 5:30 p.m., the Clearon representatives left the site for the evening.

At approximately 6:00 p.m., Optima Belle then restarted the dryer's rotation and re-introduced steam to its jacket. By 7:00 p.m., the internal dryer temperature began to rise as anticipated.

2.3 Dryer Inspection

At approximately 7:30 p.m., a sample of granular material from the dryer indicated similar moisture levels as previous samples taken throughout the day (greater than 11% moisture) but failed its visual inspection. Dark specks were observed in the white material.

At approximately 8:13 p.m., after a text message between Optima Belle and Clearon regarding the dark specks, Optima Belle stopped the steam flow to the dryer jacket, stopped the dryer's rotation, and raised the dryer

[a] Clearon supplied Optima Belle the CDB-56® inside nonrefillable flexible bulk bags called sacks or super sacks, each holding approximately 2205 lbs. of material. Clearon provided Optima Belle with sixteen super sacks of CDB-56®.

[b] A hoist and dump station were used to add the material. The dump station was removed after the material was added.

[c] The Optima Belle Lab analyzed the first sample, which had a moisture content of 11.83% and passed its visual inspection at 2:27 p.m. on December 8, 2020.

[d] At approximately 5:04 p.m., the dryer's internal temperature was approximately 39°C.

[e] At approximately 6:00 p.m., the dryer's internal temperature was approximately 40.86°C.

pressure to atmospheric pressure to investigate the cause of the dark specks observed in the samples. While the dryer itself was corrosion-resistant, the valves were stainless steel and, therefore, susceptible to corrosion. Optima Belle and Clearon suspected that corrosion of the stainless steel valves could have caused the dark specks.[a,b] Optima Belle employees examined the two stainless steel valves and observed that they both were coated with a “black tarry-looking substance” and “a brown, tacky substance,” which they thought could be from corrosion of the steel. An Optima Belle employee told the U.S. Chemical Safety and Hazard Investigation Board (CSB) that upon looking inside the dryer, the product appeared lumpy with a “yellowish” tint, but it was unclear whether the yellowish color was a flashlight reflection.[c] Optima Belle employees also described a strong chlorine smell when they opened the dryer. At 8:25 p.m., the lab analyzed its last sample, which also failed visual inspection.

The dryer’s rotation remained off while Optima Belle investigated the cause of the black specks and inspected the two stainless steel valves. Contrary to the “Emergency Shutdown Procedure” (**Figure 6**), Optima did not apply cold water to the jacket and did not apply a vacuum while the dryer’s rotation was stopped. The dryer’s internal temperature continued slowly increasing (**Figure 8**) despite no steam being supplied to the jacket.[d] By this point, unidentified by Optima Belle, the dryer contents had likely started to decompose at a rate sufficient to cause a runaway reaction. With no rotation and no applied vacuum, any released water vapor would have remained in contact with the material in the dryer.

At 8:37 p.m., Optima Belle had closed the dryer’s 12-inch to 10-inch reducing manual ball valve (**Figure 4**) and again pulled a vacuum on the dryer. Optima Belle did not restart the dryer’s rotation. At this time, the recorded dryer’s internal temperature was 77°C.[e]

---

[a] To inspect both valves attached to the dryer, the dryer had to be rotated 180 degrees. This rotation occurred at approximately 8:33 p.m.

[b] Clearon had previously identified that “[a]ll metals in contact with the product or dust should be Inconel 600. Other materials may corrode – causing damage to the equipment and black speck issues in the product.”

[c] The Optima Belle employee explained that a valve on the rotary dryer was opened, allowing them to shine a flashlight inside and see the product.

[d] Optima Belle’s internal dryer pressure unit of measurement was inches of mercury (in. Hg) in the DCS.

[e] Because the dryer was not rotating, the recorded dryer’s internal temperature likely did not represent the entire mass inside the dryer.

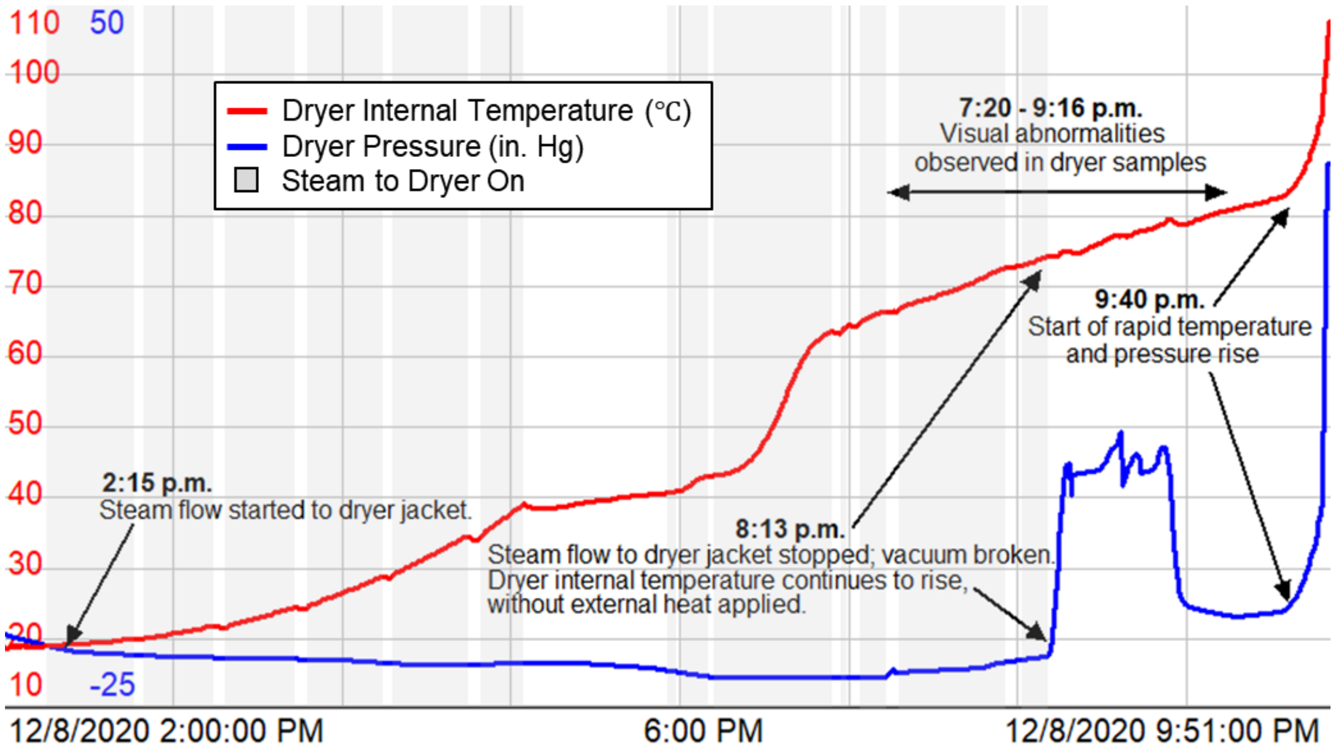


Figure 8. Optima Belle's rotary dryer operating conditions on December 8, 2020. Areas shaded with gray indicate times during which steam was applied to the dryer jacket. (Credit: CSB)

At approximately 9:16 p.m., Optima Belle called Clearon to discuss the possible corrosion and the plan moving forward. At approximately 9:20 p.m., while the dryer temperature continued to rise without the application of steam to the jacket, the main scrubber's pH dropped below 8.[a] Unknown by Optima Belle, this drop in pH was likely the result of decomposition products, including chlorine, exiting the dryer.[b] Concerned primarily with avoiding an environmental permit deviation rather than interpreting this pH drop as an indicator of decomposition activity inside the vessel, Optima Belle took action to increase the scrubber pH.[c] Due to a non-functioning automated caustic supply valve, two Optima Belle employees began manually adding caustic soda to the scrubber to prevent the pH from dropping below 7.[d]

By approximately 9:30 p.m., Optima Belle and Clearon agreed during a telephone call to stop the batch operation for the night and continue troubleshooting the black specks in the morning.[e] Optima Belle planned to take one final sample from the dryer, replace the reducing stainless steel valve with a 12-inch blind flange, apply cooling water to the jacket, and rotate the dryer for the remainder of the night until the team could regroup in the morning. Around the same time, Optima Belle began performing a nitrogen blowdown of the dryer jacket.[f]

[a] At the time of the incident, Optima Belle's air permit required its main scrubber pH to be greater than 7 and included a low-level pH alarm setpoint of 7.5.

[b] Post-incident, a Clearon employee told the CSB that he was unaware of the drop in the scrubber pH and explained that the pH would decrease as traces of chlorine were being released from the NaDCC dihydrate depending on the scrubber design/scrubbing agent.

[c] Optima Belle personnel told the CSB that the scrubber pH was to be maintained above the limit of 7 as specified in Optima Belle's air permit.

[d] The automated caustic supply valves are manipulated from the control room when functioning.

[e] The CSB does not have evidence that Clearon was aware of the dryer's internal temperature or the pH drop in the scrubber at that time.

[f] Optima Belle's dryer jacket heating and cooling system design required the jacket to be blown with nitrogen to remove the steam before applying cooling water. Mechanical failures, equipment damage, and/or thermal issues may occur if steam and cooling water is mixed in the jacket.

Following the call, the board operator left the control room to manually open valves to stop the nitrogen blowdown to the jacket and apply cooling water (see Section 4.3.2), as the two field operators were occupied with trying to raise the scrubber pH.[a] At this time, the dryer's recorded internal temperature was slightly above 80°C.

2.4 Explosion

At approximately 9:40 p.m., before Optima Belle could resume rotating the dryer, the dryer temperature and pressure sharply increased as the NaDCC dihydrate (CDB-56®) decomposed (**Figure 8**).[b] The last recordings in the historian data indicate the dryer temperature reached 108°C and the dryer pressure reached 33 inches of Hg (in. Hg) before the dryer catastrophically exploded.

Debris and metal projectiles from the exploded dryer struck a nearby methanol pipe owned by another site tenant,[c] and the releasing methanol caught fire (**Figure 9**). Metal fragments were also found off-site on U.S. Route 60 and roughly a half mile from the site.[d]

Figure 9. Fire following the Optime Belle dryer explosion. (Credit: The New York Times [9])

The Optima Belle board operator, who was working to apply cooling water to the dryer's jacket,[e] was fatally injured. He was found alive, trapped under debris but died later at the hospital. His death was ruled as an

[a] The main scrubber's pH dropped below 7 at approximately 9:32 p.m.

[b] After the incident, water was observed in the bottom of the tank (**Figure 3**) below the height of the impeller blades, indicating that the release of the water of hydration from the CDB-56® had started and was being collected in the tank, despite the liquid level likely not reporting on the radar device (see Section 1.6.2).

[c] The methanol pipe was less than 100 feet from the Optima Belle process building, where the dryer was installed.

[d] The Chemours Belle site fire brigade, Belle Volunteer Fire Department, Kanawha County Emergency Management, West Virginia Emergency Management, and others responded to the incident. Chemours FC, LLC Belle provides Optima Belle fire protection and emergency response under a 2015 service agreement.

[e] Cooling water had been applied to the dryer's jacket just before the explosion.

NaDCC intoxication from the fumes he had inhaled. The two Optima Belle field operators were evaluated for respiratory irritation, and one Kanawha County resident reported an injury.[a] Optima Belle's estimated property damage from the incident is $33.1 million.

[a] The Kanawha County resident told the police that he went to the hospital for leg pain after a large fragment from the explosion landed on Route 60, resulting in an accident involving two personal vehicles.

3 Technical Analysis

3.1 Chlorinated Dry Bleach (CDB) Decomposition

3.1.1 Post-Incident Chemical Reaction Hazard Testing

After the incident, DEKRA Services, Inc., a third-party process safety laboratory (among other specialties), was commissioned[a] to conduct Differential Scanning Calorimetry (DSC) and Accelerating Rate Calorimetry (ARC) testing using samples of CDB-56® material supplied by Clearon to Optima Belle [10]. **Appendix C** details the testing methods and conclusions. DSC and ARC are two tests used to determine the thermal data necessary for evaluating thermal process safety.

Differential Scanning Calorimetry (DSC)

DSC is a thermal analysis technique that assesses a material's heat energy uptake as its temperature is raised [11]. The technique can be used for various analyses, including thermal stability, thermal phase transition characterizations, the heat of fusion, and oxidation behavior. DSC tests use very small samples and have a fast turnover, typically only a few hours. The post-incident DSC testing for CDB-56® was performed in test cells under an air headspace that represented the likely conditions inside the dryer on December 8, 2020, and under nitrogen. The DSC test results for both conditions measured two absorptions of heat (endotherms) and two evolutions of heat (exotherms), with the total heat of reaction (energy released during decomposition) greater than one kilojoule per gram (1,000 joules per gram [J/g]).[b,c] The detected onset of the first endotherm was at 63.93°C, and the first exotherm was detected at 114.10°C. **Figure 10** shows the DSC results of the test performed under air.[d]

[a] Optima Belle commissioned DEKRA Services, Inc. to conduct the CDB-56® DSC and ARC testing per compiled chemical sampling and analysis protocols written by Exponent on behalf of Optima Belle and approved by RCI, the CSB, and The Chemours Company. The protocols were also made available to Clearon.

[b] As an industry reference, 2,4,6-Trinitrotoluene, commonly known as TNT, has a heat of decomposition of 5.1 KJ/g [93, p. 541] and is used as a high explosive for military and industrial applications. 8,820 lbs. of NaDCC is equivalent to 2,272 lbs. (1.14 tons) of TNT.

[c] A 6.69-milligram test sample of CDB-56® was used for the DSC tests.

[d] No significant difference was seen in the DSC test results measured under air and nitrogen (see **Appendix C**).

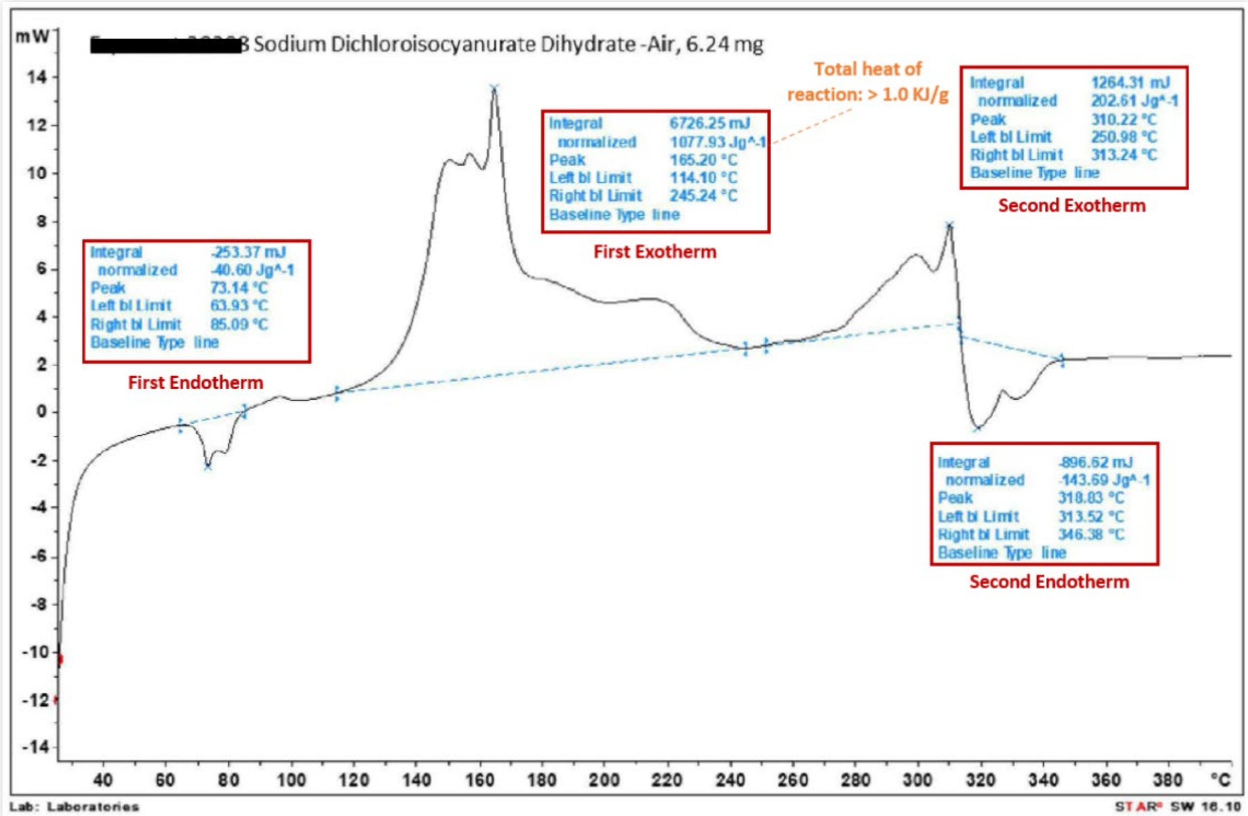


Figure 10. Post-incident NaDCC dihydrate energy vs. temperature DSC results. (Credit: Optima Belle; DEKRA Services, Inc.)

Accelerating Rate Calorimetry (ARC)

ARC is "a technique in which a substance is heated in stages until very slow decomposition [or other reaction] is detected [12]." ARC testing detects the onset temperature and other relationships of exothermic reactions in a confined adiabatic environment.[a] It can be used to measure both the amount of heat released and the rate at which the heat is released. For CDB-56®, the ARC testing showed exothermic activity detected at 81.90°C, leading to a thermal runaway and subsequent failure/destruction of the test cell.[b] **Figure 11** shows the ARC test's temperature and pressure versus time plot of a 3.86-gram test sample. The laboratory reported that the increases in pressure and temperature in the explosive reaction at the end of the test were so rapid that data could not be fully recorded. **Figure 12** shows the test cell before it was used to conduct the NaDCC dihydrate ARC test and after it exploded during the test. The highest exotherm self-heat rate recorded was approximately 810.35°C/min at 150.57°C, and the highest pressure rate recorded was approximately 17,571 psi/min at 128.18°C.

[a] In an adiabatic environment there is no exchange of heat or mass between the environment or thermodynamic process.

[b] The test cell is a sample container or "spherical bomb" for the calorimeter, as shown in Figure 1 of the ASTM E1981-98 *Standard Guide for Assessing Thermal Stability of Materials by Accelerating Rate Calorimetry* [98, p. 2].

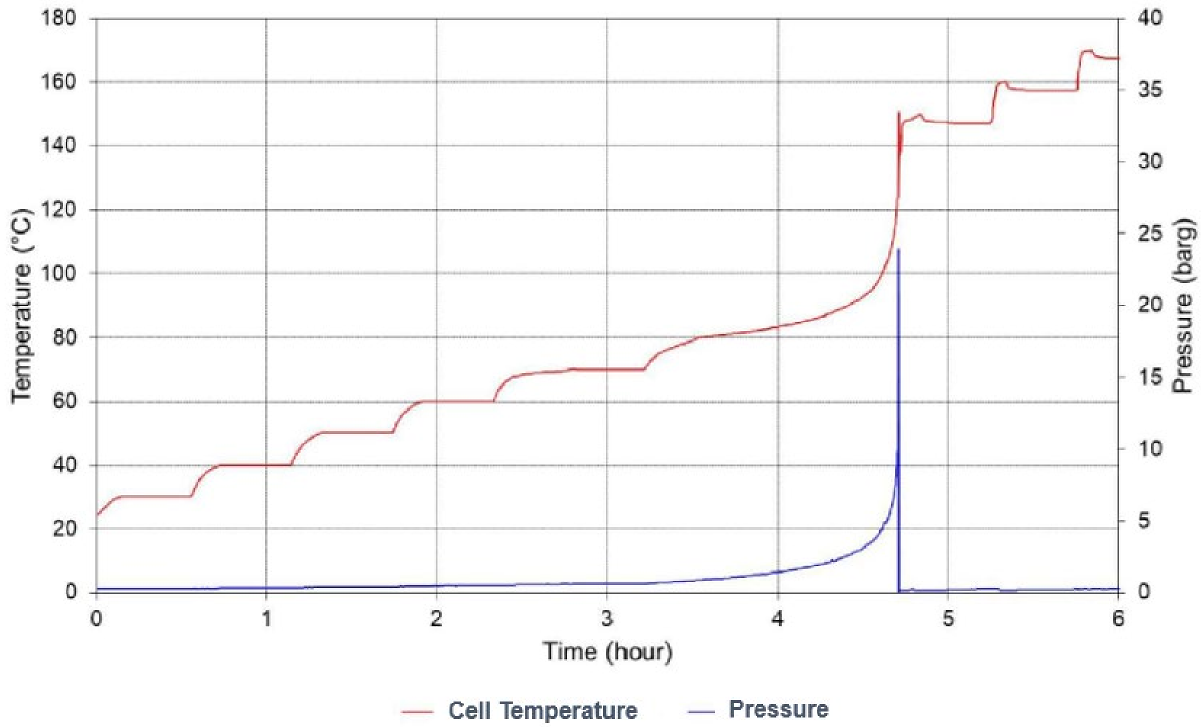


Figure 11. NaDCC dihydrate temperature and pressure vs. time. (Credit: Optima Belle; DEKRA Services, Inc.)

Figure 12. Cell used in the post-incident ARC test for NaDCC dihydrate (see **Appendix C**). (Credit: Optima Belle; DEKRA Services, Inc.)

3.1.2 Process Data

Dryer Temperature and Pressure

The CSB reviewed recorded process data leading up to the incident. Dryer internal temperature and pressure versus time are shown in **Figure 8**. Even after the steam to the jacket was shut off, the temperature inside the dryer continued to slowly increase up to approximately 83°C before both the temperature and pressure began increasing exponentially until the dryer exploded.

Vapor Scrubber pH

The vapors and gases that were expected by Optima Belle to release from the dryer during the dehydration process included traces of chlorine. These vapors and gases were routed through a caustic scrubber before they were vented to the atmosphere (**Figure 3**).[a] Optima Belle equipped the scrubber with a pH meter, and the scrubber pH was typically controlled automatically via control valves. As shown below in **Figure 13**, the scrubber's pH read approximately 12 at the start of the dehydration process. As the dehydration process progressed, the scrubber's pH started decreasing. Beginning at approximately 8:10 p.m., the pH fell sharply, from approximately 11.4 to under 7 in less than 1.5 hours. The CSB concludes that the sharp drop in the scrubber pH was an indication that decomposition was likely occurring in the dryer since a CDB-56® decomposition reaction releases much higher amounts of chlorine than the CDB-56® dehydration process.

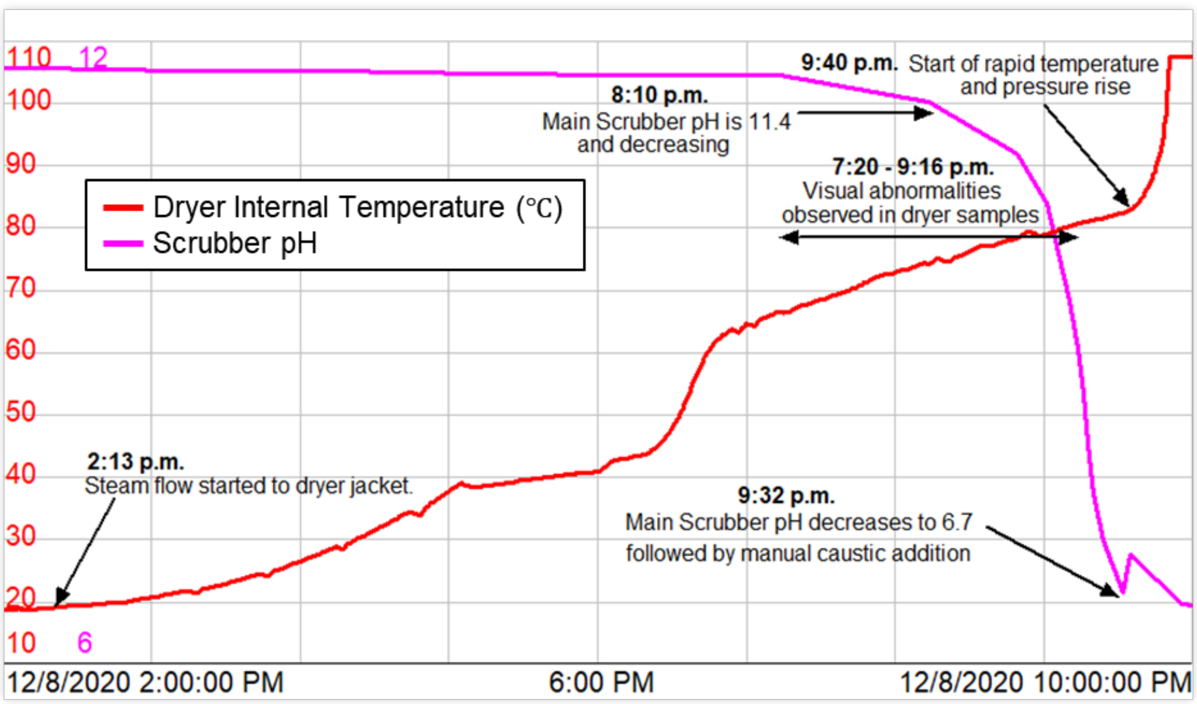


Figure 13. Dryer's internal temperature and scrubber pH on December 8, 2020. (Credit: CSB)

At approximately 9:32 p.m. (**Figure 13**), over an hour after the pH started decreasing, Optima Belle employees began manually adding caustic soda to the scrubber because one of two automated caustic supply valves to

[a] The caustic scrubber also serves as Optima Belle's main scrubber in its process building as referenced in this report.

maintain pH was not functioning. An employee also described a strong chlorine smell when they had the dryer open to look inside and after the explosion during the emergency response.

3.1.3 Analysis

ARC testing showed that NaDCC dihydrate can achieve detectable self-accelerating exothermic activity at approximately 81°C when the released water vapor is confined and in close contact with the product (Section 3.1.1). Process data show that the Optima Belle dryer temperature began increasing exponentially once the dryer reached approximately 83°C (Section 3.1.2. Process data also show that the pH in the vapor scrubber began sharply decreasing from 11.4, indicating acidic gas was venting to the scrubber. Operators stated that they smelled a chlorine-like smell during both product sampling and after the explosion (Section 3.1.2). Chlorine is a known decomposition product of NaDCC dihydrate (Section 1.4) that reacts with water (such as the water being removed from the dihydrate or the water in the vapor scrubber) to produce hypochlorous acid and hydrochloric acid. The CSB concludes that the NaDCC dihydrate in Optima Belle's rotary dryer underwent a self-accelerating decomposition reaction.

Optima Belle's dryer was designed for 30 psi and was equipped with a relief system set at the same pressure (Section 1.6.3). However, as discussed in further detail in Section 4.3.3, Optima Belle's dryer pressure relief system was not sized for an NaDCC dihydrate decomposition and was unable to evacuate the generated gas at a sufficient rate to prevent the pressure in the dryer from increasing beyond the dryer's maximum allowable working pressure. Process data show that the pressure inside the double cone dryer began increasing exponentially moments before the explosion (Section 3.1.2). The CSB concludes that excessive pressure produced by the NaDCC dihydrate decomposition reaction caused over-pressurization of the Optima Belle rotary dryer and its subsequent catastrophic failure.

4 Safety Issues

The following sections discuss the safety issues contributing to the incident, which include:

- Process Knowledge Management
- Thermal Hazard Assessment
- Equipment Selection and Design
- Product Tolling Guidance
- Regulatory Coverage of Reactive Hazards

4.1 Process Knowledge Management

As part of their tolling agreement, Clearon provided Optima Belle with a "Technology Package" to assist Optima Belle in the development of its process design and operating procedures for the dehydration process. The Technology Package could be analogous to a process safety information (PSI) package based on its content. Optima Belle then used the information in that Technology Package as the basis for its technical evaluation in the development and hazard analysis of its proposed NaDCC dihydrate dehydration process. As will be described in this section, Clearon lacked effective process knowledge management practices, which contributed to Optima Belle's inadequate understanding of the hazards of the CDB-56® dehydration process and ultimately the dryer explosion.

4.1.1 CCPS and OSHA Guidance

Optima Belle's batch drying process was not subject to regulation by either the OSHA Process Safety Management (PSM) standard or the EPA Risk Management Program (RMP) rule. As a result, there was no requirement beyond those organizations' respective "general duty" requirements for Optima Belle to have a process safety management system.

Despite the lack of regulatory coverage for many processes and chemicals, including those involved in this incident, industry groups have issued extensive guidance that companies can voluntarily adopt to manage the risk of their hazardous chemical processes. One such group is the CCPS within the American Institute of Chemical Engineers (AIChE).

CCPS and Risk Based Process Safety

According to CCPS, process safety management systems are "comprehensive sets of policies, procedures, and practices designed to ensure that barriers to episodic incidents are in place, in use, and effective [13]." In response to what it perceived as stagnation in many organizations' process safety management activities in the years since OSHA and EPA promulgated the PSM standard and the RMP rule, respectively, CCPS has created an example framework intended for use by organizations of all sizes, which it calls Risk Based Process Safety (RBPS) [14, p. 1].

CCPS, in *Guidelines for Risk-Based Process Safety,* identifies four foundational blocks that support 20 elements for its RBPS framework, as illustrated below in **Figure 14**. The four foundational blocks are as follows:

1) Commit to Process Safety – through elements such as process safety culture, workforce involvement, and stakeholder outreach;
2) Understand Hazards and Risk – through elements such as process knowledge management and hazard identification and risk analysis;
3) Manage Risk – through elements such as operating procedures, asset integrity and reliability, and management of change; and
4) Learn from Experience – through elements such as incident investigation and auditing (of safety systems) [14, pp. 23-24].

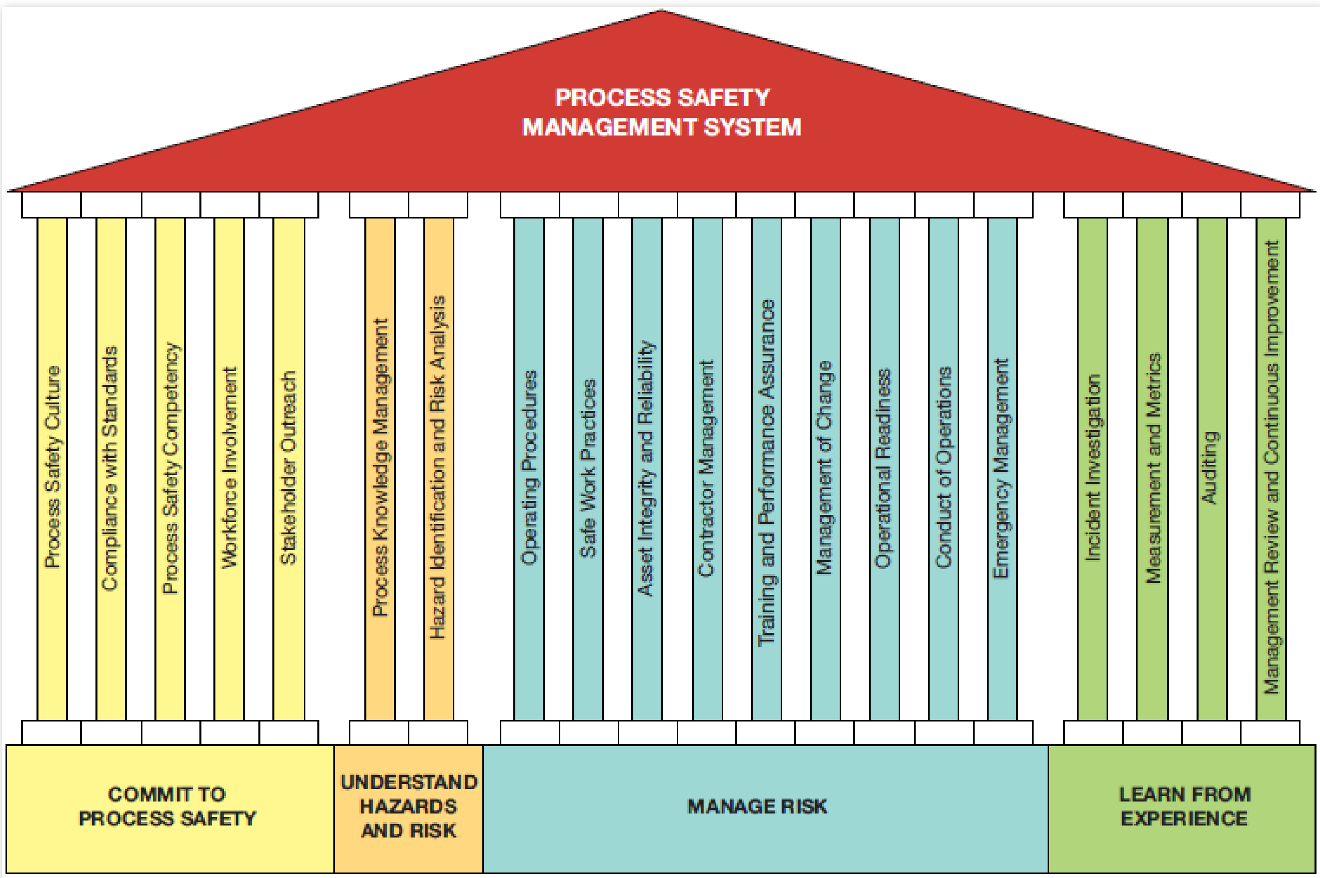


Figure 14. The CCPS Risk Based Process Safety Management System. (Credit: CCPS [14, p. 4])

PSI is one of the elements of the OSHA PSM standard. CCPS defines PSI as:

> Physical, chemical, and toxicological information related to the chemicals, process, and equipment. It is used to document the configuration of a process, its characteristics, its limitations, and as data for process hazard analyses [15].

The RBPS management element most analogous to the PSM PSI element is Process Knowledge Management. CCPS states:

> [T]he primary objective of the [Process Knowledge Management] element is to maintain accurate, complete, and understandable information that can be accessed on demand [14, p. 171].

CCPS further elaborates on the importance of process knowledge management, and states:

> Risk understanding depends on accurate process knowledge. Thus, this element underpins the entire concept of risk-based process safety management; the RBPS methodology cannot be efficiently applied without an understanding of risk. […] Accurate and complete process knowledge is vital to identifying hazards and evaluating risk [14, pp. 171, 173].

According to CCPS, the responsibility for development and maintenance of process knowledge is as follows:

> Knowledge grows and evolves throughout the life cycle of the process and thus is the responsibility of a number of organizations. Early in the life cycle of a process, knowledge is normally developed by the central research, development, and engineering groups. […] Around the time of plant commissioning and startup, responsibility for maintaining and expanding knowledge typically shifts to the facility at which the unit is located. In other cases, the knowledge is maintained by a group external to the facility, such as central engineering […]. Chemical hazard information is developed mainly by suppliers or corporate research and provided to the facility. For example, much of the hazard information on raw materials is documented in [Safety Data Sheets] and product- or chemical-specific guidelines published by the company that manufactures the material [14, p. 172].

OSHA Process Safety Management

OSHA explains the importance of PSI in its PSM guidance publication:

> Complete and accurate written information concerning process chemicals, process technology, and process equipment is essential to an effective process safety management program and to a process hazard analysis [16, p. 2].

For covered processes, OSHA requires companies to compile and maintain PSI on the chemicals and the technology used in the process. For the chemicals used or produced by a covered process, PSI must include, among other things:

- physical data,
- reactivity data, and
- thermal and chemical stability data [17, p. 7].

4.1.2 Technology Package Inadequacy

Technology Package Contents

As part of the CDB-56® tolling agreement, Clearon submitted a "Toll Manufacturing Technology Package" to Optima Belle. The Technology Package included:

- General manufacturing, quality, logistics, and safety instructions for the conversion of CDB-56® to CDB-63®;
- Contact information for relevant Clearon personnel;
- "Technical Product Bulletins" for both CDB-56® (the raw material to be dehydrated) and CDB-63® (the final product);
- Clearon's SDSs for both CDB-56® and CDB-63®;
- A product specification sheet for CDB-63®;
- Instructions for lab QC analysis of CDB-63®; and
- A lab drying curve showing the moisture content versus time of a 5.6-gram sample of CDB-56® dehydrated at 130°C and at atmospheric pressure.

The Technology Package provided information discussed with RCI and Optima as of the date the Technology Package was issued. After discussing the initial Technology Package, Clearon subsequently sent Optima Belle and RCI a technical paper written in 1968 by the FMC Corporation (FMC) Inorganic R&D Department, titled "Thermal Decomposition Studies of CDB-63." The paper discusses the decomposition of CDB-63®. Importantly, CDB-63® was the intended product of the dehydration process, and not the raw material, which was CDB-56®.

The 1968 FMC Report

The report abstract states:

- "The thermal decomposition of sodium dichloroisocyanurate (CDB-63®) was initiated at temperatures as low as 60C to 90C…"
- "In a tightly sealed system NCL_3 build up is rapid enough to cause a detonation."

The report includes:

- Physical properties of NaDCC (CDB-63®);
- A description of the thermal decomposition process of NaDCC (CDB-63®);
- A discussion of the heats of solution, hydration, de-hydration, and hydrolysis, as well as heating studies by thermogravity and DSC for CDB-63®;
- The effect of water on the decomposition of NaDCC (CDB-63®) in both open and closed systems; and
- Data on the CDB-63® decomposition products.

1989 Olin Paper

In March 2022, Clearon provided the CSB with another white paper, which was written in 1989 by Olin. In contrast to the 1968 paper Clearon gave Optima Belle, this paper contains thermal decomposition information for CDB-56®, which was the raw material for the dehydration process and source of the decomposition reaction in this incident, and for CDB-63®, the desired product. The paper was not submitted to Optima Belle as part of the Technology Package. As discussed below, Clearon told the CSB that it did not submit the paper to Optima Belle because it was duplicative of other materials in the Technology Package.

The document compiles various technical reports and analyses performed by and for Olin beginning roughly in 1977 and continuing throughout the 1980s. Among other things, the report details:

- ARC and DSC calorimetry data for NaDCC dihydrate (CDB-56®);
- Various circumstances that can result in NaDCC dihydrate (CDB-56®) decomposition;
- The impact of water vapor on the decomposition of NaDCC dihydrate (CDB-56®);
- The source data for Clearon's CDB-56® storage temperature restriction of 60°C;
- Details on the quantities and identities of gas produced in an NaDCC dihydrate decomposition reaction; and
- Data detailing NaDCC dihydrate decomposition temperatures.[a,b]

Clearon believed that the 1968 FMC paper provided all the necessary information and context that Optima Belle would have needed for the analysis and design of its dehydration process and that the 1989 Olin report would have been redundant. Despite Clearon's assertions to the contrary, the information on CDB-56® contained in this report would have provided important context for the design and operation of the dehydration process.

CDB-56® SDS Inadequacies

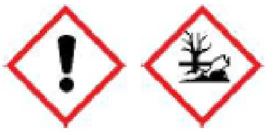
At the time of the incident, the Clearon SDS for CDB-56® lacked key information. For example, the Hazards Identification section (**Figure 15**) contained the following information:

[a] Post-incident ARC testing found that NaDCC dihydrate begins a runaway exotherm at approximately 81°C when heated in a closed container.

[b] The CSB notes that this report provides temperatures in degrees Celsius because this is the temperature unit predominantly used by Clearon, Optima Belle, and NaDCC literature. **Appendix B** includes the temperature conversions to degrees Fahrenheit.

2. Hazards Identification

Acute Toxicity: Oral, Category 4
Serious Eye Damage/Eye Irritation, Category 2
Specific Target Organ Toxicity (single exposure), Category 3
Aquatic Toxicity (Acute), Category 1
Aquatic Toxicity (Chronic), Category 1



GHS Signal Word:	**Danger**
GHS Hazard Phrases:	H302 - Harmful if swallowed. H319 - Causes serious eye irritation. H335 - May cause respiratory irritation. H400 - Very toxic to aquatic life. H410 - Very toxic to aquatic life with long lasting effects.
GHS Precaution Phrases:	P261 - Avoid breathing dust/fume/gas/mist/vapors/spray. P264 - Wash hands thoroughly after handling. P270 - Do not eat, drink or smoke when using this product. P271 - Use only outdoors or in a well-ventilated area. P273 - Avoid release to the environment. P280 - Wear protective gloves/protective clothing/eye protection/face protection.
GHS Response Phrases:	P301+312 - IF SWALLOWED: Call a POISON CENTER or doctor/physician if you feel unwell. P304+340 - IF INHALED: Remove victim to fresh air and keep at rest in a position comfortable for breathing. P305+351+338 - IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing. P312 - Call a POISON CENTER or doctor/physician if you feel unwell. P330 - Rinse mouth. P337+313 - If eye irritation persists, get medical advice/attention. P391 - Collect spillage.
GHS Storage and Disposal Phrases:	P403+233 - Store container tightly closed in well-ventilated place. P405 - Store locked up. P501 - Dispose of contents/container to an approved disposal facility.
Potential Health Effects (Acute and Chronic):	Hazards not otherwise classified (HNOC) or not covered by GHS.
Additional Hazards Information	Contact with acids liberates toxic gas.

Figure 15. Excerpt from the Hazards Identification section of the CDB-56® SDS. (Credit: Clearon)

This section of the CDB-56® SDS contained no information on the substance's ability to undergo a hazardous decomposition reaction, only mentioning that contact with acids liberates toxic gases. As shown in **Table 2** below, other manufacturers of NaDCC dihydrate list more specific information about this effect on their SDS. The absence of this information here in the Clearon SDS is problematic given that there are other scenarios known to Clearon that cause the liberation of toxic gases from CDB-56®, including contact with water, contact with organic contaminants, and by simply heating the material. None of these scenarios are mentioned in this section of the SDS. Such information could have been listed under "Additional Hazards Information." Further, neither the SDS for CDB-56® nor for CDB-63® indicated that the maximum safe storage temperature was 60°C (**Figure 16** and **Figure 17**).

7. Handling and Storage	
Precautions To Be Taken in Handling:	Do not get in eyes, on skin or clothing. Avoid formation of dust and aerosols. Provide appropriate exhaust ventilation at places where dust is formed. Keep away from sources of ignition - No smoking.
Precautions To Be Taken in Storing:	Keep container tightly closed in a dry and well-ventilated place. Never allow product to get in contact with water during storage. Do not store near acids. Store away from incompatible substances.
Other Precautions:	Contact with acids liberates toxic gas.

Figure 16. Excerpt from the Clearon CDB-56® SDS. (Credit: Clearon)

7. Handling and Storage	
Precautions To Be Taken in Handling:	Do not get in eyes, on skin or clothing. Avoid formation of dust and aerosols. Provide appropriate exhaust ventilation at places where dust is formed. Keep away from sources of ignition - No smoking.
Precautions To Be Taken in Storing:	Keep container tightly closed in a dry and well-ventilated place. Never allow product to get in contact with water during storage. Do not store near acids. Store away from incompatible substances.
Other Precautions:	Contact with acids liberates toxic gas.

Figure 17. Excerpt from the Clearon CDB-63® SDS. (Credit: Clearon)

The only place in the Technology Package where this storage requirement appeared was in the technical product bulletin for CDB-56®. The technical product bulletin offered no explanation or context for the storage temperature requirement, instead stating that:

> [CDB-56®] should be stored in a cool, dry, well ventilated fireproof area where the temperature never exceeds 60°C (140°F)." […] [CDB-56®] decomposes at 240–250°C (464–482°F).

Both the technical product bulletin and the CDB-56® SDS stated explicitly that the decomposition temperature for the substance was approximately 240°C. No explanation was given for the difference between the storage temperature requirement (less than 60°C) and the listed decomposition temperature (240–250°C) for CDB-56®. Post-incident testing results found that NaDCC dihydrate begins a runaway exotherm (indicative of a runaway decomposition) at approximately 81°C when heated in a closed container.

Without the underlying information contained in the 1989 Olin paper, it was unlikely that a reader of the CDB-56® Technology Package would adequately understand the circumstances that could lead to a hazardous decomposition reaction of CDB-56® below the listed decomposition temperature. Optima Belle focused its decomposition prevention efforts on preventing water intrusion into the dryer and avoiding temperatures in excess of 240°C, the listed CDB-56® decomposition temperature in the Technology Package.

The "Stability and Reactivity" section of the Clearon CDB-56® SDS also did not communicate information necessary to understand that the material could decompose at a temperature far lower than the listed 240°C decomposition temperature. Additionally, Clearon was aware that chlorine gas (a toxic gas) and NCl_3 (a toxic and explosive liquid) are products of NaDCC decomposition, but the Clearon CDB-56® SDS did not indicate either of them as decomposition products. Additionally, the SDS indicated that hazardous reactions "Will not occur," despite listing other hazardous decomposition products and listing multiple types of incompatible materials (**Figure 18**):

10. Stability and Reactivity	
Reactivity:	No data available.
Stability:	Unstable [ ] Stable [X]
Conditions To Avoid - Instability:	Stable. However, may decompose if heated.
Incompatibility - Materials To Avoid:	Strong oxidizing agents. Acids. Strong reducing agents, Organic solvents and compounds.
Hazardous Decomposition or Byproducts:	nitrogen oxides (NOx), Hydrogen chloride gas, Carbon oxides, Sodium oxides.
Possibility of Hazardous Reactions:	Will occur [ ] Will not occur [X]
Conditions To Avoid - Hazardous Reactions:	No data available.

Figure 18. Excerpt from the Clearon CDB-56® SDS. (Credit: Clearon)

In summary, the CSB concludes that Clearon's SDS for NaDCC dihydrate was inadequate in the following ways:

- It did not accurately reflect the temperatures at which the compound could decompose, which was known to Clearon to be far lower than the listed decomposition temperature of 240°C–250°C, based on studies conducted in the 1970s and 1980s. Post-incident testing results found that NaDCC dihydrate begins a runaway exotherm (indicative of a runaway decomposition) at approximately 81°C when heated in a closed container;
- It did not contain Clearon's storage temperature restriction of 60°C;
- It did not list chlorine or NCl_3 in the list of decomposition products. Both products of decomposition were known to Clearon;
- It stated that hazardous reactions "Will not occur" despite listing several chemicals with which NaDCC dihydrate is incompatible and listing multiple hazardous decomposition products other than chlorine and NCl_3;
- It stated that hazardous reactions "Will not occur" despite Clearon's knowledge that NaDCC dihydrate can undergo a hazardous decomposition reaction;
- It stated that hazardous reactions "Will not occur" despite also stating that the compound "may decompose if heated"; and
- It did not list the material as an oxidizer despite it being classified as such by the NFPA, and despite that designation appearing on the material's technical bulletin.

NaDCC Dihydrate SDS Comparison

The CSB compared the Clearon CDB-56® SDS with five other NaDCC dihydrate suppliers' SDSs available at the time of the incident to determine whether supplier SDS data were consistent. As shown in the SDS excerpts in **Table 2** below, a comparison of SDSs indicates a variety of inconsistencies, including decomposition details. The red text in **Table 2** below indicates an inconsistency between suppliers.

Table 2. Comparison of six separate SDSs for NaDCC dihydrate obtained by the CSB.

	Clearon	Supplier B	Supplier C	Supplier D	Supplier E	Supplier F
Suitable Extinguishing Media	Water spray, fog (flooding amounts)	Flood with copious amounts of water	Water	**Dry powder**	Flood with water	Water in large quantities
Unsuitable Extinguishing Media	Do not use halogenated extinguishing agents or foam. Dry chemical or CO_2	DO NOT use ABC or other dry chemical extinguishers DO NOT USE carbon dioxide as an extinguishing agent. DO NOT USE halogenated extinguishing agents	Do not use dry chemical extinguisher containing ammonia compounds	**Do NOT use water jet**		Do not use dry chemical extinguisher containing ammonia compounds
Safe Storage Conditions	Keep container tightly closed in a dry and well-ventilated place	**Store in original container and in a dry area where temperatures do not exceed 52°C for 24 hours**	**Do not store at temperatures above 60°C**	Keep container tightly closed in a dry and well-ventilated place.	**Keep at temperature not exceeding 40°C**	**Temperature may not exceed 50°C**
Decomposition Temperature	**240°C–250°C**	Decomposes at temperatures **above 210°C** with liberation of harmful gases	Begins to lose 1 mole water at approx. 50°C; second mole water at 95°C; Decomposes at **240–250°C**	**240°C** - (anhydrous) Explosive properties May mass explode in fire	**Not applicable**. Explosive properties: Not explosive. Oxidizing properties: After prolonged exposure **above 40°C** the product could decompose and release excessive heat	Begins to lose 1 mole water at approx. 50°C; second mole water at 95°C; decomposes at **240–250°C**
Conditions To Avoid – Instability	Stable. However, may decompose if heated	Wet material may generate **NCl_3** **Any quantity of NCl_3 is potentially explosive. Liquid NCl_3 will explode … on heating to 60°C or above.**	Heating above decomposition temperature	**No data available**	**After prolonged exposure above 40°C the product could decompose** and release excessive heat	Heating above decomposition temperature
Hazardous Decomposition or Byproducts	Nitrogen oxides (Nox), Hydrogen chloride gas, Carbon oxides, Sodium oxides	**Chlorine**, nitrogen, **nitrogen trichloride**, cyanogen chloride, Oxides of Carbon, Phosgene, Chloramines	**Nitrogen trichloride**, **chlorine**, carbon monoxide	Carbon oxides, Nitrogen oxides (NOx), Hydrogen chloride gas, Sodium oxides **Other decomposition products - No data available**	**Chlorine**	**Nitrogen trichloride**, **chlorine**, carbon monoxide
Globally Harmonized System (GHS)		**Heating over 80°C can initiate a self-sustaining decomposition which releases large amounts of heat and gas including toxic fumes**				

The CSB concludes that the NaDCC dihydrate chemical hazard information contained in SDSs varies substantially between suppliers. Such inconsistencies are in alignment with the CCPS observation that SDS chemical hazard information can vary substantially between suppliers [18, p. 74]. In 1999, the EPA issued a Safety Alert that warned "[SDS] chemical hazard information can vary substantially depending on the provider [19, p. 2]."

One of Clearon's direct competitors (anonymized as Supplier B in **Table 2**) explicitly states in its SDS for NaDCC dihydrate that the compound can initiate a self-sustaining decomposition reaction at temperatures as low as 80°C, which is consistent with the data gathered in post-incident calorimetry testing of CDB-56®, which showed the onset of decomposition at approximately 81°C. In several responses to CSB information requests, Clearon insisted that its SDS for CDB-56® is compliant with OSHA regulations. The CSB draws no conclusions in this report as to the regulatory compliance of Clearon's SDS.

However, the CSB concludes that:

- The SDS for Clearon CDB-56® did not fully reflect the known hazards of the substance.
- Given that important information and context were missing from the CDB-56® SDS, an end user of the document may not have completely understood the material's propensity to decompose, the circumstances that could result in a decomposition, or the potential consequences of a decomposition.

KEY LESSON

Safety Data Sheet (SDS) chemical hazard information can vary substantially between suppliers. Chemical tollers and other end users should not rely solely on hazard information contained in the SDS when using the chemical at elevated temperatures or pressures, or with other chemicals with which the chemical could react. Additional hazard analyses may be needed to prevent process safety incidents. Companies should seek additional publicly available information, or obtain additional information through testing, to supplement information contained in a material's SDS.

Other Technology Package Deficiencies

Despite the deficiencies of the CDB-56® SDS, Clearon did include other information in the Technology Package that provided some additional context and considerations specific to decomposition. For example, the Technology Package stated that if there is "any mechanical problem preventing rotation of the dryer, remove heat from the dryer." This information appeared in the general manufacturing instructions, which stated:

> Heat dryer to a temperature range of approximately 100–130°C, and no more than 140°C.

and:

> Safety Recommendation: Only begin or maintain heating the dryer if it is rotating. If there is any mechanical problem preventing rotation, remove heat from the dryer. This is to avoid localized hot spots since the material would not be moving/mixing in this situation.

The Technology Package also included the following safety information that provided some additional context for CDB-56® decomposition:

> Decomposition can occur with either CDB-56 or CDB-63 – resulting in high temperatures and gas releases. The following conditions may contribute to potential decompositions:
>
> - Excessive temperature including localized friction with stagnant material
> - Localized heat input
> - Contamination with organics
> - Contamination of bulk material […] with small amounts of water. Note: Copious/Continuous water is acceptable for cleanup or extinguishing a decomposition.
> - Material with out-of-specification moisture concentrations (roughly between 4-10% moisture). For example, do not stop an in-process batch and allow the material to remain at the in-between moisture concentration.

The warnings against localized heat input and excessive temperature, however, are not stated quantitatively, and there was no explicit means for the reader to understand what "excessive temperature" or "localized heat input" meant in terms of process conditions. After assessing the Technology Package, Optima Belle arrived at the conclusion that CDB-56® decomposition as a result of overheating was not a credible risk.[a] The following circumstances led to this incorrect conclusion:

- The Technology Package stated that CDB-56® should not be stored in temperatures greater than 60°C;
- The process was intended to heat the material to temperatures between 100-130°C, which Optima Belle believed was sufficiently below the SDS-listed decomposition temperature of 240°C to avoid decomposition;[b]
- As designed, Optima Belle's steam system could only produce temperatures in the double cone dryer up to 130°C;
- Clearon's Technology Package stated that temperatures should not exceed 140°C; and
- The Technology Package stated that CDB-56® decomposes at 240°C.

Finally, as discussed in further detail below in Section 4.3.2, Optima Belle did not ensure the adequacy of the dryer's cooling and relief systems. Chiefly, Optima Belle did not perform calculations to verify that the dryer's cooling system could remove sufficient heat in the event of a potential CDB-56® decomposition reaction and did not perform calculations to verify whether the dryer's relief system was sufficiently sized to remove decomposition gases to prevent the buildup of excessive pressure inside the dryer in the event of a decomposition reaction. To perform such calculations, Optima Belle would have required:

- thermal decomposition data including the heat of decomposition (the amount and rate of heat energy released during exothermic decomposition), which Optima Belle could have compared with the heat

[a] Optima Belle's PHA identified the risk of CDB-56® decomposition as follows: Prompt: "Have the effects of [abnormal temperatures] been evaluated?" Response: "Too hot- greater than 200C decomposition including some [chlorine]." The PHA documented no responsive action for an abnormal temperature condition.

[b] Heat dryer to a temperature range of approximately 100–130°C, and no more than 140°C. Note, a somewhat lower temperature may achieve drying if the unit is under vacuum.

removal capability of the dryer's existing cooling system;

- decomposition reaction kinetics, stoichiometry, and mass balances, which Optima Belle could have used to determine the amount and rate of vapor and pressure generation during a decomposition reaction. Such information would be necessary to assess the adequacy of the dryer's existing relief system during a decomposition reaction; and
- in the absence of this information, DSC and ARC testing data may have sufficed, as ARC can determine pressure generation rates, and DSC can determine heat generation during a runaway exotherm (indicative of a runaway decomposition).

None of this information for CDB-56® was included in Clearon's Technology Package, and Optima Belle did not ask for this information. Clearon included calorimetry data for CDB-63® via the 1968 FMC report, but the thermal properties of the two compounds are different, as shown in **Table 3**.

Table 3. NaDCC dihydrate and NaDCC physical and thermal properties comparison.

Chemical Name	**Sodium dichloroisocyanurate dihydrate (NaDCC dihydrate)**	**Sodium dichloroisocyanurate (NaDCC)**
Synonym(s)	Sodium dichloro-s-triazinetrione dihydrate Troclosene sodium, dihydrate	Sodium dichloro-s-triazinetrione Troclosene sodium
Trade Name	CDB-56®	CDB-63®
CAS	51580-86-0	2893-78-9
Molecular Formula	$C_3H_4Cl_2N_3NaO_5$	$C_3Cl_2N_3NaO_3$
Molecular Weight	255.97 g/mol	219.94 g/mol
Differential Scanning Calorimetry		
Exotherm start temperature	114.1°C	160.2°C
Exotherm energy	1077 J/g	434 J/g
Accelerating Rate Calorimetry		
TD24[a]	49.3°C	40.9°C
Temperature of first exotherm	81.9°C	117.8°C
TMR at first exotherm	0.2 hours	6.4 hours
Pressure rate of test	17,571 psi/minute at 128.18°C[b]	18,286 psi/minute at 245°C

The CSB obtained the data shown above from post-incident testing of NaDCC and NaDCC dihydrate. The data for NaDCC dihydrate was discussed previously in this report in Section 3.1.1, and the data for NaDCC was obtained by testing commissioned by the CSB after the incident. Because DSC and ARC tests are mostly conducted using samples in sealed test cells, the results are directly applicable to products stored in sealed containers or heated in closed vessels, such as was done leading up to the explosion at Optima Belle.

As shown, NaDCC and NaDCC dihydrate, despite any chemical or molecular similarities, have disparate thermal properties, as shown in the DSC and ARC testing results. For example, the compounds have different energies of decomposition, times to maximum rate, and temperatures at which maximum pressure generation

[a] TD24 is the temperature at which the TMR is 24 hours. ASTM E1231-19 defines TMR as "an estimate of the time required for an exothermic reaction, in an adiabatic container (that is, no heat gain or loss to the environment), to reach the maximum rate of reaction" [65, p. 2].

[b] The cell exploded before the next data point was taken.

occurs. When used to size a cooling system, or to analyze worst-case pressure relief scenarios, data from the two compounds would likely yield different results. For a company to exercise sufficient diligence in designing a process involving these chemicals, relevant data for both chemicals would be required.

The CSB concludes that:

- Clearon's Technology Package, including particularly Clearon's NaDCC dihydrate SDS, was inadequate and lacked critical information on the decomposition of NaDCC dihydrate, and as a result it did not enable Optima Belle to perform an effective assessment of the adequacy of its existing toll manufacturing equipment for the dehydration process.
- Had Clearon provided the 1989 Olin white paper, or other relevant data on the decomposition of CDB-56® to Optima Belle, Optima Belle would have had the necessary, critical context to understand the circumstances that could lead to the decomposition of CDB-56®.
- Clearon's Technology Package led Optima Belle to an inadequate understanding of the hazards of the dehydration process and CDB-56® material. Had Clearon developed a robust process Technology Package and submitted such information to Optima Belle in advance of their tolling agreement, Optima Belle could have used it to better inform its process design and hazards analysis, and this incident could have been prevented.

4.1.3 Clearon Process Knowledge Management Systems

The CSB requested information from Clearon regarding corporate procedures or guidelines governing the creation, review, approval, and oversight of Clearon's NaDCC dihydrate SDS. Clearon's response indicated that Clearon used third-party software and services to generate its SDSs, and included website links to and marketing excerpts from those third-party providers' websites.

Clearon's responses did not indicate that the company had any process or procedure to govern how, when, and by whom SDS content was generated, updated, or audited for accuracy or completeness. It is the company's responsibility to supply the third party preparing the SDS with the data required for the SDS since the third party will typically not have access to much of the required data.

In addition, Clearon did not provide the CSB with evidence that the company conducted any literature search of the reactive properties of CDB-56® beyond the 1968 FMC Report (Section 4.1.2) before Optima Belle started the dehydration trial.

The CSB also requested information related to the following:

- Whether Clearon has a corporate procedure to assess a chemical's thermal and/or reactive properties. Clearon did not have such a procedure.
- Whether Clearon has a corporate procedure to transfer information pertaining to the thermal and/or reactive properties of chemicals involved in batch tolling operations to the toller and broker. Clearon's response did not indicate the presence of such a policy or procedure.

The gaps in Clearon's process knowledge management systems are perhaps best illustrated by the absence of the 1989 Olin paper or other relevant CDB-56® data from the tolling Technology Package. A single Clearon employee assembled the Technology Package. In an interview conducted in March 2022, over a year after the incident at Optima Belle, the CSB asked the Clearon employee whether he was aware of any CDB-56® analytical testing (such as ARC or DSC) conducted either before the incident or afterward. He responded, "I am not aware of any" and "I am not familiar with any." Clearon's attorney informed the CSB during the interview of the 1989 paper, which discusses CDB-56® analytical testing.

It is likely that the employee who compiled the Technology Package was simply unaware of the paper's existence or of other relevant data in Clearon's possession, as he so indicated in an interview statement. A critical employee's lack of awareness of critical information indicates problems with Clearon's management of process knowledge.

As CCPS states:

> …facilities should implement management systems to … maintain knowledge in a manner that helps promote risk-informed decision making, and [should] share the information with other facilities (including, in some cases, competitors) [14, p. 93].

And

> Organizations that maintain a broad understanding at all levels of what can go wrong, how bad it might be, how likely it may be, and what can or should be done to manage risk are likely to manage risk more effectively than organizations in which people […] are unaware of risk [14, p. 98].

KEY LESSON

Knowledge Management and Sharing: Companies must ensure that chemical hazard information identified from previous incidents, studies, and laboratory tests are maintained and organized in a manner that will allow employees to be aware of the information's existence and to use it appropriately for future applications.

In summary, Clearon did not have a formalized, documented process or procedure by which it generated or maintained its NaDCC dihydrate Technology Package.[a] Clearon had no formalized processes or procedures to collect and transmit PSI to contract tolling manufacturers.[b] Clearon had ineffective systems in place, which did not ensure that essential employees had critical process knowledge and data. The result was that the Clearon employee responsible for compiling the Technology Package was likely not aware of the 1989 Olin paper (even over a year after the incident), and the paper was not included in the Technology Package. The paper, along with other information missing from the Technology Package, contained important data and context on the thermal decomposition of NaDCC dihydrate, the raw material for the dehydration process. Optima Belle could have

[a] Clearon stated in a response to CSB that it "created a Technology Package specifically for RCI and Optima and does not maintain Technology Packages in the normal course of business."

[b] Clearon cited its lack of any prior experience working with toll manufacturers, prior to RCI and Optima, as the reason for its lack of such formalized systems.

used such information to better inform its analysis and design of the NaDCC dihydrate dehydration process, which could have prevented the incident.

Thus, the CSB concludes that Clearon lacked effective process knowledge management practices. Such practices should have documented and maintained information critical to the safe dehydration of NaDCC dihydrate and should have made that information easily accessible. As a result of Clearon's ineffective process knowledge management practices, Clearon's Technology Package lacked important process and product knowledge, and the company did not transmit important safety information to its tolling manufacturer, Optima Belle.

The CSB recommends that Clearon develop and implement a comprehensive process knowledge management program or evaluate and revise existing process safety management procedures to ensure consistency with industry guidance publications such as the CCPS's *Guidelines for Risk Based Process Safety*. The program should:

a) assign specific responsibilities for compiling content and maintaining robust process technology and safety information packages that incorporate relevant knowledge for all hazardous processes and substances operated, manufactured, and/or handled by Clearon;

b) ensure that key process personnel are aware of critical reactive chemistry information, including thermal stability and calorimetry data, chemical compatibility information, and descriptions of any past reactive incidents and safety studies involving the materials; and

c) define procedures for the transmittal of such information to toll manufacturers.

4.1.4 Clearon Post-Incident Actions

Since the incident, Clearon has developed a standard operating procedure for "requesting [SDS] authoring from third party vendors as well as updating and maintaining SDS to maintain compliance with OSHA's Hazard Communication Standard […] and updating Clearon's technical data sheet."

In June 2022, Clearon produced an updated SDS for CDB-56®. Among the changes are:

- the inclusion of a storage temperature requirement of less than 53°C;
- multiple references to chlorine and NCl_3 as decomposition products;
- a warning that "if this material becomes damp/wet or contaminated in a container, the formation of nitrogen trichloride gas may occur and an explosive condition may exist";
- removal of language stating that hazardous reactions "will not occur";
- a change in the listed decomposition temperature from 240°C–250°C to 220°C;
- multiple statements that the compound "loses water of hydration at 50–150°C"; and
- the inclusion of the NFPA's Class 1 Oxidizer classification for NaDCC dihydrate.

Despite these positive changes, the Clearon NaDCC dihydrate SDS still contains ambiguities. For example, the document lists a storage temperature maximum of 53°C but still offers no context for that maximum other than the statement "loses water of hydration at 50–150°C" and does not state that the compound can decompose if that temperature is exceeded. In other parts of the document, it states that the compound "may decompose when exposed to excessive heat" but does not meaningfully quantify "excessive heat" and does not connect that statement to any specific temperature or circumstance. Further, the document clearly states in other sections that the compound loses water of hydration at 50–150°C and decomposes without melting at 220°C. This implies that the material can safely exist at temperatures greater than 53°C (the stated storage maximum) but less than 220°C (the stated decomposition temperature), but the document does not make clear the circumstances under which that may be true. It is unclear to the reader whether the warning against "excessive heat" applies to the 53°C storage temperature maximum or the 220°C decomposition temperature, as the company still offers no context for the two different temperatures.

One of Clearon's direct competitors includes in its SDS (Section 4.1.2) for the same compound a warning that "heating over 80°C can initiate a self-sustaining decomposition which releases large amounts of heat and gas including toxic fumes." This warning is consistent with both the 1989 Olin paper and the post-incident calorimetry testing confirming the ability of NaDCC dihydrate to achieve self-accelerating decomposition at temperatures much lower than 220°C.

The CSB concludes that:

- Regardless of whether Clearon's SDS is compliant with OSHA's Hazard Communication Standard, the OSHA regulations are minimum requirements. Clearon's NaDCC dihydrate SDS could have exceeded the regulatory minimums in the OSHA Hazard Communication Standard.
- The June 2022 Clearon SDS for NaDCC dihydrate still falls short of clearly communicating the known hazards of the material.

As a result, the CSB recommends that Clearon update the NaDCC dihydrate (CDB-56®) SDS. At a minimum, the document should:

a) provide the underlying reasoning for the storage temperature maximum and the consequences of exceeding that temperature;

b) provide the underlying reasoning for the decomposition temperature and the consequences of exceeding that temperature;

c) explain or make clear the reason(s) for and/or the circumstance(s) resulting in the differences between the decomposition temperature and the lowest temperature at which self-accelerating decomposition may occur; and

d) provide the exothermic decomposition energy in the Physical Properties section.

4.2 Thermal Hazard Assessment

4.2.1 Thermal Hazard Assessment Methods

In 2002 during the AIChE 36th Annual Loss Prevention Symposium, a speaker reminded the attendees that "it is possible to obtain a good idea of the nature and degree of hazards that may be encountered in a particular operation involving the storing, handling, or reactions of chemicals from a variety of readily available sources" [20, pp. 508-523]. He also explained that most reactive chemical accidents could have been foreseen by using laboratory tests, hazard analysis, and chemical reaction engineering techniques. Incidents involving chemical reactions continue to result in injuries, fatalities, environmental impact, and property or economic loss.

According to *Chemical Engineering Progress*, "The thermal risk linked to a chemical reaction is the risk of loss of control of the reaction or of triggering a runaway reaction.[a] Hence, it is necessary to understand how a reaction can 'switch' from its normal course to a runaway reaction" [21]. The evaluation of thermal hazards and the management of chemical reactivity hazards are critical in the chemical process industry to aid in identifying or understanding the risk involved in chemical processing operations. Probability and severity may also be considered when assessing the thermal hazards of chemical reactions or understanding thermodynamics and chemical kinetics. Avoiding a runaway reaction is important for exothermic batch reactions— chemical reactions that liberate heat.

KEY LESSON

There are many tools available to identify whether a chemical has thermal or reactive hazards that could lead to a process safety incident. These tools include the Oxygen Balance method, Differential Scanning Calorimetry (DSC), Accelerating Rate Calorimetry (ARC), Yoshida Correlations, the CHETAH tool, the CCPS screening tool, the Chemical Reactivity Worksheet (CRW), the O.R.E.O.S. Method, and the Stoessel Criticality tool. Some of these tools involve simple calculations that can be conducted to determine whether further laboratory testing is required.

Multiple industry resources, including recognized and generally accepted good engineering practices (RAGAGEP), are readily available to evaluate chemical reactivity or explosivity. RAGAGEP are generally used for engineering, operation, or maintenance based upon recognized codes, standards, recommended practices, or similar technical documents to ensure safety and prevent process safety incidents [22]. One tool, the oxygen balance calculation, has existed since the 1940s.[b] In a 1949 *Chemical Reviews* article, W.C. Lothrop and G.R. Handrick "demonstrated quantitative correlations between oxygen balance and various measures of explosive effectiveness for several classes of organic explosives" [23]. Other examples are summarized below. Additional thermal assessment guidance and reactive hazard RAGAGEP are also discussed in Section 4.5.1.

- ***Thermal Analysis/Calorimetry.*** DSC and ARC are two tests used to determine the quantitative thermal data necessary for thermal process safety. DSC assesses a material's heat energy uptake or release as its temperature is raised [11]. It uses very small samples and provides results quickly, typically in only a few hours. ARC testing detects the onset temperature and other relationships of exothermic reactions in a confined adiabatic environment.[c] Since DSC and ARC tests are mostly conducted using samples in sealed test cells, the results are directly applicable to products stored in sealed containers or heated in closed vessels, such as the CDB-56® heated inside the closed pressure-rated vessel/dryer during the dehydration process leading up to the explosion at Optima Belle.

[a] A runaway reaction occurs when one or more chemicals suddenly react or decompose, accompanied by steep and accelerating temperature increases capable of creating dangerous pressure increases, a vessel rupture, or an explosion.

[b] It is of significance to note, "Although the hazard ranks of many substances are correctly identified by the [oxygen balance] calculation, several compounds are either ranked at too high or too low of a hazard…This serves as a powerful reminder that the [oxygen balance] calculation is oversimplistic and should not be used as the only method for predicting the energy release from a material" [27, pp. 216-217].

[c] An adiabatic environment suggests that there is no heat exchanged—"no heat is drawn into a process or expelled from that process" [109, p. 105].

- ***Mathematical or Tabular Methods.***
  - The Yoshida correlations of highly energetic reactions use an empirical relationship based on DSC data. The mathematical equations date back to at least 1987 and are useful for pinpointing potential explosion risk or shock sensitivity.
  - In 1995, the periodical *Process Safety Progress* published *The Oxygen Balance Criterion for Thermal Hazards Assessment* by E.S. Shanley and G.A. Melhem [24]. It provided a formula for correlating the proportion of oxygen in chemicals that can be "calculated and compared with the amount of oxygen required for complete oxidation of fuel elements, i.e., hydrogen and carbon." The oxygen balance concept is widely used in explosives technology.
  - In 2002, *Process Safety Progress* published *An Index-Based Method for Assessing Exothermic Runaway Risk* by C. Kao et al. It "proposed a simplified mathematical and tabular method for assessing the risk of exothermic runaway reactions, based on the calculated hazard index" [25].

- The ***CHETAH*** (Chemical Thermodynamic and Energy Release Evaluation) program. The CHETAH tool is currently available from ASTM International.[a] It may be used to predict thermal properties and certain "reactive chemicals" hazards associated with a pure chemical, a mixture of chemicals, or a chemical reaction, and can classify materials for their ability to decompose and estimate the heat of reaction.

- ***Preliminary Screening Method***. CCPS developed a simple screening tool to screen facilities for chemical reactivity [18, pp. 31-63]. The tool is based on a series of 12 "yes" or "no" questions to aid in quickly determining whether a facility has chemical reactivity hazards. The questions may be completed individually or by a team of persons with diverse expertise.[b]

- The ***Chemical Reactivity Worksheet*** (CRW) software program/database is owned and maintained by the CCPS [26]. It can be used to determine the chemical reactivity of common hazardous chemicals, compatibility information, and materials of construction suitability. The National Oceanic and Atmospheric Administration (NOAA) refined the original basic worksheet procedure, which was developed by the Hazardous Materials Management Section of the California Department of Health Services.

- ***The O.R.E.O.S. Method.*** This assessment tool combines three traditional methods for screening explosive properties (oxygen balance calculations, the Rule of 6, and the explosive functional group list[c]) with the onset temperature of decomposition as determined by DSC, and the proposed scale of use. It was developed to identify materials with the potential to pose a risk early before large-scale chemistry is planned. In 2021, the American Chemical Society periodical *Organic Process Research & Development* published *Explosive Hazard Identification in Pharmaceutical Process Development: A Novel Screening Method and Workflow for Shipping Potentially Explosive Materials* by Sperry et al. It states, "the Rule of 6 is as follows: If a molecule presents at least six atoms of carbon (or other atoms of approximately the same size or greater) per energetic functionality, this should render the molecule relatively safe to handle. When the Rule of 6 is applied to known explosive organic compounds, the method is reliably able to predict compounds containing explosive properties" [27, p. 217].

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[a] ASTM International was formerly the American Society for Testing and Materials.

[b] Using a team approach has the "possibility of better identifying and assessing the potential for chemical reactivity hazards" [18, p. 31].

[c] The United Nations *Manual of Tests and Criteria* includes examples of chemical groups indicating explosive properties in organic materials [8, p. 494].

- ***Stoessel Criticality*** is a tool for the risk assessment of a chemical reaction. It classifies a chemical reaction into five criticality classes ranging from 1 to 5. The higher the criticality class, the higher the risk of thermal runaway. Identifying the Stoessel criticality class for a chemical reaction requires the process temperature (T_p), the maximum temperature of synthesis reaction (MTSR), the temperature at which the maximum rate under adiabatic conditions is 24 hours (T_{D24}), and the maximum temperature for technical reasons (MTT) [28].

Appendix E contains thermal assessments of NaDCC dihydrate performed by the CSB using readily available resources, which all identified NaDCC dihydrate as a highly hazardous substance that warrants further reactivity testing.

Additional published literature, including guidance from the European Process Safety Centre[a] and AIChE, provides safe operational principles to avoid hazardous chemical incidents with the potential for severe consequences [14, 29]. AIChE formed the CCPS in 1985 to provide technical information and guidance to prevent and eliminate chemical incidents. A 2017 AIChE *Chemical Engineering Progress* article also states, "Industry experience has shown a facility must review chemical reactive hazards and the potential for runaway reactions in batch operations. If left unexamined, these issues can lead to serious process safety incidents." OSHA's Chemical Reactivity Hazards website also provides resources [30], including the index-based tabular method by Kao et al. [25] that may aid in evaluating potential chemical runaway reaction hazards. Companies should use caution when using this method since it was concluded that "limited knowledge derived from the statistical data must be taken into account. Organized and systematic thermal hazard reviews of chemical processes are needed to acquire more, and more accurate, information about runaway reaction hazard."

Optima Belle employees told the CSB that PubChem [31],[b] CAMEO [32],[c] and the American Chemical Society website were used in addition to the Clearon Toll Manufacturing Technology Package to conduct literature searches of NaDCC dihydrate and its possible reactivity or hazardous properties before completing the PHA or starting the first dehydration batch. One of the Optima Belle employees explained, "[there] wasn't much information available." As discussed above, the Clearon Technology Package did not include underlying data for CDB-56® thermal stability (see Section 4.1). Clearon did not provide the CSB with evidence that the company conducted any literature search of the reactive properties of CDB-56®, excluding the 1968 FMC Report (Section 4.1.2), before the start of the first trial batch. Clearon and Optima Belle agree that there was a discussion on December 2, 2020, about avoiding excess heat and water to prevent a CDB-56® decomposition reaction.

Post-incident, the CSB conducted a web-based literature search and found SADTs estimated as low as 45°C for NaDCC dihydrate based on ARC testing [6, p. 604]. The CSB also found that the European Chemicals Agency (ECHA) Registration, Evaluation, and Authorization of Chemicals (REACH) dossier[d] for NaDCC or NaDCC dihydrate section on the explosive properties of NaDCC stated that "[M]etal containers, such as steel drums or cans, are generally not suitable for anhydrous NaDCC or NaDCC dihydrate, since metal containers are pressure tight and could produce an explosion hazard if heated. However, neither anhydrous NaDCC or NaDCC

[a] The European Process Safety Centre is an international not-for-profit organization of member companies that work together on process safety [83].

[b] PubChem is a freely accessible database of chemical information, including safety and toxicity information, at the National Institutes of Health.

[c] CAMEO Chemicals is a hazardous chemical database used by emergency responders and others to predict hazards and get response recommendations. NOAA owns the database.

[d] REACH dossiers are maintained by ECHA [99]. This dossier was submitted by a subcommittee of the Isocyanurate Industry Ad Hoc Committee, of which Clearon is a member.

dihydrate are packaged in metal containers due to the corrosive properties of these products. Plastic containers, fibre drums and bulk bags are much more suitable for these products, and are less expensive, than metal drums" [33]. Optima Belle did not locate any of this information as part of its literature search prior to the incident.

4.2.2 CCPS Guidance

4.2.2.1 Hazard Identification and Risk Analysis

CCPS discusses the importance of hazard identification and risk analysis in its *Guidelines for Risk Based Process Safety* [14, pp. 209-242]. It explains that once a hazard is identified, the risks should be evaluated and mitigated. As discussed in Section 4.1, a thorough review of possible hazards must be based on accurate process knowledge. Each recommendation made by the risk analysis team(s) should be formally resolved by implementing the recommendation or rejection and acceptance of the risk. The rationale for the rejection or risk acceptance should be documented. Standard designs and processes that conform to RAGAGEP may be helpful to evaluate when assessing risk and making risk-based decisions.

4.2.2.2 Process Safety Competency Including Knowledge Sharing

"[E]nsuring that appropriate information is available to people who need it" has been identified as one of the core components in developing and maintaining process safety competency [14, p. 90]. Learning process safety competency may include conducting experiments as necessary and structured means to retain people-based knowledge. The CCPS states that "only competent people can transform information into knowledge [14, p. 91]." Business and human factors, including acquisitions, divestitures, resignations, and other factors, make it difficult to maintain competency by relying on the knowledge in people's heads. Sharing information is a critical principle of process safety competency for facilities that manufacture, store, or handle hazardous chemicals.

4.2.3 Company Thermal Hazard Assessment Practices

Neither Optima Belle, RCI, nor Clearon had a formalized policy or practice for assessing thermal or reactive properties at the time of the incident. Optima Belle cited its company's process safety management program and its use of PHAs, and stated, "[a]s corporate practice when introducing a new tolling process, Optima Belle identifies potential chemical reactivity and thermal reactivity hazards of chemicals to be used. In addition to relying on a client's/manufacturer's data, information (*e.g.*, Tech Transfer Package), specifications, guidance, participation, and direction, Optima Belle uses a PHA (Checklist or HazOp) to guide its assessment of potential process hazards." Clearon further explained that the company has a process safety management system in place, has many policies related to the safety of its operation, and uses the hazard and operability methodology to evaluate specific nodes throughout its process.

4.2.4 Reactivity Evaluation Gaps by Clearon, Optima Belle, and RCI

Non-Use of Publicly Available Reactive Hazard Tools

As described above, all chemical facilities can use various readily available tools to identify and provide a realistic assessment of serious potential reactive hazards. The assessment tools shared in this report vary in their needed resources and time requirement.

Neither Optima Belle nor RCI utilized available thermal and reactivity assessment tools, including the preliminary screening, calorimetry testing, or mathematical or tabular methods for CDB-56®, as described in Section 4.2.1. Post-incident, Clearon provided the CSB with CDB-56® thermal decomposition data from 1989 (Section 4.1.2). However, such information was not made available to Optima Belle or RCI representatives supporting the CDB-56® dehydration tolling agreement before the first batch was run at the Optima Belle facility. The CSB concludes that had Clearon, Optima Belle, and RCI performed an extensive thermal hazard assessment, shared the 1989 Olin data, or located adequate publicly available information, all parties could have understood the associated NaDCC dihydrate reactivity hazards, and the explosion could have been avoided.

As previously stated, one of the resources Optima Belle used prior to the incident was PubChem, which is an online resource maintained by the National Institutes of Health through the National Center for Biotechnology Information (NCBI).[a] PubChem did not contain sufficient information to indicate the hazardous decomposition potential of NaDCC dihydrate. Because PubChem is a widely known tool that can be used to search for publicly available chemical information, public safety would benefit from having more complete NaDCC dihydrate reactivity information located there. Therefore, the CSB issues a recommendation to NCBI to update the safety information in PubChem for NaDCC dihydrate, to include publicly available reactivity and decomposition information including but not limited to the SADT, the explosion hazard when heating metal containers containing NaDCC dihydrate, and the DSC and ARC results presented in this report. When compiling this information, review sources including the REACH dossier and other publications.

In addition, OSHA offers chemical reactivity hazards resources and evaluation information on its website [30]. However, the information on the OSHA website does not adequately embody the current industry best practices or knowledge of chemical reactivity hazards as described in Section 4.2.1 and **Appendix E**. As concluded by Kao et al., companies should use caution when using the index-based tabular method introduced in 2002 and listed on OSHA's Chemical Reactivity Hazards website because "limited knowledge derived from the statistical data must be taken into account. Organized and systematic thermal hazard reviews of chemical processes are needed to acquire more, and more accurate, information about runaway reaction hazard [25]." The CSB concludes that OSHA should update its Chemical Reactivity Hazards website. Therefore, the CSB recommends that OSHA update the Chemical Reactivity Hazards website (https://www.osha.gov/chemical-reactivity) to include various reactivity assessment tools developed since the 2002 Index-Based Method for Assessing Exothermic Runaway Risk and the 2004 Preliminary Screening Method. Mathematical methods, thermal analysis methods (e.g., ARC testing), ASTM E1231-19 *Standard Practice for Calculation of Hazard Potential Figures of Merit for Thermally Unstable Materials*, Stoessel Criticality, and the O.R.E.O.S. Method are tools that could be considered for the update. The "Additional Resources" section of the website should also be evaluated for necessary changes and updates.

Despite OSHA offering the Chemical Reactivity Hazard website as a public resource, neither Optima Belle, Clearon, nor RCI appeared to be aware of its existence. To aid in bridging this awareness gap, the CSB recommends that OSHA, following the implementation of CSB recommendation 2021-02-I-WV-R11, ensure that the chemical industry is aware of the Chemical Reactivity Hazards website (https://www.osha.gov/chemical-reactivity) by developing and implementing a comprehensive outreach plan that actively targets the chemical industry and related trade associations. The outreach plan may include such

[a] The NCBI is a division of the National Library of Medicine at the National Institutes of Health. "As a national resource for molecular biology information, NCBI's mission is to develop new information technologies to aid in the understanding of fundamental molecular and genetic processes that control health and disease" [101]. Its PubChem Compound Database contains validated chemical depiction information, including chemical structures, identifiers, chemical and physical properties, safety, and toxicity data [102].

means as a national news release and OSHA's "*QuickTakes*" newsletter and/or *Safety and Health Information Bulletins*.[a] This outreach plan should coordinate with OSHA's On-Site Consultation Program partners.

Missed Opportunity for Inherently Safer Design

More robust safety management systems at Optima Belle could have prevented this incident and protected the workers and the public from the hazards of exploding pressure vessels. Inherently safer design considerations for the dehydration process could also have been utilized. For example, *Designing and Operating Safe Chemical Reaction Processes* [34, p. 16] discusses the importance of inherently safer synthesis routes which include:

> Replacement of batch reaction processes with semi-batch or continuous processes. This reduces the quantity of reactant present and controlling the addition rate may stop the reaction in the event of a hazard arising …

Optima Belle's Belief that NaDCC Dihydrate Decomposition Was Not a Credible Scenario

Optima Belle's technical lead for the dehydration process (see Section 1.6.2) reviewed the 1968 FMC white paper provided by Clearon and issued a summary to Optima Belle, RCI, and Clearon personnel. The summary stated, "If allowed to escape, the NCl_3 does not reach a critical level, and no detonation occurs." The technical lead also explained that the Optima Belle dehydration process could stay in the safe range with "a few adjustments to their normal operating procedures[,]" including limiting the concentration of NCl_3 (by pulling vacuum and purging with nitrogen), cooling the batch below 50°C before pack out, and minimizing both product degradation and NCl_3 formation by "drying at the lowest possible temperature." Therefore, the formation of NCl_3 was not considered likely with these "few adjustments" to Optima Belle's normal operating procedures for the first CDB-56® dehydration batch; however, the amount of nitrogen required to remove NCl_3 was never determined. Further, the Clearon technical lead, a chemical engineer who was also a process engineer, told the CSB, "we don't see a need to do [a nitrogen sweep]."

Ultimately, Optima Belle did not believe NaDCC dihydrate decomposition due to overheating to be a credible scenario. The basis for this assumption was that the temperature of the steam used to heat the NaDCC dihydrate was roughly 100°C lower than the understood decomposition temperature (240°C–250°C). However, as discussed in Sections 1.4 and 3.1.1, the material can decompose at far lower temperatures under certain conditions. Instead, Optima Belle focused on preventing water intrusion and avoiding contaminating the material. As previously discussed, post-incident testing results found that NaDCC dihydrate begins a runaway exotherm (indicative of runaway decomposition) at approximately 81°C when heated in a closed container.

The CSB concludes that:

- None of the parties involved in the NaDCC dihydrate tolling operation effectively assessed the hazards of the material or operation. The deficiencies included:
  - failure to identify the initiation of a self-accelerating decomposition of NaDCC dihydrate as a credible scenario, except as a result of water intrusion or contamination of the product with other contaminants;
  - inadequate literature searches for publicly available or internal Clearon-owned NaDCC dihydrate data; and

[a] OSHA's *Safety and Health Information Bulletins* replaced its *Hazard Information Bulletins* and *Technical Information Bulletins* in 2003.

- failure to utilize available reactive hazard screening methods to assess the potential reactivity or explosivity of heated NaDCC dihydrate inside a metal pressure vessel.

- Optima Belle's ineffective hazards assessment was due in part to the lack of adequate process knowledge.

- Although Clearon did not submit sufficient CDB-56® thermal decomposition data and information to Optima Belle, Optima Belle did not adequately seek additional information that could have resulted in an effective hazards assessment.

- The effective use of publicly available thermal hazards evaluation methods or of publicly available or Clearon-owned data could have resulted in a more robust and effective assessment of the hazards of the dehydration operation, which could have prevented the incident.

The CSB issues a recommendation to Optima Belle to develop and implement a written thermal and reactive hazards evaluation and management program. The program should adhere to industry guidance provided in publications such as the CCPS's *Essential Practices for Managing Chemical Reactivity Hazards.* At a minimum, the program should identify the process that Optima Belle will use to manage chemical reactivity hazards, resources for collecting and assessing reactivity hazards, steps for determining how and when to test for chemical reactivity, documentation requirements, and training.

4.3 Equipment Selection and Process Design

In a tolling contractual agreement such as the one in place for the CDB-56® dehydration, "[b]oth parties need to identify responsibilities for choosing the right equipment for the process" [35, p. 64]. The equipment selected (**Figure 2** and **Figure 3**) and the process developed (Section 1.6.4) to dehydrate the CDB-56® could not prevent the CDB-56® decomposition and ultimate explosion of the vessel. The flaws with the equipment selection and process development are described in this section.

4.3.1 Dryer Technology Selected to Convert CDB-56® to CDB-63®

As described in Section 1.6.2, Optima Belle used its existing equipment to dehydrate the CDB-56®, including its Hastelloy® C-276 rotary dryer.[a] The use of the rotary dryer to conduct the CDB-56® dehydration operation was a new process for Clearon, RCI, and Optima Belle.[b] Clearon also asserts it was unaware of any CDB-56® exothermic decomposition in a double-cone dryer similar to Optima Belle's, and its previous CDB-56® dehydration method was not like Optima Belle's.

Clearon previously used a fluidized bed dryer technology at atmospheric pressure for its CDB-56® dehydration process. Fluidized bed drying is a hot-air drying process used in batch and continuous operations [36, p. 552]. This drying technology may use an upward flow of heated air through a perforated bed and mechanical shaking to create a fluidized effect in powders [37, p. 601].[c] Advantages of fluidized bed drying include "high drying

[a] Optima Belle circulated steam through the dryer's jacket for indirect heating. The indirect heating method transfers heat to the material as it contacts a heated surface instead of immersing it directly into a heating media (called direct heating) [79]. Optima Belle also applied vacuum to the dryer.

[b] Optima Belle has previously used its dryer to remove water from other products.

[c] The fluidized effect occurs when the material lifts from the bottom and suspends in the airflow. Heat transfer is accomplished by direct contact between the material and hot gases/air.

rates" [38, p. 182] and "relatively short drying times" [39, p. 262]. Published literature states,

> Fluid-bed dryers are useful for drying heat sensitive materials where exit temperatures should not exceed 200°F. Control of temperature in stable fluidization is easily maintained with essentially no hot spots in the bed. [40, p. 254].

In addition, Clearon's initial toll manufacturing solicitation to RCI also requested a fluidized bed dryer to dry the chlorinated granular solid.[a] The CSB does not have evidence that a thorough evaluation(s) was conducted to replace the fluidized bed dryer as specified in the solicitation with an alternative drying technology, such as a rotary dryer, for CDB-56® dehydration. None of the three parties raised any process or operational concerns with using a different drying technology, and Clearon ultimately agreed to the proposal to use a rotary dryer (Section 1.6.1). However, equipment material construction concerns were discussed among the parties, which led to a site visit and compatibility studies that resulted in an agreed-upon path forward before the start of the first batch. A consultant with many years of industry experience with the chlorinated isocyanurate compound also explained to the CSB that NaDCC is a relatively good insulator with a thermal conductivity similar to rubber; therefore, a "stationary bed" can create significant temperature gradients within the product if localized heating exists. The CSB concludes:

1. A temperature sensor will have difficulty detecting a hot spot that is not in the immediate vicinity of the sensor in a stationary bed; and
2. The use of the appropriate drying technology and ancillary equipment that minimized the potential for overheating, creating hot spots, or a self-accelerating decomposition reaction during the NaDCC dihydrate dehydration process could have prevented the incident.

The CCPS publication *Guidelines for Engineering Design for Process Safety* includes in its "Equipment Design" section a subsection called "Dryers" [41, p. 213]. The subsection describes three past incidents, two of which happened when exothermic chemical reactions occurred in dryers when the material was overheated. Lessons learned presented in the section include "the consideration of a different type of dryer for [the] application that better controls the temperature" and "the need to understand the temperature sensitivity of the material being dried, as well as knowing the actual characteristics of the heating medium being used" [41, p. 214]. The publication goes on to say, "The choice between different types of dryers is often guided by the chemicals involved and their physical properties, particularly heat sensitivity" [41, p. 221]. In the case of the Optima Belle incident, the CSB concludes that key differences between the fluidized bed dryer that had previously been used by Clearon and the rotary dryer used by Optima Belle include:

1. When the rotary dryer was stationary, a large volume of the material would be compacted together. As previous studies have found, the configuration and mass of stored CDB-56® affects its thermal properties, including the decomposition temperature;
2. Fluidized bed dryers promote high rates of heat and mass transfer and uniformity of temperature and composition throughout [40, p. 254], in contrast to the rotary dryer where temperature could be less uniform; and
3. The fluidized bed dryer operated at atmospheric pressure, and the rotary dryer was a pressure vessel. Any evolved gases in the fluidized bed dryer would be swept out of the fluidized bed dryer to the atmosphere, but a rotary dryer with an undersized relief system (see Section 4.3.3) would contain

[a] Granular materials typically have a small thermal conductivity and are generally good insulators.

evolved gases, leading to a vessel explosion in a major decomposition event. Furthermore, if the rate of gas evolution is high enough, the gas flow could carry the granular product into the vent system where the product could have restricted or blocked the gas flow.[a]

The difference in design between the fluidized bed dryer and the rotary dryer and the different effects it could have on the material were not thoroughly evaluated by Clearon, Optima Belle, or RCI.

The CSB issues a recommendation to Optima Belle to develop and implement a written program for tolling process design and equipment selection using guidance from the CCPS's *Guidelines for Risk Based Process Safety* and *Guidelines for Process Safety in Outsourced Manufacturing Operations* to ensure that the equipment design basis is adequate for any new tolling process or product. This written program should incorporate the information developed in Optima Belle's thermal and reactive hazards evaluation program (see CSB recommendation 2021-02-I-WV-R1) to ensure that chemical hazards are fully understood and controlled.

The CSB also issues a recommendation to Clearon to develop and implement a formalized program for tolling process design and equipment requirements/specifications to ensure that the equipment design basis is adequate for any new tolling process, operation, or product.

4.3.2 Jacket Cooling and Heating Design

Reactive chemicals can be more sensitive to temperature than to other parameters, such as pressure [18, p. 71]. NaDCC dihydrate (CDB-56®), as described in Section 1.4, is one such chemical; thus, it requires temperature control to avoid creating reactive conditions.

In addition, the onset or critical temperature—the temperature at which the heat released by a reaction can no longer be completely removed, resulting in a runaway reaction—depends on the rate of heat generation and the rate of cooling, which are closely linked to the dimensions of the vessel. As the vessel size increases, the volume increases at a faster rate than the surface area. Kayode A. Coker states in *Modeling of Chemical Kinetics and Reactor Design*,

> This can be represented by the rate of heat generation being proportional to the volume of the reaction mixture. In other words,
>
> Rate of heat generation [is proportional to] volume
>
> The rate of natural cooling is proportional to the surface area of the vessel and is represented by
>
> Rate of cooling [is proportional to] surface area [42, p. 988]

The CSB concludes that the vessel size and area-to-volume ratio must be considered when evaluating heat generation and cooling rates involving reactive materials to ensure sufficient cooling is attainable to prevent a runaway reaction. The CSB found no evidence that Optima Belle calculated the required cooling in the event of heat generation from a CDB-56® decomposition in the dryer. As discussed in Sections 4.1 and 4.2, Optima Belle

[a] Post-incident, the CSB observed yellow granules in the vent pipe, which had a significant color change from the white NaDCC dihydrate. Preliminary analyses of the yellow granules detected elevated levels of chlorine and nitrogen and lesser amounts of oxygen, carbon, iron, neodymium, and chromium. Since no additional analytical analyses were conducted, the actual identity of the material is inconclusive.

did not have or seek out sufficient NaDCC dihydrate calorimetry data to perform such calculations.

As described in Section 1.6.2, Optima Belle's steam supply could heat the dryer and its internal contents to a maximum internal temperature of approximately 130°C. This temperature was believed to be sufficiently high to release the water of hydration and reduce the CDB-56® nominal moisture content but sufficiently low to avoid the published decomposition temperature of 240°C to 250°C (Section 1.4).

As described in Section 1.6.4, Optima Belle's prescribed procedure for the CDB-56® dehydration process also notes that "[i]f the rotation on the double cone stops, immediately shut off steam to remove heat from going to the vessel. Consult with management if cooling water needs to be applied to the jacket." In addition, the Clearon Technology Package warned Optima Belle to avoid creating localized hot spots inside the dryer during dehydration.

To control the dryer's internal temperature, steam, cooling water, or nitrogen could be selected manually using hand valves located within the building near the dryer.[a] The steam, cooling water, or nitrogen feed to the jacket was then automatically regulated from the control room through the distributed control system (DCS). The jacket cooling and heating system did not contain 1) high-temperature rise alarms, 2) rate of change of temperature over time alarms, or 3) interlocks to control the dryer temperature. At approximately 9:40 p.m., the nitrogen control valve for the dryer's nitrogen blowdown had been opened in preparation for adding the cooling water. At the same time, a rapid internal temperature increase continued until the explosion occurred.[b]

The CSB asked Optima Belle whether any automated DCS control actions or interlocks were provided to prevent a runaway reaction in the first CDB-56® batch. Optima Belle responded:

> Based on the thermal hazard information provided by Clearon, Optima Belle implemented a process that was inherently safe against overheating the CDB-56, [in as much] as the process was designed to remain at least 100 C below the 240 C minimum decomposition temperature identified by Clearon. There was a mechanical interlock in the form of a steam pressure regulator set to prevent overheating of the material beyond the temperatures specified by Clearon. There also was a DCS alarm triggered if the double cone dryer stopped rotating so that the board operator would be notified to stop heating.

The CSB concludes that:

- Optima Belle incorrectly believed that it had developed an inherently safe process that was incapable by design of achieving the conditions that would lead to the decomposition of CDB-56®, based on its inadequate understanding of the CDB-56® thermal decomposition temperature. As a result, Optima Belle's existing heating and cooling systems could not prevent a CDB-56® decomposition as designed.
- Optima Belle's jacket cooling system design was likely inadequately sized to control a CDB-56® decomposition.
- Optima Belle's jacket heating and cooling system design lacked automatic engineering controls to monitor and adequately control the dryer temperature during the CDB-56® dehydration.
- Had Optima Belle, Clearon, and RCI better understood the conditions at which CDB-56® could

[a] Steam has to be blown out of the rotary dryer's jacket before applying the cooling water.

[b] There is insufficient evidence to determine whether the cooling water that also required the opening of manual valves was applied to the dryer jacket before the explosion.

hazardously decompose, Optima Belle might have implemented improved safeguards to prevent the material from reaching its decomposition temperature.

The CSB issues a recommendation to Optima Belle to develop and implement a written program for tolling process design and equipment selection to ensure that safeguards and ancillary equipment are considered and adequately designed, installed, and function as designed and required. This process should incorporate the information developed in Optima Belle's thermal and reactive hazards evaluation program (see CSB recommendation 2021-02-I-WV-R1 and Section 4.2.4) to ensure that chemical hazards are fully understood and controlled.

4.3.3 Safety Relief Device(s) Overpressure Protection

The ASME BPVC Section VIII requires that all pressure vessels "shall be provided with overpressure protection" [43]. Safety valves and bursting discs are the most commonly used relief devices to protect against over-pressurization [44, p. 9] and are designed for the automatic relief of excessive pressure. The spring-loaded safety valve, a conventional safety valve (**Figure 19**), is the most widely used relief device for overpressure protection in the chemical process industry [44, pp. 14 - 15]. It is generally equipped with a full nozzle below the seat, a bonnet around the spring, and adjusting rings. A rupture/bursting disc is a non-reclosing device and must be replaced after it has ruptured. Safety valves and rupture discs must be carefully sized to pass the maximum flow produced by emergency conditions. The double cone dryer was equipped with a 3-inch PSV (**Figure 4**) and a 3-inch rupture disc in series.

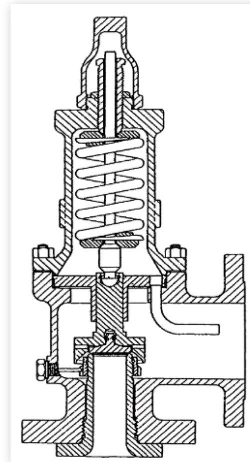

Figure 19. Conventional safety valve (Credit: API [44, p. 15])

The ASME BPVC also requires the user to identify all over-pressurization scenarios, establish how the equipment will be protected for each scenario, and ensure that the required overpressure protection is properly installed before initial operation. According to the CCPS, "For the possibility of a runaway reaction, which often results in the need for an appreciably larger relief device than other relief scenarios may require," the relief design basis should include a review of all intentional and unintentional reaction paths [41, p. 190]. The American Petroleum Institute (API) 521 *Pressure-relieving and Depressuring Systems* standard also specifies requirements and guidance in examining the causes of over-pressurization and determining relief rates for common conditions or occurrences, including chemical reactions [45, p. 16 & 31].

Industry good practice guidance, such as is contained in ASME BPVC Section VIII, API 521, and publications from CCPS, all would have required or suggested Optima Belle to consider an NaDCC dihydrate decomposition reaction relief case. However, ASME BPVC Section VIII is not a regulatory requirement for West Virginia.[a]

4.3.3.1 Optima Belle's CDB-56® Dehydration PHA

As described in Sections 1.4 and 4.5, NaDCC dihydrate is not covered under the OSHA PSM standard or EPA RMP rule; however, Optima Belle has a process safety management procedure that states, "New processes are evaluated before startup to determine if they will be covered under the PSM standards." Thus, Optima Belle voluntarily conducted a PHA for the CDB-56® dehydration. There was an action item from the PHA to "review

[a] In 2009, former CSB Chairman John Bresland discussed this gap and urged the remaining states to adopt the long-standing pressure vessel code and related boiler standards to help prevent accidents [78].

[the 3-inch PSV] pressure relief sizing for self-sustaining decomposition reaction." The double cone dryer's 3-inch PSV was originally sized for other process applications. Optima Belle told the CSB that it considered steam generation (e.g., trapped water vapor in the dryer in the event that the vacuum vent valve was closed) to be the only credible over-pressurization scenario and concluded that this scenario would not result in reaching the 30 psig PSV set point. Optima Belle's technical lead for the dehydration process also told the CSB that an external fire case for CDB-56® was not considered a credible scenario because no flammable materials were located in the building. He also explained, "I don't think we had any information on gas release in a fire case [a scenario involving a fire], which made it somewhat problematic."

The CDB-63® decomposition studies provided by Clearon to Optima Belle did contain gas evolution information that Optima Belle could have used to conduct a preliminary screening analysis of the existing pressure relief system. The data may have been sufficient to analyze a CDB-63® decomposition scenario but would not have been sufficient for a CDB-56® decomposition scenario given that the two compounds have different maximum pressure generation rates and different temperatures at which maximum pressure generation occurs (see **Table 3**). For a company to exercise sufficient diligence in designing a process involving these chemicals, relevant data for both chemicals would be required.

Optima Belle did not document its review process of the 3-inch PSV for the CDB-56® dehydration, including existing sizing calculations and over-pressurization scenario evaluations. Nor did Optima Belle perform new PSV sizing calculations for the CDB-56® dehydration. There was a verbal conversation between the Optima Belle technical lead for the dehydration process and another Optima Belle worker regarding the required Pre-Startup Safety Review action item to review the PSV sizing. After their discussion, the action item was signed off as completed. As demonstrated by the incident, the 3-inch PSV was inadequate to prevent the over-pressurization of the dryer that ultimately exploded during the CDB-56® decomposition.

The CSB evaluated the double cone dryer's relief valve sizing for the batch dehydration process using the recommended vent ratio and vent pressure from a 1961 potassium dichlorocyanurate thermal decomposition study cited in the Technology Package provided to Optima Belle.[a] Using the criteria in the study, the CSB concludes that a 30-inch rupture disc could likely have been required to protect the dryer from over-pressurization, which would be impractical to install on the 8-foot diameter conical vessel with an 18-inch manway and 12-inch discharge outlet. The CSB concludes that had Optima Belle conducted this evaluation or similar preliminary over-pressurization evaluations, they likely would have determined that the double cone dryer was not a practical equipment selection for the dehydration process.

The CSB also concludes that:

- Optima Belle incorrectly believed that steam generation was the only credible over-pressurization hazard applicable to the dryer during the CDB-56® dehydration because it believed that decomposition was not possible using the heating medium selected for the dehydration process. As a result, no analysis was performed to determine the PSV size needed to prevent over-pressurization during a CDB-56® self-accelerating decomposition reaction.

- Optima Belle's inadequate PSV evaluation was a consequence of insufficient information and its incomplete understanding of the CDB-56® decomposition temperature and decomposition characteristics, as well as Optima Belle's failure to seek additional information required to conduct the

[a] Upon request, Clearon provided the referenced study to the CSB.

PSV evaluation.

- Had Optima Belle, Clearon, and RCI better understood the conditions at which CDB-56® could hazardously decompose, Optima Belle could have evaluated and identified proper safeguards to prevent the exceedingly high pressure experienced in the double cone dryer that led to its failure.

- Optima Belle failed to adequately close out a PHA action item to review the pressure relief sizing for a self-accelerating decomposition reaction.

As stated in Section 4.3.2, the CSB recommends Optima Belle develop and implement a written program for tolling process design and equipment selection to ensure that safeguards and ancillary equipment are considered and adequately designed, installed, and function as designed and required.

The CSB also issues a recommendation to Clearon to develop and implement a written program for tolling process design and equipment specifications/requirements to ensure that safeguards and ancillary equipment are considered and adequately designed, installed, and function as designed and required.

4.3.4 Batch Scale

The control of chemical reactions is critical to operating safely in the chemical manufacturing industry [42, p. 910]. Published literature, including the CCPS's *Essential Practices for Managing Chemical Reactivity Hazards,* provides guidance on preventing uncontrolled chemical reactions. It explains that small-scale tests can be performed to indicate whether a reaction is expected, and that particular caution must be taken when scaling up chemical reactions to the manufacturing scale, as a "reaction, which is innocuous on the laboratory or pilot plant scale, can be disastrous in a full-scale manufacturing plant" and must be controlled [42, p. 912].

In the pharmaceutical industry, it is generally accepted that a chemical process cannot be executed at a large scale without a proper process safety assessment [46].[a] For example, a survey of 15 pharmaceutical companies reported that some pharmaceutical companies evaluate thermal hazards when process volumes at the "early stage" laboratory scale reach 250 milliliters to 5 liters [46, p. 2534]. In the same survey, the scale that triggers thermal hazard testing in the next stage (mid-stage) varies from 2 liters to pilot scale [46, p. 2536]. Almost half of the companies surveyed completed their thermal evaluations by the end of the mid-stage scale, "which likely reflects a desire [by the companies] to have most process safety risks understood and discharged prior to transfer to [full-scale]."

Toll manufacturers such as Optima Belle should use the PSI provided by the customer, and have their own hazard review processes, to screen new feed chemicals and products to determine whether the toll facility can produce the product safely. A 2017 article in AIChE's *Chemical Engineering Progress* publication titled "Ensuring Process Safety in Batch Tolling" recommends that tolling facilities (1) evaluate PSI on the involved chemicals to determine whether the chemicals can be safely used at the laboratory scale, (2) examine the process at the laboratory scale to determine whether the process can be scaled to a trial batch or full production, and (3) involve site safety and process engineering personnel to determine whether the process can be conducted at the tolling facility safely at full scale with the existing equipment [47].

[a] The U.S. Navy has similar scale-up policies for energetic materials and related hazardous materials operations.

Neither Optima Belle, Clearon, nor RCI performed small- or pilot-scale tests to dehydrate CDB-56® using the rotary dryer process. Rather, the first attempt at using the rotary dryer method to dehydrate the CDB-56® was conducted using approximately 8,820 lbs. of material, as discussed in Section 1.6.1.[a] Notably, the RCI proposal signed by Clearon stated, "The drying trials will be used to determine final steam/temperature settings and the resulting cycle times." The CSB concludes that Clearon and Optima Belle essentially experimented on a new method to remove water of hydration from the CDB-56® at full production scale without first experimenting at the laboratory and pilot scales, and the result was a catastrophic explosion. The CSB also concludes that had scaled studies been conducted, Optima Belle, Clearon, and RCI likely would have gained additional NaDCC dihydrate thermal stability data, reactivity information, and process knowledge before running the first production-scale batch, which might have led to changes in the process and potentially prevented the decomposition reaction and the explosion.

The CSB issues a recommendation to Optima Belle to develop and implement a written program for tolling process design and equipment selection to ensure that new processes are evaluated for potential process hazards at the laboratory and/or pilot scale before production scale.

KEY LESSON

To ensure that hazards associated with new processes are identified and controlled, facilities should (1) evaluate process safety information on the involved chemicals to determine whether the chemicals can be safely used at the laboratory scale, (2) examine the process at the laboratory and pilot scales to determine whether and how to safely scale the process to the production scale, and (3) involve site safety and process engineering personnel to determine whether the process can be conducted at the tolling facility safely at full production scale with the existing equipment.

4.4 Tolling of Hazardous Materials

Clearon is the manufacturer of CDB-56® and contracted Optima Belle through RCI to dehydrate four approximately 8,800-pound batches of CDB-56® at the Optima Belle facility to produce CDB-63®.

Companies often augment in-house production by outsourcing chemical processes and distillation, drying, formulating, blending, and packaging operations. In addition, chemical manufacturers frequently enter into agreements with outside firms to process industrial-grade materials into commercial products. These agreements are called tolling contracts. While most of these tolling, or contracted manufacturing services, proceed without incident, they are not without risk. The Optima Belle manufacturing plan was the first tolling agreement between the three companies and the first time Optima Belle attempted to dehydrate NaDCC dihydrate.

[a] RCI asserts it was not asked to or contracted to conduct scaled studies. Clearon explained to the CSB that its personnel at one point, in a call with RCI and Optima Belle, suggested using approximately 2,205 lbs. of material (one super sack) instead of the approximately 8,820 lbs. of material for the first trial. However, Clearon ultimately did not express any concerns about the final decision to use the approximate 8,820 lbs. of material in the first trial batch.

4.4.1 Industry Tolling Guidance

The CCPS publication *Guidelines for Process Safety in Outsourced Manufacturing Operations* [35] is an industry document that provides recommended guidance for safe and effective tolling operations. Its intended purpose is stated as follows:

> This Guideline describes techniques to assist the chemical processing industry in applying the CCPS chemical process safety concepts to the tolling vendor-client relationship. This Guideline book is intended to provide guidance in fundamental safety practices to technical staff and management [35, p. xii].

For the purposes of aligning terminology and guidance in the CCPS publication with the circumstances of this incident, the CSB considers Clearon to be the client, and Optima Belle to be the toller.

The guidance publication is divided into five chapters that detail the best practices for the entire life cycle of a tolling arrangement. The topics include 1) toller selection, 2) contract considerations and agreements, 3) pre-startup and startup activities, 4) considerations for the conduct of operations, and 5) closure and audit [35, pp. 11-12].

KEY LESSON

Outsourcing the production or processing of a hazardous material does not outsource the responsibility for process safety. Effective process safety and the prevention of catastrophic incidents are responsibilities that should be shared by all parties involved in a tolling operation.

4.4.2 Process Knowledge Management in Tolling Operations

According to the CCPS guidelines, the client normally prepares the technology package for the toll, which includes 1) health, safety, and environmental related data, 2) chemical process information, 3) raw material and product specifications, and 4) waste characteristics and disposition instructions [35, p. 5]. CCPS recommends that "[t]he technology package for the toll should be at least partially established prior to starting the active search for a toller." CCPS provides an example of an initial technology package that will assist the client in identifying the expertise required for the tolling project [35, pp. 15-19]. The example initial technology package is extensive and, among many other things, guides tolling clients to include the following information in an initial solicitation for tolling services, prior to selecting and entering into a contract with a toller:

- Process chemistry information including reaction kinetics and thermodynamics;
- Material balances;
- Unit operations details including block flow diagrams and technology and equipment descriptions;
- Process equipment design criteria;
- Environmental considerations;
- Physical properties of the materials involved; and
- Reactive chemistry information, including thermal stability and calorimetry data, chemical compatibility information, and descriptions of any past reactive incidents and safety studies involving the materials [35, pp. 16-19].

In addition to CCPS, other industry groups have also developed guidance on the contents of a technology package for potentially reactive or energetic materials. SEMI is an industry trade group "representing the electronics manufacturing and design supply chain" and consists of over 2,500 member companies [48]. Like other industry trade groups such as API, SEMI authors standards covering a wide range of topics, including manufacturing metrics, process and quality control, and safety [49].

SEMI authors a standard—SEMI S30 *Safety Guideline for the Use of Energetic Materials in Semiconductor R&D and Manufacturing Processes*—that provides, among other topics, guidelines for what information a user of an energetic material should expect from the supplier of that material. The information described is consistent with the types of information that CCPS recommends in its tolling *Guidelines*:

The 2019 edition of SEMI S30 states in § 10:

> 10.1 Energetic Process chemical suppliers should provide the information described in this section, at the time negotiated with the user.
>
> 10.2 *Classifications* – A determination of 'pyrophoric', 'water reactive', and 'hazardously exothermic'[a] classifications in accordance with the definitions and empirical tests specified in § 5 and including:
>
> 10.2.1 The objective test data and calculations on which the determinations were based. For determinations which were not based on objective data, the rationales used in making the determinations and the basis for considering the persons making the determination qualified to do so.
>
> 10.2.2 The completed Material Characterization Form provided in Appendix 1.
>
> 10.2.3 Stoichiometry and thermodynamics of reaction with water and with oxygen, including any byproducts which are flammable or otherwise hazardous.
>
> 10.2.4 Calorimetry results that show the time evolution of heat under defined reaction conditions.
>
> 10.2.5 A video illustrating the salient properties and reaction of the energetic process chemical with air, water, and any other materials with which the energetic process chemical is foreseen to react exothermically should be provided to users by the chemical supplier. The video should clearly illustrate, to the end user and to those who do maintenance or service, the vigor and hazards a release could create. This information should be such that first responders (to leaks or spills) and those mentioned above can be trained, appropriate PPE provided, and safe work practices (including emergency response) determined. […]
>
> 10.3 *Byproduct Information* – the chemical identity of known and anticipated products and byproducts […]. The information should include […] any safety determinations made from byproduct quantitative or predictive model evaluation(s) or during the integrated process risk assessment conducted as described in § 9.3.

[a] NaDCC dihydrate (CDB-56®) meets the SEMI S30 criteria for a "hazardously exothermic" material. For more information, see **Appendix E** Section VII.

It should be noted that neither Clearon, Optima Belle, nor RCI are member companies of SEMI, nor do they operate in the manufacturing sectors served by SEMI. However, the contents of this standard, particularly in the section quoted above, are easily applied to tolling arrangements in the chemical manufacturing sector. In the absence of further regulation of hazardous reactive chemicals by OSHA and EPA (Section 4.5), standards such as SEMI S30 provide examples of how industries other than the chemical manufacturing industry are managing the risk of hazardous substances.

As previously discussed in Section 4.1, Clearon's final Technology Package was comprised of:

- General manufacturing, quality, logistics, and safety instructions for the conversion of CDB-56® to CDB-63®;
- Contact information for relevant Clearon personnel;
- Clearon's SDSs for both CDB-56® (the raw material to be dehydrated) and CDB-63® (the final product);
- "Technical Product Bulletins" for both CDB-56® (the raw material to be dehydrated) and CDB-63® (the final product);
- A product specification sheet for CDB-63® (the final product);
- Instructions for lab QC analysis of CDB-63® (the final product); and
- A CDB-56® lab drying curve, showing the moisture content versus time of a 5.6-gram sample of CDB-56® dehydrated at 130°C and at atmospheric pressure.

The Clearon Technology Package lacked many of the components CCPS recommends, and therefore the CSB concludes that Clearon did not follow industry best practices in developing its Technology Package.[a]

CCPS states that "[t]he success of the tolling experience is directly related to the quality of the technology package [35, p. 56]," and goes on to recommend, in addition to the extensive list of information to be included in an initial technology package, many other considerations for inclusion in the final technology package [35, pp. 42-43]. CCPS elaborates:

> Engineering staff, HS&E representatives, chemists, and others should participate in the development of the technology package as demanded by the risk involved with the specific toll. The technology package, plus the operating procedures, equipment drawings, and other process safety information, become the basis of the process hazard analysis. Thoroughness will help ensure an accurate assessment of the risks associated with the tolling project [35, p. 43].

The Clearon Technology Package was developed by a single employee, and Clearon had no formalized processes or procedures governing the creation and maintenance of its Technology Package or the transmittal of the package to tolling partners (Sections 4.1.2 and 4.1.3).

Lessons learned from past incidents can also inform companies' development of technology packages. In April 1995 (roughly three years after OSHA promulgated the PSM standard, and roughly one year before the EPA promulgated the RMP rule), the Napp Technologies facility in Lodi, New Jersey experienced an explosion and fire that resulted in five worker fatalities. The incident also resulted in significant property damage, a public

[a] Clearon asserts it did not routinely prepare Technology Packages or utilize tolling partners.

evacuation, and contamination of the Saddle River with chemical-laden firefighting water. The EPA and OSHA conducted a joint accident investigation and released the report in October 1997 [50].[a]

At the time of the incident, Napp Technologies was performing toll blending operations for Technic Inc. Among the incident's reported causal factors was this:

> Communications [b]etween Napp and Technic were inadequate. Napp was carrying out a blending operation for another company. Inadequate communication of hazard information between the companies led to an inadequate process hazard review [50, p. III].

The report further states:

> Facilities need to clarify and understand their respective responsibilities for the discovery and assessment of chemical and process hazards and process safety information in tolling or other contracting agreements. Both parties must be clear as to who will be responsible for process safety information, including chemical hazards, technology of the process, consequences of upset conditions, and identification of any previous incidents involving similar processes [50, p. 30].

Unfortunately, the incident shares many common circumstances, causal factors, and lessons learned with the Optima Belle incident that is the subject of this report.

4.4.3 Hazard Identification and Risk Analysis in Tolling Operations

The CCPS Guidelines also contain specific recommendations for the tolling parties to conduct PHAs of the tolling project. The CCPS states:

> PHAs are performed primarily to reduce losses resulting from incidents that can injure plant personnel or the public, or damage or destroy buildings, equipment, and material. There are other less measurable losses that occur after incidents. Companies' reputations, the industry's reputation and the effect on customers and the public are all at stake. For every new tolling situation a process hazard analysis should be conducted using one of several acceptable methodologies in common use [35, p. 89].

CCPS elaborates:

> In order to understand the chemical and process hazards, a Process Hazard Analysis (PHA) should be conducted. For tolls involving regulated substances […], a PHA is a regulatory requirement. Both parties need to stipulate their areas of responsibility and participation with respect to:
>
> - Assignment of the PHA leader
> - Provision of PHA team members

[a] The EPA and OSHA conducted the Napp Technologies investigation even though the CSB had been created in 1990 because the CSB had not yet been funded at the time and did not begin operations until 1998.

> - Type(s) of PHA methodology acceptable for the toll
> - Process safety information update and preparation
> - Resolution of PHA action items
> - Reports on progress of action item resolution[.]
>
> Details concerning such responsibilities could be provided in the contract or in project correspondence [35, pp. 59-60].

The CCPS recommends that "[t]he toller and their client can work together to identify the appropriate method and detail required for the [PHA] [35, p. 93]." CCPS also details important inputs into the PHA process, including "a thorough final process technology package combined with the toller's equipment information," P&IDs, alarms, interlocks, operating procedures, and emergency response plans [35, p. 93]. The CCPS summarizes the importance of the PHA:

> Investigations of incidents involving tolling operations have found that the PHA can be the most important pre-startup activity for preventing problems while providing an opportunity to share information. When representatives from both parties are focused on the PHA, they may discover [issues] not previously identified [35, p. 93].

The *Guidelines* list actions to take if the process or materials are not regulated by the PSM standard or RMP rule. The guidelines recommend implementing good process safety practices even "when a candidate toll project will not trigger regulation [35, pp. 30-31]."

As recommended by industry guidance, Optima Belle conducted a PHA of its dehydration process. However, the PHA was based upon an inadequate understanding of the hazards of the NaDCC dihydrate (CDB-56®) material, and ultimately the PHA failed to identify or even consider the potential for overheating NaDCC dihydrate (CDB-56®), leading to a self-accelerating decomposition, at the intended operating conditions. Further, Clearon did not substantively participate in the PHA, contrary to industry good practice guidance.

After the hazards analysis phase, the *Guidelines* recommend augmented observation during scale-up of the critical process characteristics that were designed in pilot testing. This is to ensure that the order-of-magnitude changes in vessel size and quantity of materials that may have been engineered into the new process are fully considered. When scaling up exothermic or high-temperature processes, heat removal must be considered. The pilot or bench process design may be compromised by a lower surface to volume ratio in the reaction vessel. This may be a key factor during equipment selection for the scale-up [35, p. 107].

However, again contrary to industry guidance, Clearon and Optima Belle never performed scale-up studies for the dehydration of CDB-56® in a pressure vessel. Instead, Clearon sought "immediate," "full-scale" toll production, although that language was tied to Clearon's initial solicitation for production via a fluidized bed dryer. Ultimately, Clearon agreed to proceed with Optima Belle's rotary double cone dryer at the same production scale as it originally sought via a fluidized bed dryer.

A Clearon project implementation manager/improvement leader told the CSB that "during the pandemic, there was a need for disinfectant-type products…there was a commercial need for [the CDB-63®]." Another Clearon leader shared that CDB-63® was on the EPA's list of COVID-19 disinfectants, stating, "[the company] had made it in the past and were looking to run trials and start up production again because of its potential as a disinfectant."

4.4.4 Other Client Responsibilities

The CCPS *Guidelines for Process Safety in Outsourced Manufacturing Operations* recommends that the client become familiar with the toller's planned operation and audit the health, safety, and environmental practices as part of the client's product stewardship responsibilities [35, p. 54]. Clearon reviewed and provided comments on the Optima Belle procedure to dehydrate CDB-56®. Revision 3 of the procedure was in use at the time of the incident.

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 [35, p. 60]. The CSB found no evidence that Clearon or RCI reviewed Optima Belle's employee training program or requested any proof of adequate training addressing NaDCC dihydrate.

The *Guidelines* also recommend that the client audit the toller during ongoing operations to ensure that "operations are going as planned and obligations are being met [35, pp. 109-111]." Clearon technical coverage did not continue throughout the first dehydration batch even though the process was taking much longer than expected, and product quality issues were arising. As discussed in Section 2.2, several Clearon representatives, including Clearon's technical lead for the CDB-56® dehydration at Optima Belle, were on-site until approximately 5:30 p.m. on December 8, 2020. Clearon's technical lead told the CSB that "things had gone as expected; maybe a little slower than expected but it was a first batch…first trial." He also shared that there was a discussion with Optima Belle about staying, and it was agreed that he would be available by phone.

4.4.5 Other Toller Responsibilities

The CCPS best practice guidelines also describe typical responsibilities of the toller, which include 1) equipment, 2) operating personnel, 3) technical support, 4) utilities, 5) analytical resources, 6) maintenance resources, 7) engineering support, and 8) manufacturing products [35, p. 5 & 55]. "The toller needs to be familiar with all raw materials, intermediate materials, products, and wastes used, respectively, while operating the process" [35, p. 61]. It is essential that health, safety, and environmental data are shared between the parties. Additionally, the guidelines recommend that the toller discuss and agree on changes made to the equipment, chemicals, technology, or procedure of the tolling agreement with the client. The guidelines summarize the completion of the pre-startup phase of a new toll as follows:

> [Before starting the process,] the tolling team has analyzed the hazards, addressed the risks and modifications using a management of change system, revised and written procedures, trained the workers, performed a PSSR [Pre-Startup Safety Review], and completed any required test runs [35, p. 106].

An agreement should be made between the client and toller on how change is to be managed for a toll [35, p. 62], including changes in personnel, the process, ownership, performance monitoring, and handling of materials [35, p. 117], whether or not the process or facility "is covered under a regulatory mandate to manage change" [35, p. 117]. Any change requires the toller and client to address the hazards and risks associated with the change. The CSB found no evidence that either Clearon or Optima Belle conducted a change management review for the change in technology from a fluidized bed dryer, with which Clearon had extensive process knowledge and experience, to a pressure-rated rotary dryer.

4.4.6 Tolling Conclusions

The CSB concludes that:

- Neither Clearon nor Optima Belle adequately followed existing industry guidance concerning the safe conduct of tolling operations. Their deficiencies included:
    - Inadequate exchange of process knowledge between the tolling parties;
    - Inadequate mutual involvement in the PHA;
    - Inadequate understanding, characterization, and analysis of the hazards of NaDCC dihydrate and the dehydration operation; and
    - No evaluation of the technology change from an atmospheric fluidized bed dryer to a pressure-rated rotary dryer.
- Had Clearon and Optima Belle followed industry good practice guidance for tolling operations, this incident might have been prevented.

The CSB recommends that Clearon and Optima Belle develop and implement a formalized program for the development of toll manufacturing agreements using resources such as the CCPS's *Guidelines for Process Safety in Outsourced Manufacturing Operations* and *Guidelines for Risk Based Process Safety*. Ensure that the program provides for the following:

a) Identification of roles and responsibilities of all parties, including the client, toller, and any third-party technical service providers, for all phases of a proposed arrangement;

b) Evaluation of equipment requirements/specifications to ensure that they are adequate for the intended operation; and

c) Participation by all parties in tolling process development, including process hazards analysis and emergency planning, and appropriate stages of the pre-planning, pre-startup, and production phases.

As a tolling broker and project manager serving between Clearon (the client) and Optima Belle (the toller), RCI could have served an important role in ensuring that the two companies were aware of and following industry good practice guidance. Instead, RCI served no role other than to connect Clearon with Optima Belle and to ensure that a Technology Package was received from Clearon. The CSB found no evidence that RCI took any part in reviewing or verifying the adequacy of the Technology Package, conducting the PHA, or any subsequent tolling activities.

The CSB concludes that:

- Companies like RCI can serve an important function between tolling manufacturers like Optima Belle and tolling clients like Clearon. RCI could have ensured that Optima Belle and Clearon were aware of and adhering to tolling industry good practices.
- Companies like RCI can aid in spreading knowledge of tolling industry good practices, as they are likely to participate in many tolling arrangements between many companies.

The CSB thus recommends to RCI to develop and implement a formalized program for the development of toll manufacturing agreements using resources such as the CCPS's *Guidelines for Process Safety in Outsourced*

Manufacturing Operations and *Guidelines for Risk Based Process Safety*. Ensure that the program provides for the following:

a) Identification of roles and responsibilities of all parties, including the client, toller, and any third-party technical service providers, for all phases of a proposed arrangement; and

b) Participation by all parties in tolling process development, including process hazards analysis and emergency planning, and appropriate stages of the pre-planning, pre-startup, and production phases.

CCPS's *Guidelines for Process Safety in Outsourced Manufacturing Operations* contains extensive guidance for client companies and tolling manufacturers, but contains little guidance specific to companies like RCI, which served as the service provider between the client Clearon and the toller Optima Belle. Since CCPS published its tolling *Guidelines* in 2000, the knowledge base regarding the processing of hazardous reactive chemicals and the best practices required to do so safely has continued to grow, and standards such as SEMI S30 to safely use energetic and reactive materials have been introduced. In 2000, the PSM standard and RMP rule were less than 10 years old, and in the intervening time, the body of knowledge and best practices for process safety in general has also grown immensely. In 2007, CCPS published its *Guidelines for Risk Based Process Safety* (RBPS), which provides excellent guidance on process safety management practice in general and provides a holistic process safety management system structure that companies can follow and adapt to their operations. RBPS provides more specific guidance and expands upon the process safety practices recommended in *Guidelines for Process Safety in Outsourced Manufacturing Operations.*

Although the process safety practices detailed in CCPS's *Guidelines for Process Safety in Outsourced Manufacturing Operations* likely could have helped prevent this incident, those practices may not fully reflect the current body of knowledge of process safety or CCPS's guidance thereof. For example, terminology used in the tolling *Guidelines* does not align with the management elements and systems contained in RBPS, as RBPS had not yet been published when CCPS published its tolling *Guidelines.*

The CSB thus recommends to CCPS to update *Guidelines for Process Safety in Outsourced Manufacturing Operations* or develop a new tolling guidance document to supplement existing guidelines. The publication should include current best practices, introduce guidance specific to tolling brokers and/or project managing companies such as RCI, and cross-reference and align with the comprehensive management systems framework and terminology contained in *Guidelines for Risk Based Process Safety* and other contemporary industry good practice guidance.

4.5 Regulatory Coverage of Reactive Hazards

In 1992, OSHA promulgated the PSM standard (29 CFR § 1910.119), and in 1996 the EPA promulgated its RMP rule (40 CFR § 68) to manage chemical process safety and to help prevent major incidents. Together, these regulations require chemical facilities to manage process safety to protect workers, members of the public, and the environment. Each regulation covers facilities that process certain chemicals. The OSHA PSM standard covers processes using flammable materials and individually listed chemicals that present a range of hazards, and the EPA RMP rule identifies covered substances based on flammability and toxicity. While these regulations achieve improved process safety for many chemical processing facilities in the United States, they have a critical coverage gap: neither standard adequately covers facilities processing chemicals that could undergo a highly hazardous chemical reaction. Significantly, while NaDCC dihydrate and NaDCC are capable of undergoing a highly hazardous chemical reaction (decomposition) that can release toxic chlorine, which happened during the Optima Belle incident, the chemical is not covered in either the OSHA PSM standard or

EPA RMP rule. As such, Optima Belle was not required to implement baseline process safety management system elements to manage the safety of its NaDCC-related operations under these regulations.

OSHA and the EPA currently use predefined chemical lists to identify the processes subject to coverage under the PSM standard and RMP rule. The CSB found that OSHA and EPA did not adequately consider reactive chemical hazards when developing these chemical lists, and, as a result, many reactive chemicals, including NaDCC dihydrate and NaDCC, are not covered by these regulations. This regulatory coverage gap relating to reactive chemicals and their hazards also (1) points to a weakness with relying on fixed chemical lists to determine regulatory coverage, (2) contributed to this incident, and (3) contributed to many other reactive chemical incidents over the past three decades. OSHA has also resorted to citing companies for safety-related violations under its General Duty Clause following incidents involving reactive chemicals not covered under its PSM standard.[a] This approach is not proactive and is ill-suited for accident prevention. OSHA investigated the Optima Belle incident and cited Optima Belle for violations of the General Duty Clause of 29 CFR Section (5)(a)(1) for a total of $12,288 in penalties [51].

In 2002, the CSB published a *Hazard Investigation: Improving Reactive Hazard Management* report after completing a study on chemical hazards in the industry. In that study, the CSB examined the process safety of chemical reactivity hazards in the United States and analyzed 167 known reactive chemical incidents that occurred between 1980 and 2001. Its objectives included:

- Determining the impact of reactive chemical incidents.
- Examining how industry, OSHA, and the EPA address reactive chemicals hazards.
- Developing recommendations for reducing the number and severity of reactive chemical incidents.

In the report, the CSB concluded,

> … two elements are particularly relevant to reactive hazards–Process Safety Information (PSI; 29 C.F.R. § 1910.119(d)) and Process Hazard Analysis (PHA; 29 C.F.R. § 1910.119€). Two commonly cited causes of reactive incidents, … are inadequate understanding of reactive chemistry or inadequate hazard evaluation … [52, pp. 55-56]
>
> … the [OSHA] PSM Standard has significant gaps in coverage of reactive hazards because it is based on a limited list of individual chemicals with inherently reactive properties. [52, p. 56]
>
> When developing the [EPA's Accidental Release Prevention] list of substances, EPA considered only the inherent characteristics of a chemical that indicate a severe threat due to exposure. Well-defined criteria were used for toxicity and flammability. However, because of the complexities of site-specific factors and process conditions, EPA was unable to determine any inherent characteristic as an indicator of reactivity. EPA concluded that there was "insufficient technical information for developing criteria for identifying reactive substances." Consequently, the January 1994 RMP list of 130 chemicals does not contain any

[a] An example includes the 2017 Midland Resource Recovery (MRR) explosion where neither of the chemicals involved was covered under the OSHA PSM standard (see **Table 4**). Midland Resource Recovery Investigation | CSB

substances listed due to reactive hazards. [52, p. 60]

The CSB issued the following recommendation to OSHA and has repeatedly reiterated it in other investigation reports:

> Amend the Process Safety Management Standard (PSM), 29 CFR 1910.119, to achieve more comprehensive control of reactive hazards that could have catastrophic consequences.
>
> - Broaden the application to cover reactive hazards resulting from process-specific conditions and combinations of chemicals. Additionally, broaden coverage of hazards from self-reactive chemicals. In expanding PSM coverage, use objective criteria. Consider criteria such as the North American Industry Classification System (NAICS), a reactive hazard classification system (e.g., based on heat of reaction or toxic gas evolution), incident history, or catastrophic potential.
> - In the compilation of process safety information, require that multiple sources of information be sufficiently consulted to understand and control potential reactive hazards. Useful sources include:
>   - Literature surveys (e.g., Bretherick's Handbook of Reactive Chemical Hazards, Sax's Dangerous Properties of Industrial Materials).
>   - Information developed from computerized tools (e.g., ASTM's CHETAH, NOAA's The Chemical Reactivity Worksheet).
>   - Chemical reactivity test data produced by employers or obtained from other sources (e.g., differential scanning calorimetry, thermogravimetric analysis, accelerating rate calorimetry).
>   - Relevant incident reports from the plant, the corporation, industry, and government.
>   - Chemical Abstracts Service.
> - Augment the process hazard analysis (PHA) element to explicitly require an evaluation of reactive hazards. In revising this element, evaluate the need to consider relevant factors, such as:
>   - Rate and quantity of heat or gas generated.
>   - Maximum operating temperature to avoid decomposition.
>   - Thermal stability of reactants, reaction mixtures, byproducts, waste streams, and products.
>   - Effect of variables such as charging rates, catalyst addition, and possible contaminants.
>   - Understanding the consequences of runaway reactions or toxic gas evolution. [52, pp. 89-90]

The CSB also issued the following recommendation to the EPA and has repeatedly reiterated it in other investigation reports:

> Revise the Accidental Release Prevention Requirements, 40 CFR 68, to explicitly cover catastrophic reactive hazards that have the potential to seriously

> impact the public, including those resulting from self-reactive chemicals and combinations of chemicals and process-specific conditions … [52, p. 91]

Neither OSHA nor the EPA has implemented these recommendations [53] or improved the PSM standard or RMP rule to increase coverage of reactive chemicals.

4.5.1 Reactive Chemical Incidents Investigated by the CSB after the Reactive Hazard Study

Since the publication of the CSB Reactive Hazard Study and as of the time of publication of this report, the CSB has investigated 11 additional incidents involving reactive chemicals that are not covered by the OSHA PSM standard and EPA RMP rule. Those incidents resulted in 28 fatalities and hundreds of injuries.[a] They are listed in **Table 4**.[b]

[a] The 28 fatalities do not include the fatality in the Optima Belle incident, which is the subject of this report.

[b] The 29 fatalities listed in **Table 4** include the Optima Belle incident.

Table 4. Investigations completed by the CSB since September 2002 involving reactive chemicals that are not covered under OSHA's PSM standard or the EPA's RMP rule.

Date	Investigation Description	Chemical(s) Involved	Severity
October 13, 2002	First Chemical Corporation reactive explosion and fire[a]	Mononitrotoluene	3 injured
April 12, 2004	MFG Chemical Inc. unintended decomposition reaction[b]	Triallyl cyanurate	154 hospitalized
December 19, 2007	T2 Laboratories runaway reaction and explosion[c]	Methylcyclopentadienyl Manganese Tricarbonyl, Methylcyclopentadiene, and Diglyme	4 fatalities 32 injured
August 28, 2008	Bayer CropScience, LP runaway decomposition[d]	Methomyl	2 fatalities
April 17, 2013	West Fertilizer Company fire and explosion[e]	Fertilizer Grade Ammonium Nitrate	15 fatalities More than 260 injured
August 28, 2016	Airgas nitrous oxide decomposition reaction and explosion[f]	Nitrous Oxide	1 fatality
October 20, 2016	MGPI Processing Inc. chemical reaction and release[g]	Sulfuric Acid and Sodium Hypochlorite	More than 140 required medical attention
May 24, 2017 and June 20, 2017	Midland Resource Recovery chemical reaction and explosions[h]	Sodium Hypochlorite and Tertiary Butyl Mercaptan	2 fatalities 1 severely injured
May 3, 2019	AB Specialty Silicones chemical reaction, explosion, and fire[i]	Andisil® XL 10 and TD 6/12 Blend	4 fatalities
August 27, 2020	Bio-Lab Lake Charles reaction, decomposition, and fire[j]	Trichloroisocyanuric Acid	No reported injures
September 14, 2020	Bio-Lab Conyers reaction and decomposition[k]	Trichloroisocyanuric Acid	9 required medical attention
December 8, 2020	This incident is the subject of this report. Optima Belle chemical decomposition and explosion	Sodium Dichloroisocyanurate Dihydrate	1 fatality 3 required medical attention

[a] First Chemical Corporation Reactive Chemical Explosion | CSB Investigation
[b] MFG Chemical Toxic Chemical Vapor Cloud Release | CSB Investigation
[c] T2 Laboratories Inc. Reactive Chemical Explosion | CSB Investigation
[d] Bayer CropScience Runaway Reaction and Explosion | CSB Investigation
[e] West Fertilizer Company Fire and Explosion | CSB Investigation
[f] Airgas nitrous oxide explosion | CSB Investigation
[g] MGPI Processing Chemical Reaction and Release Investigation | CSB Investigation
[h] Midland Resource Recovery Investigation | CSB Investigation
[i] AB Specialty Silicones chemical reaction, explosion, and fire | CSB Investigation
[j] Bio-Lab Trichloroisocyanuric acid reaction, decomposition, and release | CSB Investigation
[k] Bio-Lab Trichloroisocyanuric acid reaction, decomposition, and release | CSB Investigation

During the time frame of the above incidents, various published standards and guidelines (as described in Sections 4.2.1 and 4.2.2) provided good industry practices for handling reactive chemicals. **Figure 20** shows other reactive hazard guidance issued by the EPA and OSHA before and after the CSB's reactive hazard study.

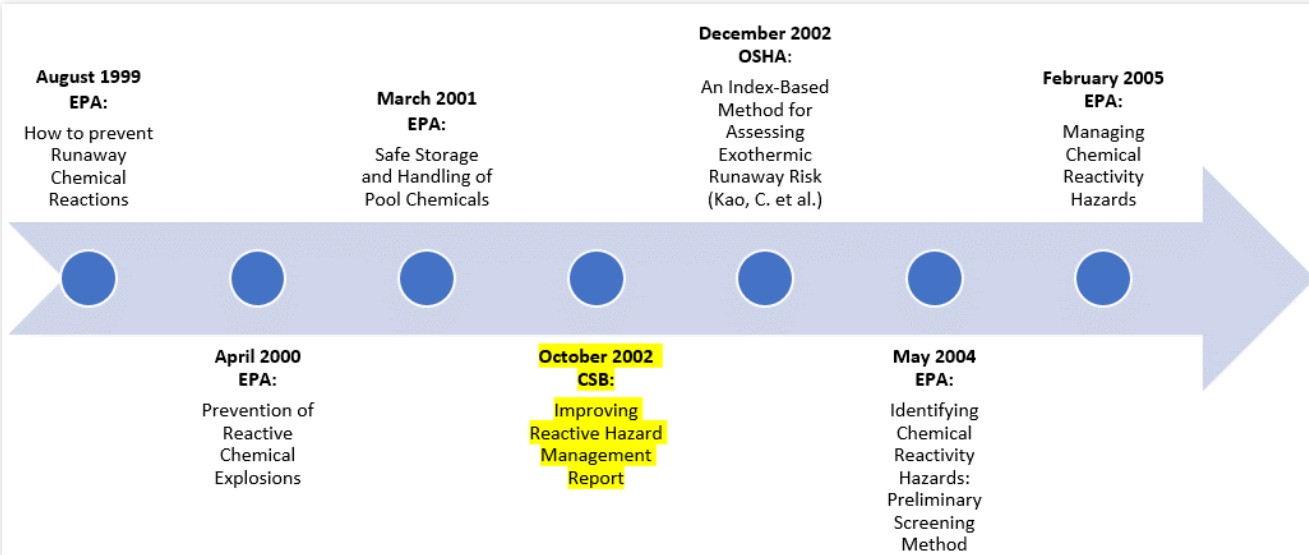

Figure 20. Timeline of EPA and OSHA reactive hazard guidance. (Credit: CSB)

In addition to the CSB investigations listed in **Table 4**, the 1995 Napp Technologies explosion and fire involved sodium hydrosulfite and powdered aluminum, which resulted in five worker fatalities. This incident (covered in Section 4.4.2) bears a striking resemblance to the Optima Belle incident that is the subject of this report. Neither sodium hydrosulfite nor powdered aluminum is covered under the RMP rule or PSM standard. In the wake of the Napp Technologies incident, which occurred approximately three years before the CSB commenced operations,[a] OSHA and the EPA conducted a joint incident investigation. Among its full list of findings, the *EPA/OSHA Joint Chemical Accident Investigation Report* contains the following facts and conclusions, which closely mirror the circumstances and conclusions presented in this report [50]:

- The incident involved a water-reactive chemical unregulated by the PSM standard or RMP rule;
- The incident involved tolling operations between multiple companies;
- The companies conducted an inadequate PHA and did not take appropriate preventive actions;
- The equipment selected for the process was inappropriate; and
- Inadequate safety and hazard information led to the inadequate PHA.

The joint EPA/OSHA investigation report made this recommendation to both the EPA and OSHA:

> The JCAIT [Joint Chemical Accident Investigation Team] developed recommendations that address the root causes and contributing factors to prevent a reoccurrence or similar event at other facilities:
>
> […]

[a] The CSB was created in 1990 but was not funded until 1998.

> OSHA and EPA should review the lists of substances subject to the [PSM] and RMP] regulations to determine whether reactive substances should be added [50, p. III][.]
>
> […]
>
> Appendix A of OSHA's existing [PSM] standard […] lists the […] chemicals covered by that standard. At the time of the [PSM] rulemaking, OSHA decided to include only [certain chemicals]. Because of this tragic event, OSHA is considering adding additional reactive chemicals [50, p. 31].

"EPA and OSHA have agreed to harmonize their lists of substances under the PSM standard and the [RMP rule]. EPA's current list only addresses toxic and flammable substances. As part of the upcoming 5-year review of its list, EPA will consider other hazards, including reactive chemicals" [50, p. 31].

Despite EPA and OSHA issuing that recommendation in the Napp Technologies investigation report in 1997, and despite the 167 reactive incidents identified in the CSB's 2002 reactive hazards study and the 11 subsequent incidents resulting in 29 fatalities and at least 450 injuries investigated by the CSB since that study, neither regulator has taken adequate action to address reactive chemical hazards. The CSB's recommendations to OSHA and the EPA remain open. The CSB has reiterated these recommendations four times since they were first issued in 2002.

In addition to regulatory guidance, the CSB has identified other thermal assessment guidance and reactive hazard RAGAGEP that existed before and after the publication of its 2002 study (**Figure 21** and **Figure 22**).

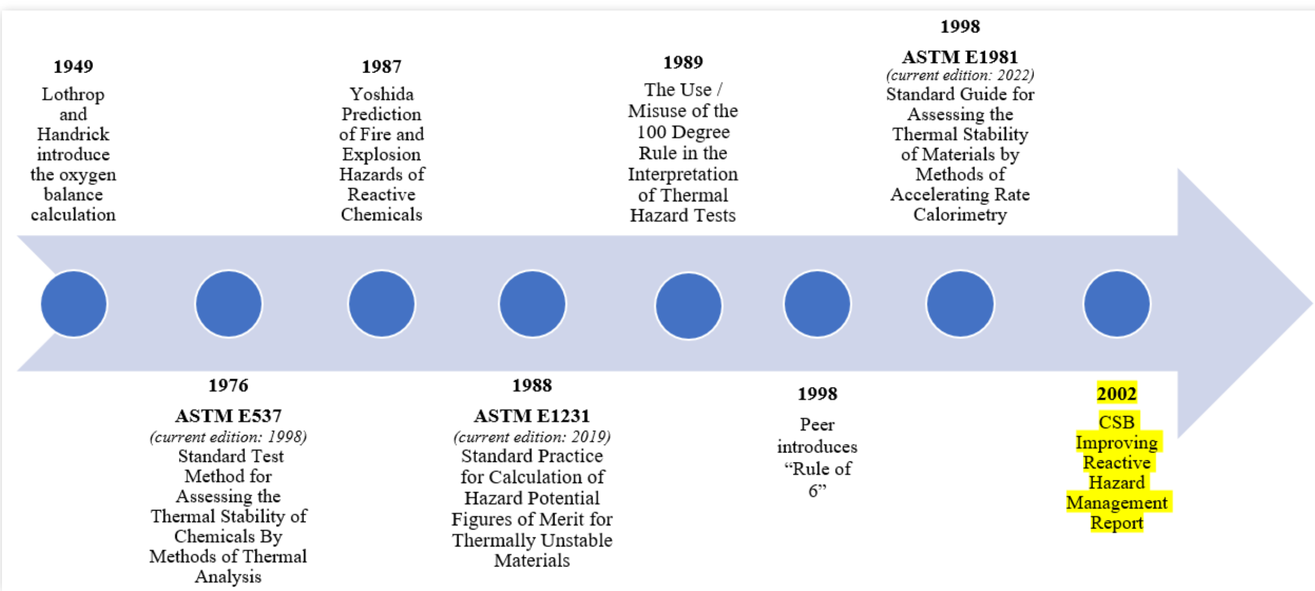

Figure 21. Thermal hazard assessment guidance and reactive hazard RAGAGEP timeline before 2002. (Credit: CSB)

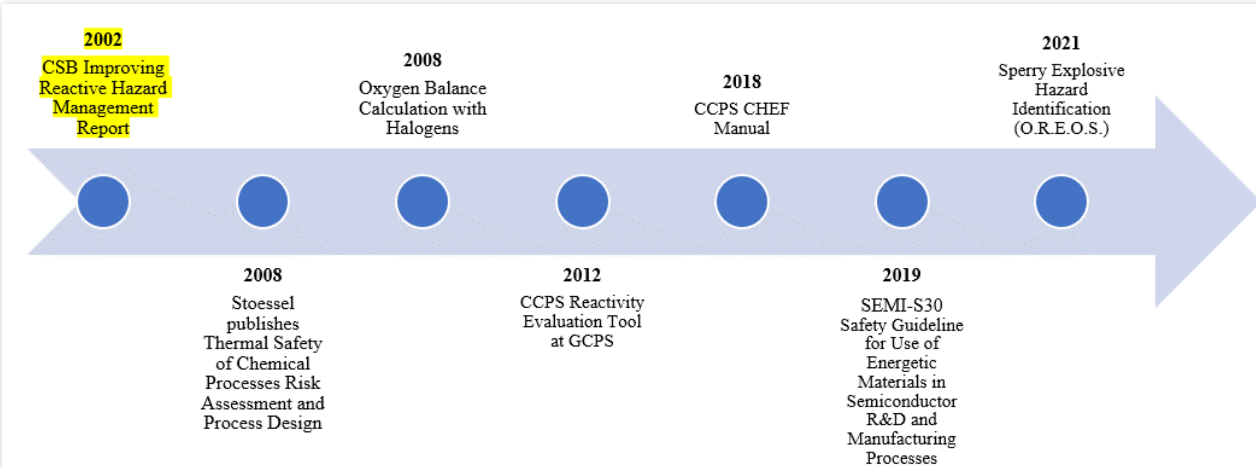

Figure 22. Thermal hazard assessment guidance and reactive Hazard RAGAGEP timeline after 2002. (Credit: CSB)

In the CSB's 2007 safety video, *Reactive Hazards: Dangers of Uncontrolled Chemical Reactions*, process safety expert Daniel Crowl[a] stated, " … we cannot avoid reactive chemical hazards. However, chemical plant accidents involving reactive hazards are unacceptable. The technology and the management systems do exist to produce these products safely." Nevertheless, as outlined herein, current federal process safety regulations do not require companies with processes like Optima Belle's to develop and implement a process safety management system to effectively control reactive chemical hazards. Although good practice guidance for managing reactive chemical hazards does exist to guide companies to establish these more robust safety management systems, they are voluntary [54, p. 47].

The CSB concludes that had NaDCC and NaDCC dihydrate been covered under the EPA's RMP rule or OSHA's PSM standard, Clearon, Optima Belle, and RCI would have been required to implement a safety management system that included provisions for PSI, including reactivity data, which might have led Optima Belle and Clearon to better analyze the reactivity hazards associated with NaDCC dihydrate.

The CSB again reiterates the recommendation to EPA (2001-01-H-R3, Section 6.2.1), but the CSB has determined that the recommendation to OSHA should be updated. Therefore, the CSB supersedes recommendation 2001-01-H-R1 to OSHA, originally published in the CSB's 2002 reactive hazards study. The CSB recommends to OSHA to amend the Process Safety Management (PSM) standard, 29 CFR 1910.119, to achieve more comprehensive control of reactive hazards that could have catastrophic consequences, as follows:

- Broaden the application to cover reactive hazards resulting from process-specific conditions and combinations of chemicals. Additionally, broaden coverage of hazards from self-reactive chemicals. In expanding PSM coverage, use objective criteria. Consider criteria such as the North American Industry Classification System (NAICS), a reactive hazard classification system (e.g., based on heat of reaction or hazardous gas evolution), incident history, or catastrophic potential.
- In the compilation of process safety information, require that multiple sources of information be sufficiently consulted to understand and control potential reactive hazards. Useful sources include but are not limited to:

[a] Daniel A. Crowl is also a professor emeritus of chemical engineering at Michigan Technological University and the co-author of *Chemical Process Safety: Fundamentals with Applications*.

   - Literature surveys (e.g., Bretherick's Handbook of Reactive Chemical Hazards, Sax's Dangerous Properties of Industrial Materials, CAS SciFinder).
   - Information developed from computerized tools (e.g., ASTM's CHETAH, CCPS's Chemical Reactivity Worksheet).
   - Chemical property data compiled in PubChem and the REACH dossiers maintained by the ECHA.
   - Chemical reactivity test data produced by employers or obtained from other sources following established standards such as:
     - ASTM E537-20, Standard Test Method for Chemicals by Differential Scanning Calorimetry;
     - ASTM E1981-22, Standard Guide for Assessing Thermal Stability of Materials by Methods of Accelerating Rate Calorimetry;
     - ASTM E2550-21, Standard Test Method for Thermal Stability by Thermogravity; and
     - ASTM E1231-19, Standard Practice for Calculation of Hazard Potential Figures of Merit for Thermally Unstable Materials.
   - Relevant incident data from the plant, the corporation, industry, and government.
- Augment the process hazard analysis (PHA) element to explicitly require an evaluation of reactive hazards. In revising this element, evaluate the need to consider relevant factors, such as:
   - Rate and quantity of heat or gas generated.
   - Maximum operating temperature to avoid a runaway reaction from decomposition.
   - Time to Maximum Rate under Adiabatic Conditions (TMR_{ad}).
   - Thermal stability of reactants, reaction mixtures, byproducts, waste streams, and products.
   - Effect of variables such as charging rates, catalyst addition, and possible contaminants.
   - Understanding the consequences of runaway reactions or hazardous gas evolution.

The CSB concludes that despite the lack of regulatory coverage of the NaDCC dihydrate dehydration process, and in the absence of regulatory changes by OSHA or the EPA, both Clearon and Optima Belle should have applied good process safety practices in accordance with industry guidance. Therefore, the CSB recommends that Clearon and Optima Belle develop and implement process safety management systems consistent with industry guidance publications such as is contained in the CCPS's *Guidelines for Risk Based Process Safety.* At a minimum, the company's process safety management system should address hazard identification, risk analysis, and management of risk.

5 Conclusions

5.1 Findings

Technical Analysis

1. The sharp drop in the scrubber pH was an indication that decomposition was likely occurring in the dryer since a CDB-56® decomposition reaction releases much higher amounts of chlorine than the CDB-56® dehydration process.
2. The NaDCC dihydrate in Optima Belle's rotary dryer underwent a self-accelerating decomposition reaction.
3. Excessive pressure produced by the NaDCC dihydrate decomposition reaction caused over-pressurization of the Optima Belle rotary dryer and its subsequent catastrophic failure.

Process Knowledge Management

4. Clearon's SDS for NaDCC dihydrate was inadequate in the following ways:
    - It did not accurately reflect the temperatures at which the compound could decompose, which was known to Clearon to be far lower than the listed decomposition temperature of 240°C–250°C, based on studies conducted in the 1970s and 1980s. Post-incident testing results found that NaDCC dihydrate begins a runaway exotherm (indicative of a runaway decomposition) at approximately 81°C when heated in a closed container;
    - It did not contain Clearon's storage temperature restriction of 60°C;
    - It did not list chlorine or NCl_3 in the list of decomposition products. Both products of decomposition were known to Clearon;
    - It stated that hazardous reactions "Will not occur" despite listing several chemicals with which NaDCC dihydrate is incompatible and listing multiple hazardous decomposition products other than chlorine and NCl_3;
    - It stated that hazardous reactions "Will not occur" despite Clearon's knowledge that NaDCC dihydrate can undergo a hazardous decomposition reaction;
    - It stated that hazardous reactions "Will not occur" despite also stating that the compound "may decompose if heated"; and
    - It did not list the material as an oxidizer despite it being classified as such by the NFPA, and despite that designation appearing on the material's technical bulletin.
5. The NaDCC dihydrate chemical hazard information contained in SDSs varies substantially between suppliers.
6. The SDS for Clearon CDB-56® did not fully reflect the known hazards of the substance.
7. Given that important information and context were missing from the CDB-56® SDS, an end user of the document may not have completely understood the material's propensity to decompose, the circumstances that could result in a decomposition, or the potential consequences of a decomposition.
8. Clearon's Technology Package, including particularly Clearon's NaDCC dihydrate SDS, was inadequate and lacked critical information on the decomposition of NaDCC dihydrate, and as a result it did not enable

Optima Belle to perform an effective assessment of the adequacy of its existing toll manufacturing equipment for the dehydration process.

9. Had Clearon provided the 1989 Olin white paper, or other relevant data on the decomposition of CDB-56® to Optima Belle, Optima Belle would have had the necessary, critical context to understand the circumstances that could lead to the decomposition of CDB-56®.
10. Clearon's Technology Package led Optima Belle to an inadequate understanding of the hazards of the dehydration process and CDB-56® material. Had Clearon developed a robust process Technology Package and submitted such information to Optima Belle in advance of their tolling agreement, Optima Belle could have used it to better inform its process design and hazards analysis, and this incident could have been prevented.
11. Clearon lacked effective process knowledge management practices. Such practices should have documented and maintained information critical to the safe dehydration of NaDCC dihydrate and should have made that information easily accessible. As a result of Clearon's ineffective process knowledge management practices, Clearon's Technology Package lacked important process and product knowledge, and the company did not transmit important safety information to its tolling manufacturer, Optima Belle.
12. Regardless of whether Clearon's SDS is compliant with OSHA's Hazard Communication Standard, the OSHA regulations are minimum requirements. Clearon's NaDCC dihydrate SDS could have exceeded the regulatory minimums in the OSHA Hazard Communication standard.
13. The June 2022 Clearon SDS for NaDCC dihydrate still falls short of clearly communicating the known hazards of the material.

Thermal Hazard Assessment

14. Had Clearon, Optima Belle, and RCI performed an extensive thermal hazard assessment, shared the 1989 Olin data, or located adequate publicly available information, all parties could have understood the associated NaDCC dihydrate reactivity hazards, and the explosion could have been avoided.
15. OSHA should update its Chemical Reactivity Hazards website.
16. None of the parties involved in the NaDCC dihydrate tolling operation effectively assessed the hazards of the material or operation. The deficiencies included:
    - failure to identify the initiation of a self-accelerating decomposition of NaDCC dihydrate as a credible scenario, except as a result of water intrusion or contamination of the product with other contaminants;
    - inadequate literature searches for publicly available or internal Clearon-owned NaDCC dihydrate data; and
    - failure to utilize available reactive hazard screening methods to assess the potential reactivity or explosivity of heated NaDCC dihydrate inside a metal pressure vessel.
17. Optima Belle's ineffective hazards assessment was due in part to the lack of adequate process knowledge.
18. Although Clearon did not submit sufficient CDB-56® thermal decomposition data and information to Optima Belle, Optima Belle did not adequately seek additional information that could have resulted in an effective hazards assessment.

19. The effective use of publicly available thermal hazards evaluation methods or of publicly available or Clearon-owned data could have resulted in a more robust and effective assessment of the hazards of the dehydration operation, which could have prevented the incident.

Equipment Selection and Process Design

20. A temperature sensor will have difficulty detecting a hot spot that is not in the immediate vicinity of the sensor in a stationary bed.
21. The use of appropriate drying technology and ancillary equipment that minimized the potential for overheating, creating hot spots, or a self-accelerating decomposition reaction during the NaDCC dihydrate dehydration process could have prevented the incident.
22. Key differences between the fluidized bed dryer that had previously been used by Clearon and the rotary dryer used by Optima Belle include:
    1. When the rotary dryer was stationary, a large volume of the material would be compacted together. As previous studies have found, the configuration and mass of stored CDB-56® affects its thermal properties, including the decomposition temperature;
    2. Fluidized bed dryers promote high rates of heat and mass transfer and uniformity of temperature and composition throughout, in contrast to the rotary dryers where temperature could be less uniform; and
    3. The fluidized bed dryer operated at atmospheric pressure, and the rotary dryer was a pressure vessel. Any evolved gases in the fluidized bed dryer would be swept out of the fluidized bed dryer to the atmosphere, but a rotary dryer with an undersized relief system would contain evolved gases, leading to a vessel explosion in a major decomposition event. Furthermore, if the rate of gas evolution is high enough, the gas flow could carry the granular product into the vent system where the product could have restricted or blocked the gas flow.

    The difference in design between the fluidized bed dryer and the rotary dryer and the different effects it could have on the material was not thoroughly evaluated by Clearon, Optima Belle, or RCI.
23. The vessel size and area-to-volume ratio must be considered when evaluating heat generation and cooling rates involving reactive materials to ensure sufficient cooling is attainable to prevent a runaway reaction.
24. Had Optima Belle conducted this evaluation or similar preliminary over-pressurization evaluations, they likely would have determined that the double cone dryer was not a practical equipment selection for the dehydration process.
25. Optima Belle incorrectly believed that it had developed an inherently safe process that was incapable by design of achieving the conditions that would lead to the decomposition of CDB-56®, based on its inadequate understanding of the CDB-56® thermal decomposition temperature. As a result, Optima Belle's existing heating and cooling systems could not prevent a CDB-56® decomposition as designed.
26. Optima Belle's jacket cooling system design was likely inadequately sized to control a CDB-56® decomposition.
27. Optima Belle's jacket heating and cooling system design lacked automatic engineering controls to monitor and adequately control the dryer temperature during the CDB-56® dehydration.

28. Had Optima Belle, Clearon, and RCI better understood the conditions at which CDB-56® could hazardously decompose, Optima Belle might have implemented improved safeguards to prevent the material from reaching its decomposition temperature.

29. Optima Belle incorrectly believed that steam generation was the only credible over-pressurization hazard applicable to the dryer during the CDB-56® dehydration because it believed that decomposition was not possible using the heating medium selected for the dehydration process. As a result, no analysis was performed to determine the pressure safety valve (PSV) size needed to prevent over-pressurization during a CDB-56® self-accelerating decomposition reaction.

30. Optima Belle's inadequate PSV evaluation was a consequence of insufficient information and its incomplete understanding of the CDB-56® decomposition temperature and decomposition characteristics, as well as Optima Belle's failure to seek additional information required to conduct the PSV evaluation.

31. Had Optima Belle, Clearon, and RCI better understood the conditions at which CDB-56® could hazardously decompose, Optima Belle could have evaluated and identified proper safeguards to prevent the exceedingly high pressure experienced in the double cone dryer that led to its failure.

32. Optima Belle failed to adequately close out a PHA action item to review the pressure relief sizing for a self-accelerating decomposition reaction.

33. Clearon and Optima Belle essentially conducted an experiment on a new method to remove water of hydration from the CDB-56® at full production scale, without first experimenting at the laboratory and pilot scales, and the end result was a catastrophic explosion.

34. Had scaled studies been conducted, Optima Belle, Clearon, and RCI likely would have gained additional NaDCC dihydrate thermal stability data, reactivity information, and process knowledge before running the first production-scale batch, which might have led to changes in the process and potentially prevented the decomposition reaction and the explosion.

Tolling of Hazardous Materials

35. Clearon did not follow industry best practice in developing its Technology Package.

36. Neither Clearon nor Optima Belle adequately followed existing industry guidance concerning the safe conduct of tolling operations. Their deficiencies included:
    - Inadequate exchange of process knowledge between the tolling parties;
    - Inadequate mutual involvement in the PHA;
    - Inadequate understanding, characterization, and analysis of the hazards of NaDCC dihydrate and the dehydration operation; and
    - No evaluation of the technology change from an atmospheric fluidized bed dryer to a pressure-rated rotary dryer.

37. Had Clearon and Optima Belle followed industry good practice guidance for tolling operations, this incident might have been prevented.

38. Companies like RCI can serve an important function between tolling manufacturers like Optima Belle and tolling clients like Clearon. RCI could have ensured that Optima Belle and Clearon were aware of and adhering to tolling industry good practices.

39. Companies like RCI can aid in spreading knowledge of tolling industry good practices, as they are likely to participate in many tolling arrangements between many companies.

Regulatory Coverage of Reactive Hazards

40. Had NaDCC and NaDCC dihydrate been covered under the EPA's RMP rule or OSHA's PSM standard, Clearon, Optima Belle, and RCI would have been required to implement a safety management system that included provisions for process safety information including reactivity data, which might have led Optima Belle and Clearon to better analyze the reactivity hazards associated with NaDCC dihydrate.
41. Despite the lack of regulatory coverage of the NaDCC dihydrate dehydration process, and in the absence of regulatory changes by OSHA or the EPA, both Clearon and Optima Belle should have applied good process safety practices in accordance with industry guidance.

5.2 Cause

The CSB determined that the cause of the Optima Belle rotary dryer's over-pressurization and its ultimate explosion was a self-accelerating decomposition of heated sodium dichloroisocyanurate dihydrate inside the dryer unit. Optima Belle did not adequately understand the potential for, analyze the hazards of, or detect and mitigate the self-accelerating thermal decomposition reaction. Contributing to the incident was Clearon Corporation's failure to transmit sufficient process safety information to Optima Belle. Also contributing to the incident were Clearon's and Optima Belle's ineffective process safety management systems, poor knowledge management, failure to follow existing industry guidance for toll manufacturing, and insufficient regulatory coverage of reactive hazards.

6 Recommendations

To prevent future chemical incidents, and in the interest of driving chemical safety excellence to protect communities, workers, and the environment, the CSB makes the following safety recommendations:

6.1 Previously Issued Recommendations Superseded in This Report

6.1.1 Occupational Safety and Health Administration (OSHA)

2001-01-H-R1 (from the 2002 CSB Reactive Hazard Study)

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

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

Superseded by **2021-02-I-WV-R13** *to OSHA in Section 6.3.4 below.*

6.2 Previously Issued Recommendations Reiterated with this Report

6.2.1 U.S. Environmental Protection Agency (EPA)

2001-01-H-R3 (from the 2002 CSB Reactive Hazard Study)

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

6.3 New Recommendations

6.3.1 Optima Belle LLC

2021-02-I-WV-R1

Develop and implement a written thermal and reactive hazards evaluation and management program. The program should adhere to industry guidance provided in publications such as the Center for Chemical Process Safety's *Essential Practices for Managing Chemical Reactivity Hazards*. At a minimum, the program should identify the process that Optima Belle will use to manage chemical reactivity hazards, resources for collecting and assessing reactivity hazards, steps for determining how and when to test for chemical reactivity, documentation requirements, and training.

2021-02-I-WV-R2

Develop and implement a written program for tolling process design and equipment selection using guidance from the Center for Chemical Process Safety's *Guidelines for Risk Based Process Safety* and *Guidelines for Process Safety in Outsourced Manufacturing Operations* to ensure that:

a) equipment design basis is adequate for any new tolling process or product;

b) safeguards and ancillary equipment are considered and adequately designed, installed, and function as designed and required; and

c) new processes to be evaluated for potential process hazards at the laboratory and/or pilot scale before production scale.

This written program should incorporate the information developed in Optima Belle's thermal and reactive hazards evaluation program (see CSB recommendation 2021-02-I-WV-R1) to ensure that chemical hazards are fully understood and controlled.

2021-02-I-WV-R3

Develop and implement a formalized program for the development of toll manufacturing agreements using resources such as the Center for Chemical Process Safety's *Guidelines for Process Safety in Outsourced Manufacturing Operations* and *Guidelines for Risk Based Process Safety*. Ensure that the program provides for the following:

a) Identification of roles and responsibilities of all parties, including the client, toller, and any third-party technical service providers, for all phases of a proposed arrangement;

b) Evaluation of equipment requirements/specifications to ensure that they are adequate for intended operation; and

c) Participation by all parties in tolling process development, including process hazards analysis and emergency planning, and appropriate stages of the pre-planning, pre-startup, and production phases.

2021-02-I-WV-R4

Develop and implement a process safety management system consistent with industry guidance publications such as is contained in the Center for Chemical Process Safety's *Guidelines for Risk Based Process Safety*. At a minimum, the process safety management system should address hazard identification, risk analysis, and management of risk.

6.3.2 Clearon Corporation

2021-02-I-WV-R5

Develop and implement a comprehensive process knowledge management program or evaluate and revise existing process safety management procedures to ensure consistency with industry guidance publications such as the Center for Chemical Process Safety's *Guidelines for Risk Based Process Safety*. The program should:

a) assign specific responsibilities for compiling content and maintaining robust process technology and safety information packages that incorporate relevant knowledge for all hazardous processes and substances operated, manufactured, and/or handled by Clearon Corporation;

b) ensure that key process personnel are aware of critical reactive chemistry information, including thermal stability and calorimetry data, chemical compatibility information, and descriptions of any past reactive incidents and safety studies involving the materials; and

c) define procedures for the transmittal of such information to toll manufacturers.

2021-02-I-WV-R6

Update the sodium dichloroisocyanurate dihydrate (CDB-56®) safety data sheet. At a minimum, the document should:

a) provide the underlying reasoning for the storage temperature maximum and the consequences of exceeding that temperature;

b) provide the underlying reasoning for the decomposition temperature and the consequences of exceeding that temperature;

c) explain or make clear the reason(s) for and/or the circumstance(s) resulting in the differences between the decomposition temperature and the lowest temperature at which self-accelerating decomposition may occur; and

d) provide the exothermic decomposition energy in the Physical Properties section.

2021-02-I-WV-R7

Develop and implement a written program for tolling process design and equipment selection using resources such as the Center for Chemical Process Safety's *Guidelines for Process Safety in Outsourced Manufacturing Operations* and *Guidelines for Risk Based Process Safety* to ensure that:

a) equipment design basis is adequate for any new tolling process or product; and

b) safeguards and ancillary equipment are considered and adequately designed, installed, and function as designed and required.

2021-02-I-WV-R8

Develop and implement a formalized program for the development of toll manufacturing agreements using resources such as the Center for Chemical Process Safety's *Guidelines for Process Safety in Outsourced Manufacturing Operations* and *Guidelines for Risk Based Process Safety*. Ensure that the program provides for the following:

a) Identification of roles and responsibilities of all parties, including the client, toller, and any third-party technical service providers, for all phases of a proposed arrangement;

b) Evaluation of equipment requirements/specifications to ensure that they are adequate for the intended operation; and

c) Participation by all parties in tolling process development, including process hazards analysis and emergency planning, and appropriate stages of the pre-planning, pre-startup, and production phases.

2021-02-I-WV-R9

Develop and implement a process safety management system consistent with industry guidance publications such as is contained in the Center for Chemical Process Safety's *Guidelines for Risk Based Process Safety*. At a minimum, the process safety management system should address hazard identification, risk analysis, and management of risk.

6.3.3 Richman Chemical Inc.

2021-02-I-WV-R10

Develop and implement a formalized program for the development of toll manufacturing agreements using resources such as the Center for Chemical Process Safety's *Guidelines for Process Safety in Outsourced Manufacturing Operations* and *Guidelines for Risk Based Process Safety*. Ensure that the program provides for the following:

a) Identification of roles and responsibilities of all parties, including the client, toller, and any third-party technical service providers, for all phases of a proposed arrangement; and

b) Participation by all parties in tolling process development, including process hazards analysis and emergency planning, and appropriate stages of the pre-planning, pre-startup, and production phases.

6.3.4 Occupational Safety and Health Administration (OSHA)

2021-02-I-WV-R11

Update the Chemical Reactivity Hazards website (https://www.osha.gov/chemical-reactivity) to include various reactivity assessment tools developed since the 2002 Index-Based Method for Assessing Exothermic Runaway Risk and the 2004 Preliminary Screening Method. Mathematical methods, thermal analysis methods (e.g., Accelerating Rate Calorimeter (ARC) testing), ASTM E1231-19 *Standard Practice for Calculation of Hazard Potential Figures of Merit for Thermally Unstable Materials*, Stoessel Criticality, and the O.R.E.O.S. Method (an assessment that combines Oxygen balance calculations, the Rule of 6, and the Explosive functional group list with Onset decomposition and scale) are tools that could be considered for the update. The "Additional Resources" section of the website should also be evaluated for necessary changes and updates.

2021-02-I-WV-R12

Following the implementation of CSB recommendation 2021-02-I-WV-R11, ensure that the chemical industry is aware of the Chemical Reactivity Hazards website (https://www.osha.gov/chemical-reactivity) by developing and implementing a comprehensive outreach plan that actively targets the chemical industry and related trade associations. The outreach plan may include such means as a national news release and OSHA's "QuickTakes" newsletter and/or *Safety and Health Information Bulletins*. This outreach plan should be coordinated with OSHA's On-Site Consultation Program partners.

2021-02-I-WV-R13

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

- Broaden the application to cover reactive hazards resulting from process-specific conditions and combinations of chemicals. Additionally, broaden coverage of hazards from self-reactive chemicals. In expanding PSM coverage, use objective criteria. Consider criteria such as the North American Industry Classification System (NAICS), a reactive hazard classification system (e.g., based on heat of reaction or hazardous gas evolution), incident history, or catastrophic potential.
- In the compilation of process safety information, require that multiple sources of information be sufficiently consulted to understand and control potential reactive hazards. Useful sources include but are not limited to:
  - Literature surveys (e.g., Bretherick's Handbook of Reactive Chemical Hazards, Sax's Dangerous Properties of Industrial Materials, CAS SciFinder).
  - Information developed from computerized tools (e.g., ASTM's CHETAH, CCPS's Chemical Reactivity Worksheet).
  - Chemical property data in PubChem and the REACH (Registration, Evaluation, and Authorization of Chemicals) dossiers maintained by the European Chemicals Agency (ECHA).
  - Chemical reactivity test data produced by employers or obtained from other sources following established standards such as:
    - ASTM E537-20, Standard Test Method for Chemicals by Differential Scanning Calorimetry;
    - ASTM E1981-22, Standard Guide for Assessing Thermal Stability of Materials by Methods of Accelerating Rate Calorimetry;
    - ASTM E2550-21, Standard Test Method for Thermal Stability by Thermogravity; and

    - ASTM E1231-19, Standard Practice for Calculation of Hazard Potential Figures of Merit for Thermally Unstable Materials.
  - Relevant incident data from the plant, the corporation, industry, and government.
- Augment the process hazard analysis (PHA) element to explicitly require an evaluation of reactive hazards. In revising this element, evaluate the need to consider relevant factors, such as:
    - Rate and quantity of heat or gas generated.
    - Maximum operating temperature to avoid a runaway reaction from decomposition.
    - Time to Maximum Rate under Adiabatic Conditions (TMR_{ad}).
    - Thermal stability of reactants, reaction mixtures, byproducts, waste streams, and products.
    - Effect of variables such as charging rates, catalyst addition, and possible contaminants.
    - Understanding the consequences of runaway reactions or hazardous gas evolution.

6.3.5 National Center for Biotechnology Information (NCBI)

2021-02-I-WV-R14

Update the safety information in PubChem for sodium dichloroisocyanurate (NaDCC) dihydrate, to include publicly available reactivity and decomposition information including but not limited to the Self Accelerating Decomposition Temperature (SADT), the explosion hazard when heating metal containers containing NaDCC dihydrate, and the Differential Scanning Calorimetry (DSC) and Accelerating Rate Calorimetry (ARC) results presented in this report. When compiling this information, review sources including the Registration, Evaluation, Authorization, and Restriction of Chemicals Regulation (REACH) dossier and other publications.

6.3.6 Center for Chemical Process Safety (CCPS)

2021-02-I-WV-R15

Update *Guidelines for Process Safety in Outsourced Manufacturing Operations* or develop a new tolling guidance document to supplement existing guidelines. The publication should include current best practices, introduce guidance specific to tolling brokers and/or project managing companies such as Richman Chemical Inc., and cross-reference and align with the comprehensive management systems framework and terminology contained in *Guidelines for Risk Based Process Safety* and other contemporary industry good practice guidance.

7 Key Lessons for the Industry

To prevent future chemical incidents, and in the interest of driving chemical safety excellence to protect communities, workers, and the environment, the CSB urges companies to review these key lessons:

1. Safety Data Sheet (SDS) chemical hazard information can vary substantially between suppliers. Chemical tollers and other end users should not rely solely on hazard information contained in the SDS when using the chemical at elevated temperatures or pressures, or with other chemicals with which the chemical could react. Additional hazard analyses may be needed to prevent process safety incidents. Companies should seek additional publicly available information, or obtain additional information through testing, to supplement information contained in a material's SDS.
2. Companies must ensure that chemical hazard information identified from previous incidents, studies, and laboratory tests are maintained and organized in a manner that will allow employees to be aware of the information's existence and to use it appropriately for future applications.
3. There are many tools available to identify whether a chemical has thermal or reactive hazards that could lead to a process safety incident. These tools include the Oxygen Balance method, Differential Scanning Calorimetry (DSC), Accelerating Rate Calorimetry (ARC), Yoshida Correlations, the CHETAH tool, the CCPS screening tool, the Chemical Reactivity Worksheet (CRW), the O.R.E.O.S. Method, and the Stoessel Criticality tool. Some of these tools involve simple calculations that can be conducted to determine whether further laboratory testing is required.
4. To ensure that hazards associated with new processes are identified and controlled, facilities should (1) evaluate process safety information on the involved chemicals to determine whether the chemicals can be safely used at the laboratory scale, (2) examine the process at the laboratory and pilot scales to determine whether and how to safely scale the process to the production scale, and (3) involve site safety and process engineering personnel to determine whether the process can be conducted at the tolling facility safely at full production scale with the existing equipment.
5. Companies need a robust safety management system in place to prevent reactive chemical incidents. If a process has the potential for uncontrolled chemical reactions, the company should conduct a formal evaluation of the reactive chemistry, perform a hazard analysis, and ensure that sufficient safeguards are in place to prevent reactive chemical incidents.
6. Outsourcing the production or processing of a hazardous material does not outsource the responsibility for process safety. Effective process safety and the prevention of catastrophic incidents are responsibilities that must be shared by all parties involved in a tolling operation.

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Appendix A—Demographic Information for Optima Belle Surrounding Area

Figure 23 shows the census blocks immediately surrounding the Optima Belle facility. The census information for the blocks shown in **Figure 23** is presented in **Table 5**.[a]

Figure 23. Census blocks within the approximately 1-mile distance from the Optima Belle facility. (Credit: Census Reporter, annotations by CSB)

[a] This information was compiled using 2020 Census data as presented by Census Reporter [80]. "Census Reporter is an independent project to make data from the American Community Survey easier to use. [It is] unaffiliated with the U.S. Census Bureau. A News Challenge grant from the Knight Foundation funded the initial build-out of the site. … Support for [Census Reporter's] 2020 Decennial Census features was provided by the Google News Initiative. … [T]he Medill School of Journalism at Northwestern University, home of the Knight Lab, [] provides in-kind support for some of Census Reporter's ongoing development. Most of [Census Reporter's] server hosting infrastructure is [] provided by the Oregon State University Open Source Lab" [81].

Table 5. Tabulation of demographic data for the populations within the census blocks and tracts Shown in **Figure 23**.

Tract Number	Population	Median Age	Race and Ethnicity		Per Capita Income	% Persons Below Poverty Line	Number of Housing Units	Types of Structures	
1	3,320	47.6	81.0%	White	$ 27,177	11.3%	1,884	77%	Single Unit
			11.0%	Black				13%	Multi-Unit
			0.0%	Native				9%	Mobile Home
			0.0%	Asian				1%	Boat, RV, van, etc.
			0.0%	Islander					
			1.0%	Other					
			4.0%	Two+					
			3.0%	Hispanic					
2	3,108	48.8	99.0%	White	$ 30,002	13.5%	1,605	78%	Single Unit
			0.0%	Black				4%	Multi-Unit
			0.0%	Native				19%	Mobile Home
			0.0%	Asian				0%	Boat, RV, van, etc.
			0.0%	Islander					
			0.0%	Other					
			1.0%	Two+					
			0.0%	Hispanic					
3	4,854	37.5	92%	White	$ 22,725	24.7%	1,751	68%	Single Unit
			2%	Black				2%	Multi-Unit
			0%	Native				30%	Mobile Home
			0%	Asian				0%	Boat, RV, van, etc.
			0%	Islander					
			0%	Other					
			5%	Two+					
			1%	Hispanic					
4	2,318	51	98%	White	$ 25,267	9.3%	1115	71%	Single Unit
			1%	Black				8%	Multi-Unit
			0%	Native				21%	Mobile Home
			0%	Asian				0%	Boat, RV, van, etc.
			0%	Islander					
			0%	Other					
			1%	Two+					
			0%	Hispanic					

Appendix B—Unit Conversions

The CSB offers the below unit conversion tables to aid the readers of this investigation report.

Table 6. Temperature conversion table

Celsius (°C)	Fahrenheit (°F)
40°C	104°F
45°C	113°F
50°C	122°F
52°C	125.6°F
53°C	127.4°F
55°C	131°F
60°C	140°F
63.93°C	147.07°F
65°C	149°F
68°C	154.4°F
77°C	170.6°F
80°C	176°F
81°C	177.8°F
81.72°C	179.1°F
81.9°C	179.42°F
82°C	179.6°F
82.54°C	180.57°F
83°C	181.4°F
85°C	185°F
90°C	194°F
95°C	203°F
100°C	212°F
108°C	226.4°F
114.1°C	285.98°F
120°C	248°F
128°C	262.4°F
128.18°C	262.74°F
130°C	266°F
135°C	275°F
140°C	284°F
150.57°C	303.03°F
200°C	392°F
210°C	410°F
240°C	464°F
250°C	482°F
280°C	536°F
810.35°C	1,490.63°F

Appendix C—Chemical Reaction Hazard Testing

DEKRA Services, Inc. tested NaDCC dihydrate using differential scanning calorimetry (DSC) and accelerated rate calorimetry (ARC).[a]

Thermal stability data can be used to assess potential heat release. The results including exotherm onset temperatures and total energy release can be used to evaluate product or process safety.

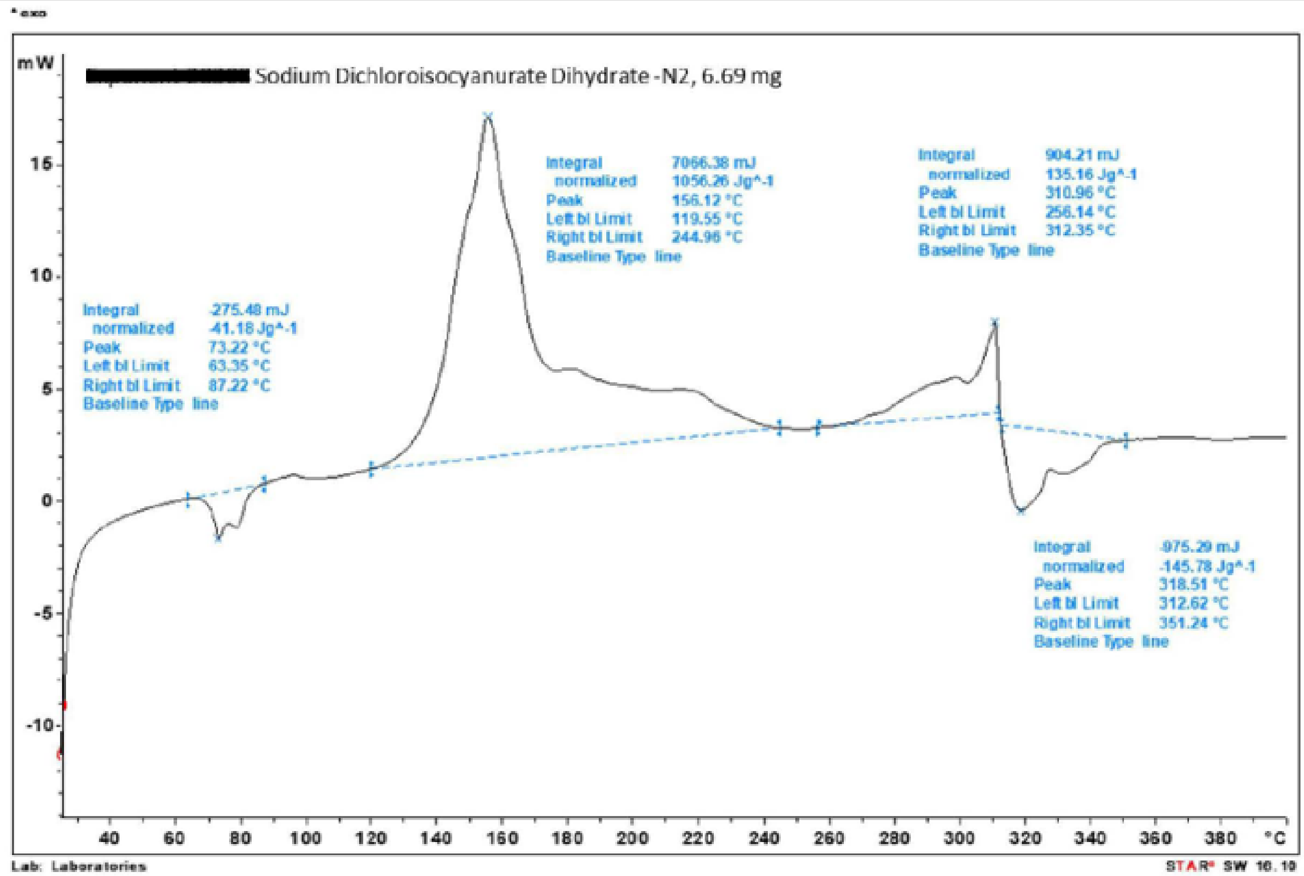
DSC test

DSC is conducted by charging a sample to a crucible and heating the crucible at a constant rate to a designated final temperature. The heat flow into and out of the sample crucible is measured throughout the test and is graphed. By calculating the area under the heat flow curve via integration, DSC determines the total energy release from chemicals upon heating [55, pp. 67-70]. The NaDCC dihydrate was tested by DSC under both air and nitrogen atmosphere in "high pressure, gold plated crucibles" and the temperature range of 25°C to 400°C at 4°C/min ramp rates. All tests showed two endotherms and two exotherms (**Figure C1, Figure C2, and Figure C3**).

Sample	Event	Start Temperature °C	Peak Temperature °C	End Temperature °C	Energy J/g
Sodium Dichloroisocyanurate Dihydrate -N2	Endotherm	63.35	73.22	87.22	41.18
	Exotherm	119.55	156.12	244.96	-1056.26
	Exotherm	256.14	310.96	312.35	-135.16
	Endotherm	312.62	318.51	351.24	145.78
Sodium Dichloroisocyanurate Dihydrate -Air	Endotherm	63.93	73.14	85.09	40.60
	Exotherm	114.10	165.20	245.24	-1077.93
	Exotherm	250.98	310.22	313.24	-202.61
	Endotherm	313.52	318.83	346.38	143.69

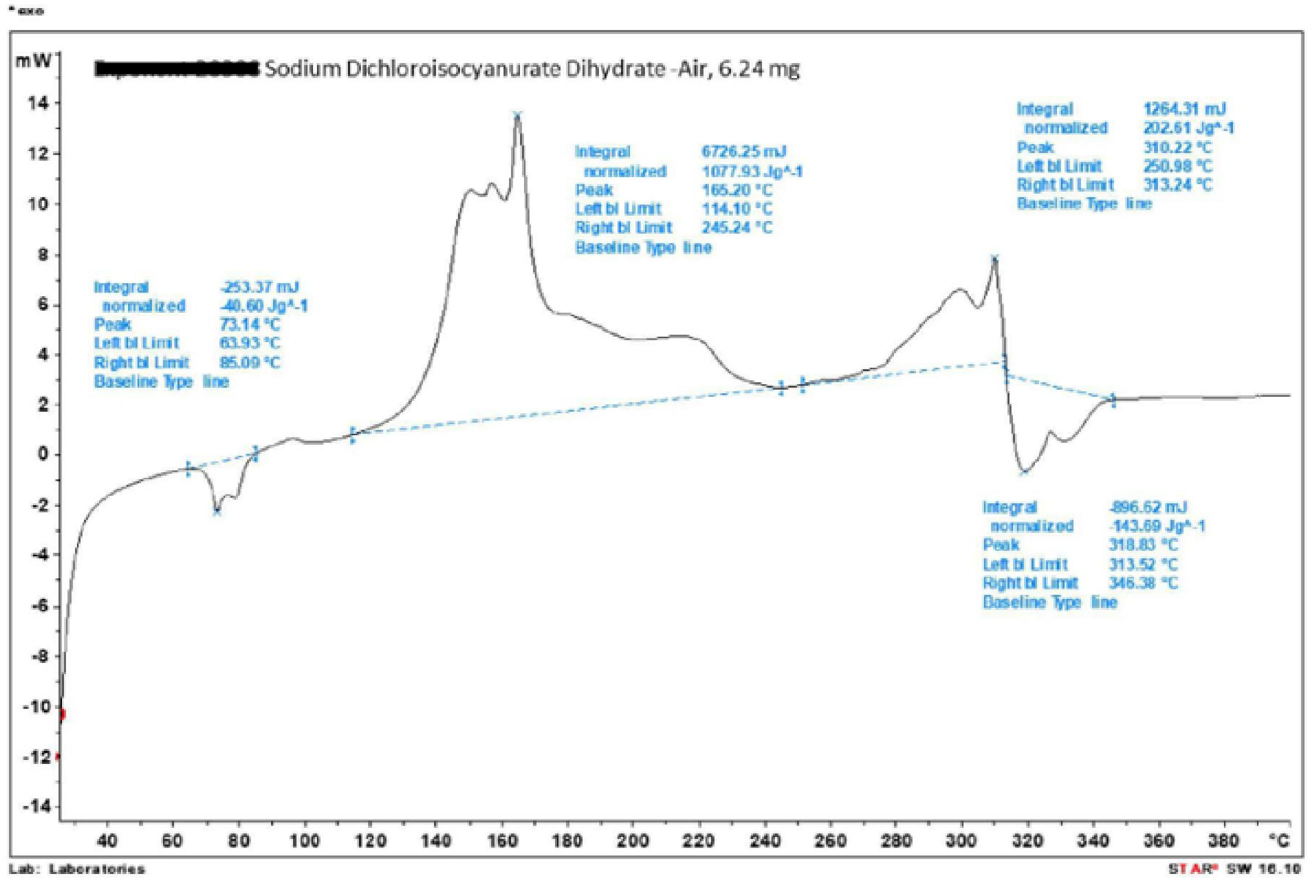
Figure C1. NaDCC dihydrate DSC test results summary. (Credit: DEKRA Services, Inc. [10, p. 7])

[a] DEKRA's disclaimer: "DEKRA performs services using generally accepted guidelines, standards, and practices which are considered reliable within our industry and which assume the accuracy of information/data provided…DEKRA is not responsible for Client's use, interpretation or application thereof."



Date performed	5/6/2021
Performed by	[redacted]
Sample holder	HP Gold Plated 40ul, Material: Stainless Steel
Method	25 to 400°C, 4°C/min GPHP
Module	DSC 3+ /700/839, 14.02.2019 16:54:57
Software	STARe Default DB V9.20
Sample	[redacted] Dichloroisocyanurate Dihydrate-N2
Weight (mg)	6.69
Percentage of Weight change after test (%)	-0.60
Atmosphere that the sample was loaded	Nitrogen

Figure C2. NaDCC dihydrate DSC thermal traces in sealed crucible under nitrogen. (Credit: DEKRA Services, Inc. [10, p. 8])



Date Performed	5/6/2021
Performed by	[redacted]
Sample holder	HP Gold Plated 40ul, Material: Stainless Steel
Method	25 to 400°C, 4°C/min GPHP
Module	DSC 3+ /700/839, 14.02.2019 16:54:57
Software	STARe Default DB V9.20
Sample	[redacted] Sodium Dichloroisocyanurate Dihydrate-Air
Weight (mg)	6.24
Percentage of weight change after test (%)	0.00
Atmosphere that the sample was loaded	Air

Figure C3. NaDCC dihydrate DSC thermal traces in sealed crucible under air. (Credit: DEKRA Services, Inc. [10, p. 9])

ARC test

The ARC test was performed in a sealed 10 cubic centimeter sample bomb enclosure (test cell) under nitrogen atmosphere, connected to a pressure transducer, with heat-wait-search (HWS) mode under adiabatic conditions to determine the onset of any self-accelerating exothermic activity and gas generation. The bomb enclosure is contained within the safety chamber of the apparatus. The sample is heated in regular temperature steps and held at each temperature for a set time to allow the sample to reach equilibrium at each temperature step. The cycle is repeated until the testing control system detects exothermic activity [42, p. 926]. **Figure C4** and **Figure C5** are the ARC test results. **Figure C4** shows the experimental parameters that were employed for the NaDCC dihydrate ARC test.

Sample	sodium dichloroisocyanurate dihydrate
Test date	5/22/2021
Test condition	Standard HWS
Test atmosphere	N_2
Total sample weight	3.859 g
Bomb type	Hastelloy C
Bomb weight	13.535 g
Bomb heat capacity	0.414 $J.g^{-1}.K^{-1}$
Sample heat capacity	2.1 $J.g^{-1}.K^{-1}$ *
Phi Factor	1.7
Slope sensitivity	0.02°C min^{-1}
End temperature	400°C
Wait time	15 minutes
Pressure trip	170 barg
Self-heating rate trip	1000 $Kmin^{-1}$
Pressure drop trip	20 barg

* Estimated

Figure C4. Experimental parameters employed for NaDCC dihydrate ARC test. (Credit: DEKRA Services, Inc. [10, p. 11])

Maximum temperature of test*	150.57	°C
Maximum self-heat rate of test*	1083.5	K min^{-1}
Temperature at maximum self-heat rate*	150.57	°C
Maximum pressure of test*	23.9	Bar gauge
Maximum pressure rate of test*	1211.48	Bar min^{-1}
Temperature at maximum pressure rate**	128.18	°C
Percent of weight loss after test	100.0	%

*Cell exploded before next data point taken. It is not known if higher rates would have been measured if the cell had not failed.

**Cell exploded at the temperature

Item	Value	Units	Exotherm
Mass of sample:	3.86	grams	3.86
Heat capacity of sample:	2.10**	J/(gm*K)	2.10
Mass of bomb:	13.54	grams	13.54
Heat capacity of bomb:	0.42	J/(gm*K)	0.42
Phi factor (Φ):	1.70		1.70
Onset temperature of exotherm:		°C	81.90
Final temperature of exotherm*:		°C	150.57
ΔT*:		°C	68.67
ΔTadiabatic*:		°C	116.84
ΔHreaction*:		Joule/gram	-245.36

*This was a runaway exotherm. The cell exploded before the exotherm was ended. The heat of reaction was not fully recorded.

** Estimated. Literature value not available.

Figure C5. NaDCC dihydrate ARC test results. (Credit: DEKRA Services, Inc. [10, p. 12])

The temperature and pressure versus time is plotted in **Figure C6**. The self-heat and pressure rate for the exotherm before the explosion is shown in **Figure C7**.

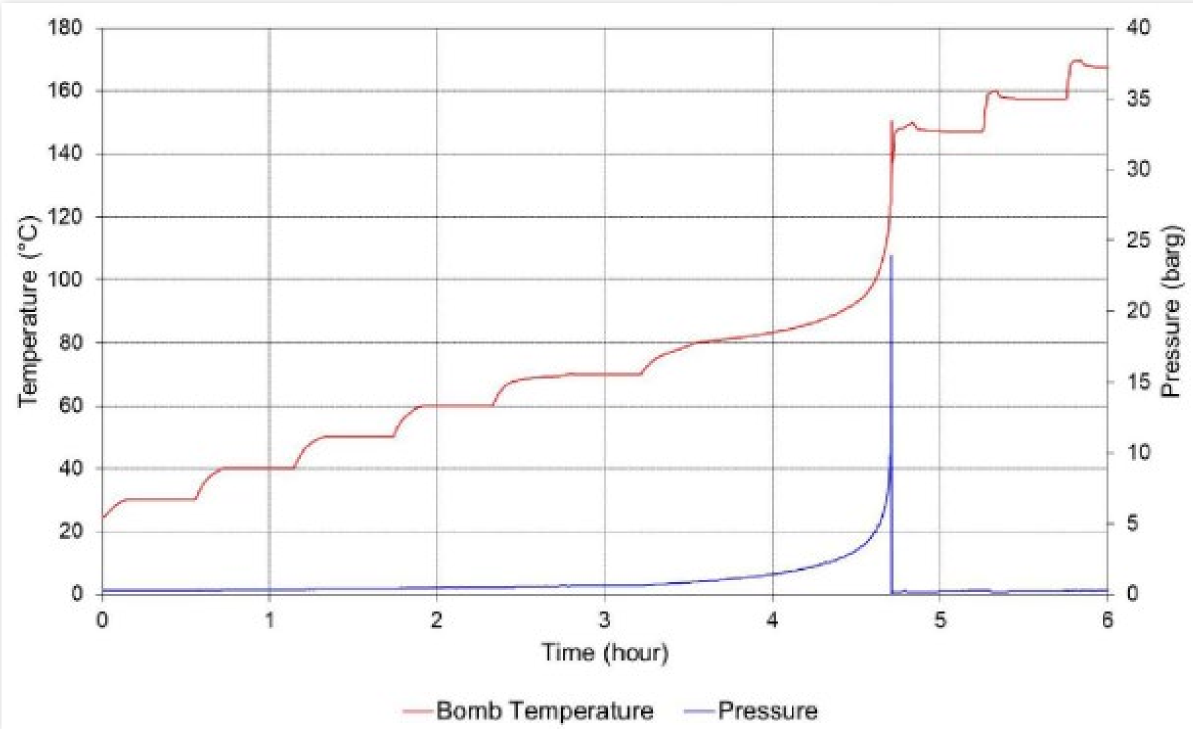


Figure C6. Temperature and pressure vs. time plot for NaDCC dihydrate. (Credit: DEKRA Services, Inc. [10, p. 13])

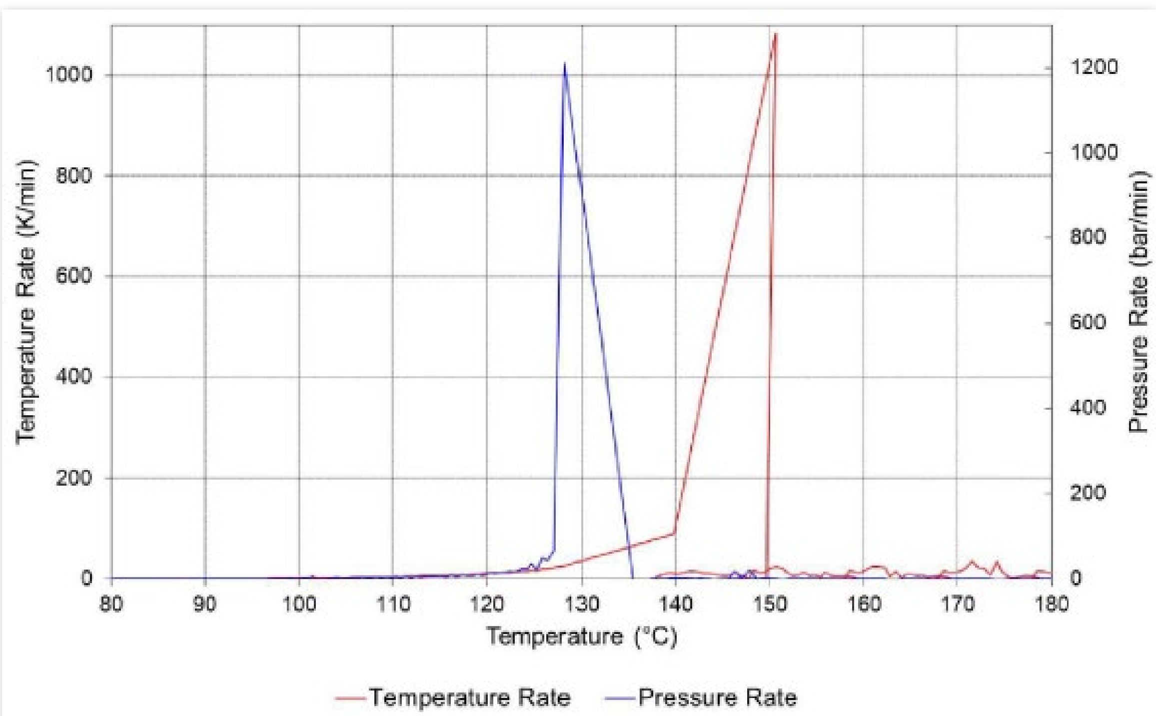


Figure C7. Self-Heat and pressure rate vs. temperature plot for NaDCC dihydrate. (Credit: DEKRA Services, Inc. [10, p. 14])

The Arrhenius theory (equation) is generally viewed as "an empirical relationship" to model the temperature variance of various chemical processes where a chemical reaction rate/constant increases exponentially with increasing temperature [56, pp. 6-8, 57, p. 25]. "An Arrhenius plot plots the log or natural log of the measured parameter […] against the inverse absolute temperature (1/K)" [56, p. 8].

Figure C8 plots Log_{10} of the measured heat rate (self-heat rate) measured in units of degree C per minute (°C/min) versus -1000/Temperature in Kelvin. The plot shows the ARC test data using the Arrhenius theory. Thus, in Arrhenius's kinetic theory, the ARC plot should initially (at low conversions) be a straight line, and the slope proportional to the activation energy for a well-behaved reaction following a single chemical mechanism. The NaDCC Dihydrate data shows a linear plot from the detected onset temperature of approximately 82°C (shown on the x-axis below as -2.81). Because the ARC test cell ruptured prematurely, the heat rate plot never reaches a peak at the maximum rate.

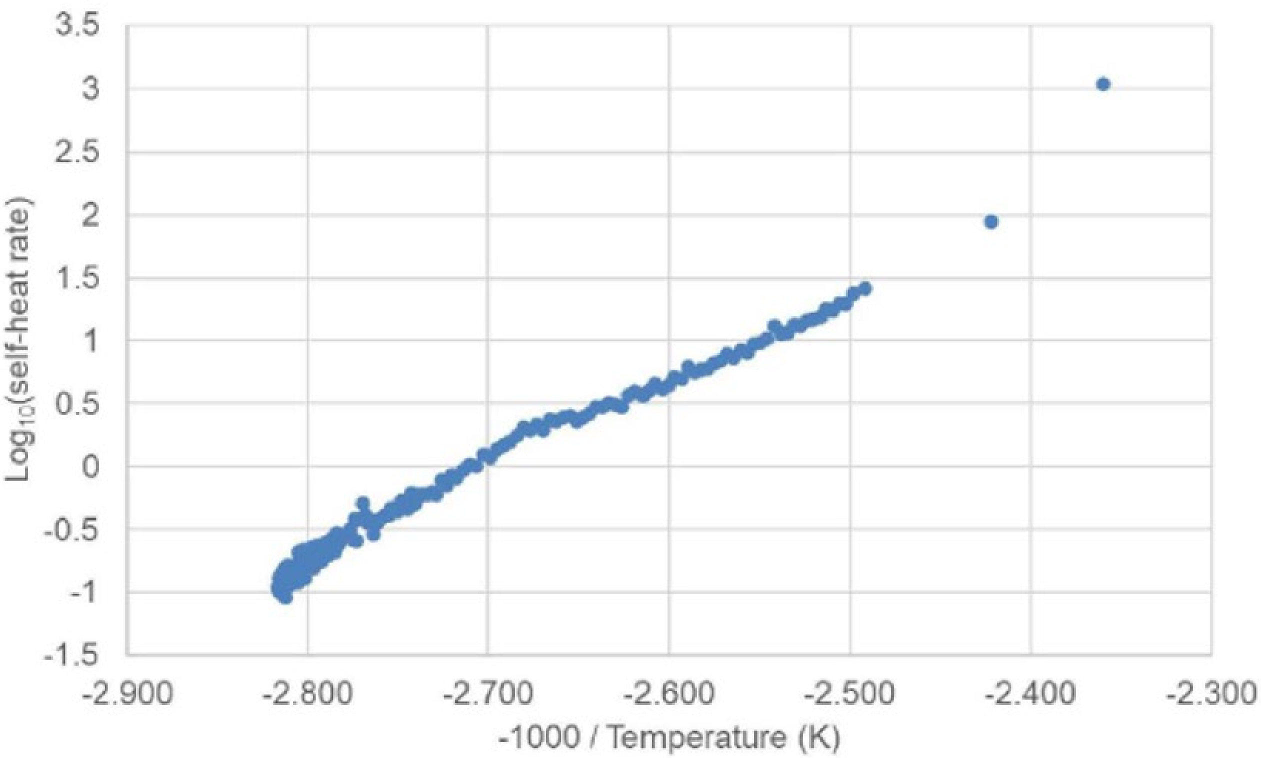


Figure C8. Self-Heat rate vs. -1000/Temperature for NaDCC dihydrate. (Credit: DEKRA Services, Inc. [10, p. 14])

Figure C9 shows the Antoine plot of pressure versus the negative reciprocal of temperature. "The Antoine plot indicates that the pressure deviates from Antoine behavior at about 80.1°C, and 127.2°C."

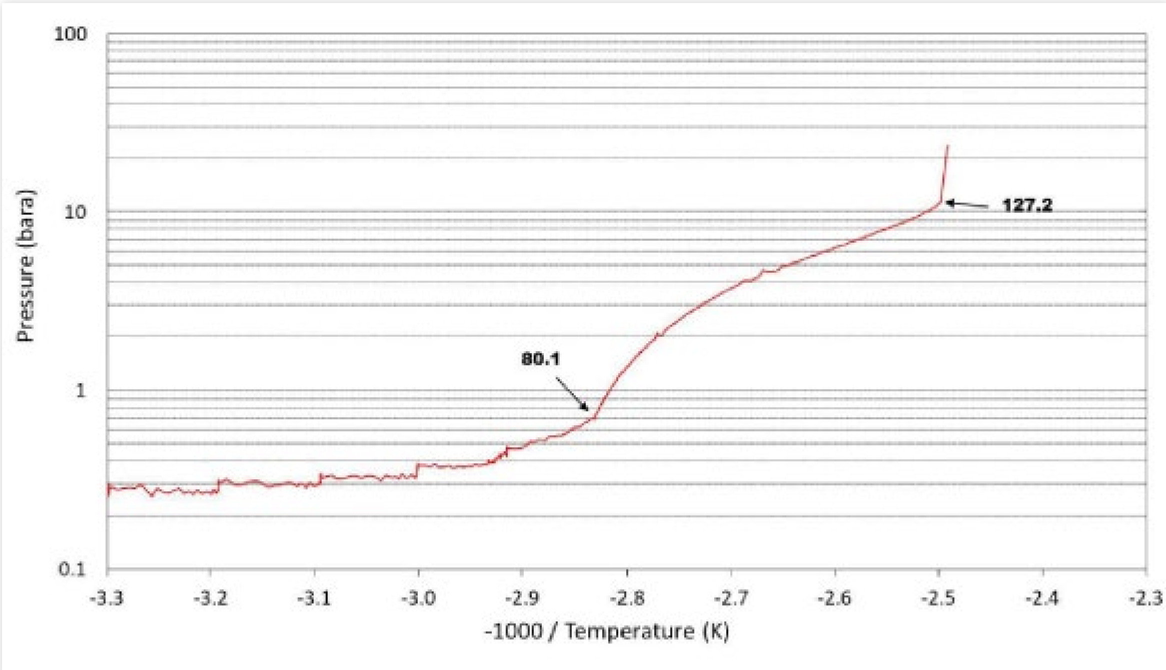


Figure C9. Antoine Plot - Log_{10} Pressure vs. -1000/T(K) Plot for NaDCC dihydrate. (Credit: DEKRA Services, Inc. [10, p. 15])

The Time to Maximum Rate (TMR) is an important parameter in chemical process design. TMR is the time needed for a reaction to reach its maximum self-heat rate or pressure rate in a thermal runaway reaction [58]. The TMR increases as the batch temperature decreases. For particularly energetic reactions, TMR is sometimes referred to as a Time to Explosion since the time when the heat rate is maximized typically corresponds to the time when the pressure rate is maximum, and the vessel may fail catastrophically [58].

DEKRA Services, Inc. determined the TMR using the ARC test data until the test cell failed. The estimated adiabatic TMR based on the ARC test data for the dryer contents from approximately 82°C is 12 minutes (**Figure C10**). Using recorded temperature data from the Optima Belle December 2020 explosion, the CSB graphically determined a time of approximately 11 minutes from when the dryer's internal temperature measured 82°C until the last value was recorded,[a] where the heat rate was rising extremely rapidly just before the explosion. This time determination is very close to the ARC prediction—11 minutes vs. 12 minutes. This close match further verifies the validity of the conclusion that the experimental ARC and DSC results were extremely useful in investigating the cause of the dryer's over-pressurization.

DEKRA Services, Inc. also concluded that it is unknown if higher self-heat rates would have been obtained at longer times if the test cell had not failed.

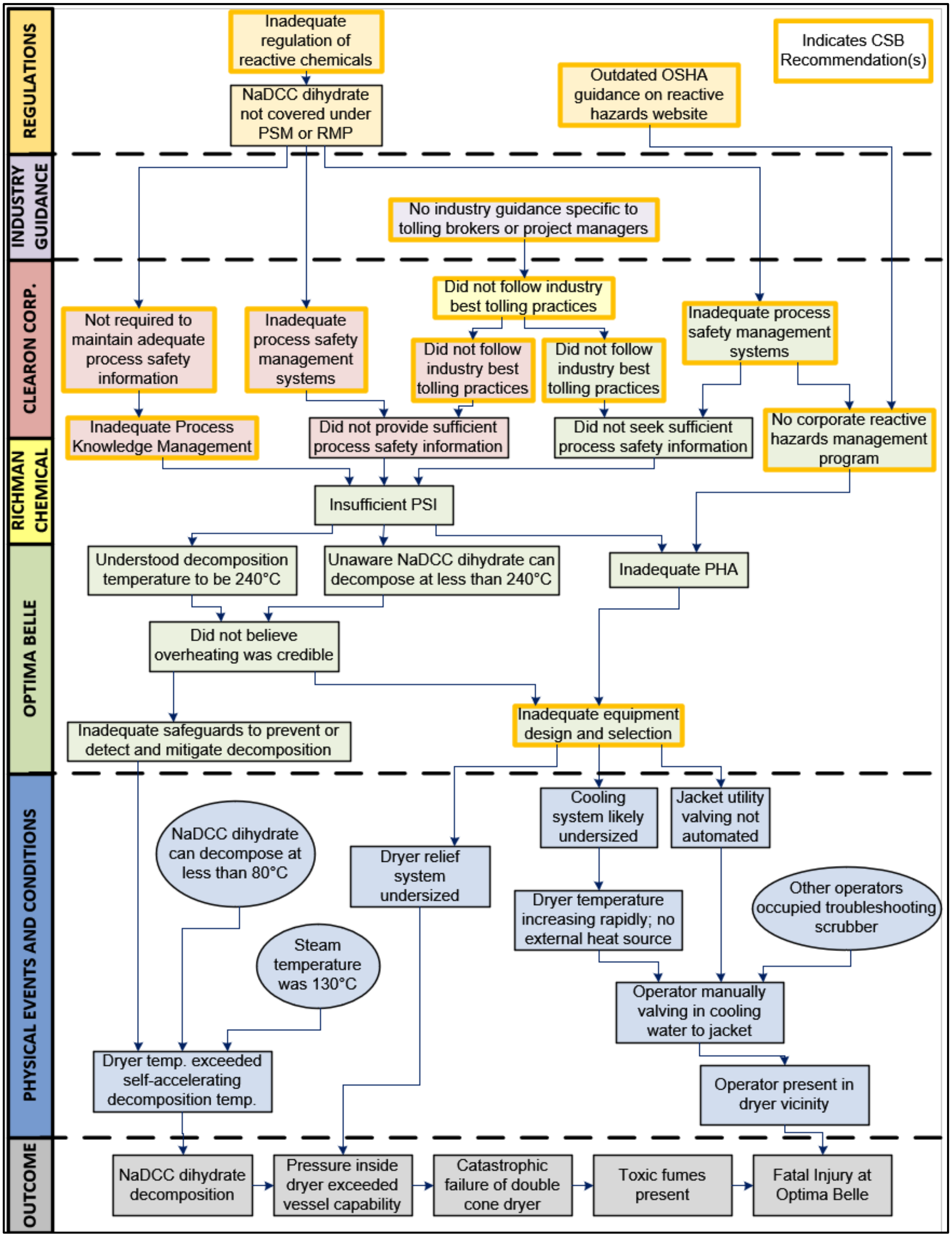
[a] See **Figure 8** in the Optima Belle investigation report.

Temperature (°C)	Hours
45.0	48.9
49.3*	24.0
55.0	9.6
81.9**	0.2

*: At 49.3 °C, the time to maximum rate (TMR) is 24 hours. TMR_{24} is a good basis for safety but is dependent on the process conditions.
**: Onset temperature of the exotherm (runaway reaction).

Figure C10. Time to Maximum Rate results. (Credit: DEKRA Services, Inc. [10, p. 17])

Appendix D—Causal Analysis (AcciMap)



Appendix E—Hazard Assessments Conducted for NaDCC Dihydrate Post-Incident

Below are available published tools that the CSB used post-incident to assess and better understand the potential hazards of sodium dichloroisocyanurate (NaDCC) dihydrate (i.e., Clearon's CDB-56®). Others not illustrated in this report may also be considered to predict potential thermal or chemical reactions hazards. The CSB suggests that companies use assessment evaluation tools, including detailed testing as deemed necessary, versus relying on rules-of-thumb (i.e., 100 Degree Rule) to predict a chemical's heat rates or other exothermic behavior.[a] The 100 Degree Rule states "that if the operating temperature of a process is 100°C away from the nearest detectable exotherm observed in a DSC experiment, the operation will not "experience" this thermal event, and it is not necessary to obtain more detailed information via a technique such as ARC."

I. Preliminary Screening Method

The CSB used the flowchart and yes/no questions (**Figure E.1**) introduced by the CCPS and further communicated by the EPA in 2004 as a preliminary screening for NaDCC dihydrate. It was concluded that facilities storing or handling NaDCC dihydrate and other hazardous substances could "expect chemical reactivity hazard(s) to be present" according to the preliminary screening method as illustrated below.

[a] Hofelich presented "The Use/Misuse of the 100 Degree Rule in the Interpretation of Thermal Hazards Test" [86] at the 1989 CCPS Annual International Conference.

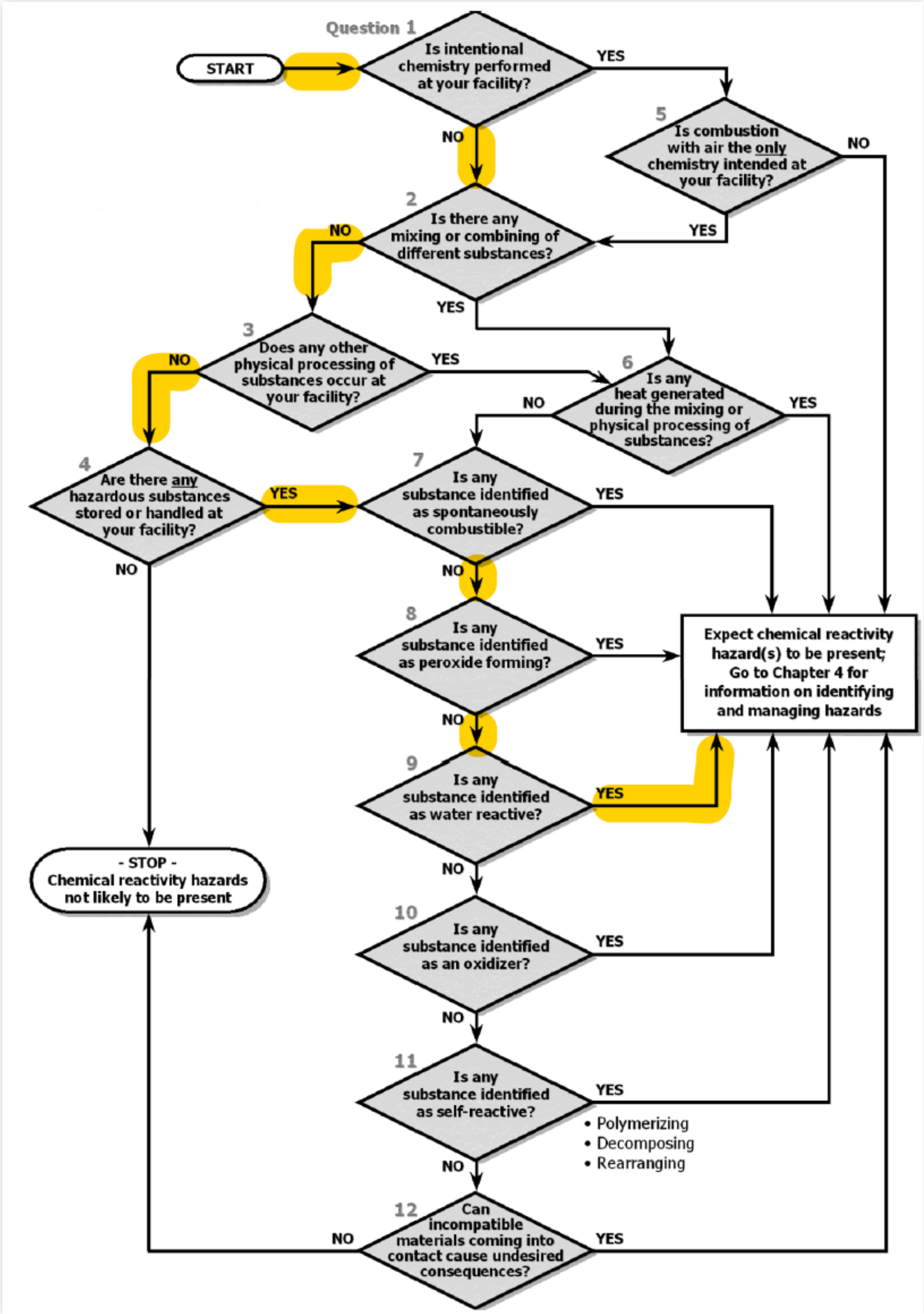


Figure E.1. Preliminary Screening Flowchart for Chemical Reactivity Hazards [18, p. 32] highlighting the path of a facility storing or handling NaDCC dihydrate and other hazardous substances. (Credit: CCPS, annotations by CSB)

II. Oxygen Balance Calculation

In 2000 the *Journal of Pyrotechnics* published the below formula for evaluating the oxygen balance of energetic materials, expressed as a mass percent, for the reaction of an oxidizer represented by the molecular formula $C_aH_bN_cO_dCl_eS_f$ with a known molecular weight (*M*) [59, p. 28]. Later in 2008, different authors published the same oxygen balance (Ω) formula [60, p. 3332]:

a, *b*, *c*, *d*, *e*, and *f* represent the number of atoms of respective elements, including carbon, hydrogen, nitrogen, oxygen, chlorine, sulfur, and halogens. This approach is more complex and may be used by explosive manufacturers. The calculated oxygen balance value represents "the (theoretical) ability of a [composition] to perform complete combustion (that is, a complete and residue-free consumption of the fuel): An oxygen balance of 0 indicates a stoichiometric mixture of fuel atoms and oxidizing atoms. A negative oxygen balance (negative Ω values) indicates a [composition] in which unburned fuel is left behind or that requires atmospheric oxygen for complete combustion. A positive oxygen balance indicates a [composition] in which these is excess of oxygen for the combustion of the fuel atoms" [60, p. 3332]. The oxygen balance (OB) does not provide information on possible heat of explosion or energy changes that occur during an explosion.

The CSB concluded that the decomposition of NaDCC dihydrate does not match the reaction or oxidized products for the above OB formula and could misidentify the compound's hazard rank. Thus, other hazard evaluations should be considered for predicting the energy releases for NaDCC dihydrate, including those presented in this report or other thermochemical and kinetic assessments.

Published literature explains how the pharmaceutical industry has used the OB calculation and hazard rank (**Table E-1**) for thermal stability assessments [27, 61].

Table E-1. Oxygen Balance correlation to hazard rank [27].

Oxygen Balance	Hazard Rank
> +160	Low
+80 to +160	Medium
-120 to +80	High
-240 to -120	Medium
< -240	Low

Below is an example of using the OB formula as a desktop calculation for applicable substances to identify preliminary warning signs (red flags). ***NaDCC dihydrate is used in this example only for computation purposes***.

1. For *NaDCC dihydrate (*$C_3H_4Cl_2N_3NaO_5$):
   $a = 3$ $c = 3$ $e = 2$ $M = 255.97$
   $b = 4$ $d = 5$ $f = 0$
   Assumption: the water oxygen molecules have not been removed from the NaDCC dihydrate
   ***Determination of oxygen balance (Ω) of NaDCC dihydrate*:**

2. For *NaDCC dihydrate less two water oxygen molecules (*$C_3H_0Cl_2N_3NaO_3$):
   $a = 3$ $c = 3$ $e = 2$ $M = 219.97$
   $b = 0$ $d = 3$ $f = 0$
   Assumption: two water molecules of hydration have been removed from the NaDCC dihydrate
   ***Determination of oxygen balance (Ω) of NaDCC dihydrate less two water molecules*:**

III. Rule of 6 Calculation

The Rule of 6 calculation is another qualitative tool the CSB used to screen NaDCC dihydrate's potential to exhibit explosive properties and the potential for rapid energy release by confirming whether its molecular weight balances with the energetics of the same molecule. The following is stated in published literature:

> "The Rule of 6 is as follows: It a molecule presents at least six atoms of carbon (or other atoms of approximately the same size or greater) per energetic functionality, this should render the molecule reactivity safe to handle. When the Rule of 6 is applied to known explosive organic compounds, the method is reliably able to predict compounds containing explosive properties. One challenge in applying the Rule of 6 is consistently counting the number of explosive functional groups (ExFGs) within a molecule." [27, p. 217].

The United Nations published list of chemical groups indicating explosive properties in organic materials are shown in **Table E-2**.

Table E-2. Examples of chemical groups indicating explosive properties in organic materials [8, p. 494].

Structural feature	Examples
C-C unsaturation	Acetylenes, acetylides, 1,2-dienes
C-Metal, N-Metal	Grignard reagents, organo-lithium compounds
Contiguous nitrogen atoms	Azides, aliphatic azo compounds, diazonium salts, hydrazines, sulphonylhydrazides
Contiguous oxygen atoms	Peroxides, ozonides
N-O	Hydroxylamines, nitrates, nitro compounds, nitroso compounds, N-oxides, 1,2-oxazoles
N-halogen	Chloramines, fluoroamines
O-halogen	Chlorates, perchlorates, iodosyl compounds

The CSB used NaDCC dihydrate's chemical structure (**Figure E.2**) to apply the Rule of 6 and count the number of potential explosive functional groups (ExFGs). As illustrated below, the NaDCC dihydrate molecule has two ExFGs, the molecule's N-Cl bonds.

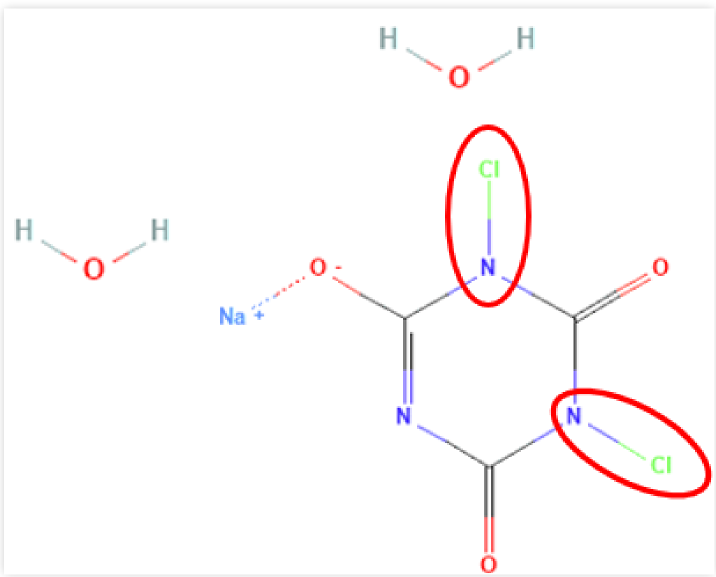


Figure E.2. NaDCC dihydrate chemical structure. (Credit: PubChem [62], annotations by CSB)

The NaDCC dihydrate's chemical structure also contains the following:

- 3 **Carbon** atoms
- 1 **Nitrogen** atoms (excluding the two Nitrogen atoms counted in the N-Cl bonds)
- 5 **Oxygen** atoms

The resulting calculated summation of heavy atoms for NaDCC dihydrate is:

Assumption: Six carbons (or other atoms of approximately the same size) per energetic functional group should provide sufficient dilution to render the compound relatively safe [63, p. 18].

Conclusion:

1. NaDCC dihydrate would need 12 heavy atoms (Carbon or similar) to render it safe to handle based on the two ExFGs.
2. 9 available heavy atoms (Carbons or similar) versus 12 required for NaDCC dihydrate suggests a risk analysis or testing such as DSC should be conducted.

IV. O.R.E.O.S. (for Oxygen Balance, Rule of 6, Explosive functional group, Onset Temperature, and the Scale)

The O.R.E.O.S. Method recognizes that the oxygen balance hazard rank has limitations and may not accurately predict the hazard of some materials, so this component of the method is weighed more conservatively in the CSB's assessment of NaDCC dihydrate to account for such. In the Rule of 6 calculation, a material that does not have at least six heavy atoms per the ExFGs fails the assessment and is awarded 8 points for the O.R.E.O.S. method. Materials containing ExFGs should be thoroughly studied before scale-up. For the ExFG score, the presence of one or more ExFGs is awarded 8 points.

Onset temperature is the temperature at which the heat released by a chemical reaction can no longer be completely removed, resulting in a temperature increase. For the onset temperature of decomposition, the highest score (8 points) is awarded to materials that begin to decompose below 125°C. "With a 100°C margin of safety applied to DSC data, these materials should be handled at or below ambient temperature until additional data are obtained [27, p. 217]." Post-incident differential scanning calorimetry (DSC) testing for NaDCC dihydrate under air showed an exotherm started at an onset temperature of 114.10°C. Therefore, NaDCC dihydrate is awarded 8 points for onset temperature for the O.R.E.O.S. method.

As published, the CSB used **Table E-3** to assign a score of 1, 2, 4, or 8 points for each part of the assessment and to assign the O.R.E.O.S. hazard rank to NaDCC dihydrate. A result of "high hazard" is summarized in **Table E-4**.

Table E-3. O.R.E.O.S. Method for Assigning Hazard Rank of Potentially Explosive Materials [27, p. 218].

	Points			
	1	**2**	**4**	**8**
Oxygen Balance Hazard		Low	Med	High
Rule of 6 calculation		Pass		Fail
Explosive Functional Group?	No			Yes
Onset temperature [°C]	>300	200-300	125-200	<125
Scale	<5g	5g to <100g	100g to 500g	>500g
O.R.E.O.S. Total:				
		Low Hazard	Medium Hazard	High Hazard
	Points:	7 to 17	18 to 27	28 to 40

Table E-4. NaDCC dihydrate Assessment Results using the O.R.E.O.S. Method.

	OB	Rule of 6	ExFG	Onset (°C)	Scale
NaDCC dihydrate to be dehydrated at Optima Belle*	N/A for NaDCC dihydrate decomposition	Fail (8)	Yes (8)	<125 (8)	>500g (8)
				O.R.E.O.S. Assessment Result:	**High Hazard**

* *Approximately 8,820 pounds of NaDCC dihydrate was planned for each batch at Optima Belle*

Below in **Table E-5** is a list of suggested industry guidance for each O.R.E.O.S. hazard rank level published by Sperry et al.

Table E-5. Example Recommendations for Each Level of the O.R.E.O.S. Hazard Rank [27, p. 221][a]

O.R.E.O.S. Hazard Rank	Example Recommendations
Low Hazard	• Proceed using internal guidance on handling energetic compounds
	• ARC testing ***recommended -or-*** • Quantitative small-scale explosivity screening is ***recommended***
Medium Hazard	• Proceed using internal guidance on handling energetic compounds
	• ARC testing ***required -or-*** • Quantitative small-scale explosivity screening is ***required***
	• Select Test Series 1 is ***recommended*** based on ARC testing, likely failure modes and available material (Koenen Test, Time/Pressure Test, and/or U.N. Gap)
High Hazard	• Consider alternative methods
	• ARC testing ***required -or-*** • Quantitative small-scale explosivity screening is ***required***
	• Select Test Series 1 is ***required*** based on ARC testing, likely failure modes and available material (Koenen Test, Time/Pressure Test, and/or U.N. Gap)

V. Yoshida Correlation

The Yoshida correlation may be used to evaluate a material's explosion propagation with DSC stability data using the below mathematical equation where Q_{DSC} is the energy of the exotherm (in calories/gram), and T_{DSC} is the onset temperature of the exotherm (in °C) [64, 27, p. 213].

If EP is ≥ 0, the material is "classified as potentially explosive and will require additional testing such as drop hammer and explosivity testing." Post-incident DSC testing of NaDCC dihydrate resulted in the following data.

Condition	Measured Result	Unit Conversion
Q_{DSC} (energy of the exotherm in air)	1,077.93	
T_{DSC} (onset temperature of the exotherm in air)	114.1°C	

EP is ≥ 0 using the DSC measured results for energy and onset temperature conducted in air. Therefore NaDCC dihydrate can be classified as potentially explosive in similar conditions and requires additional testing.

The ASTM E1231-19 "Standard Practice for Calculation of Hazard Potential Figures of Merit for Thermally Unstable Materials" provides guidance, techniques, and measurements for estimating potential thermal hazards such as Yoshida, Stoessel, shock sensitivity, and explosion potential [65]. For example, Section X1.6 "Explosion Potential," states:

[a] The listed recommendations are suggestions and can be modified to fit internal company guidance [27, p. 222].

> "Positive values of explosion potential are considered highly hazardous."
>
> "The greater the positive numerical value for explosion potential, the greater the hazard."
>
> "Negative values of explosion potential are considered low hazardous."

Conclusion: An explosion potential of 0.0000045 suggests that NaDCC dihydrate would be considered highly hazardous.

VI. Stoessel Calculations and Criticality Classes

The five Stoessel Criticality classes require the following temperatures to be defined.

- Process Temperature (Tp),
- Maximum temperature of synthesis reaction (MTSR),*
- Temperature at which the maximum rate under adiabatic conditions is 24 hours (T_{D24}): the highest temperature at which the thermal stability of the reaction mass is unproblematic, and
- Maximum temperature for technical reasons (MTT) [28].

* The MTSR must be known/calculated to predict the consequences of a runaway reaction (the loss of control of a desired reaction) [66, p. 112]. "If a cooling failure occurs while an exothermal reaction is being performed, the nonconverted reactants will react away without cooling, causing a temperature rise above the intended reaction temperature. Therefore, a temperature range may be reached where secondary reactions could become dominant or where the vapor pressure of the system could surpass the maximum allowed working pressure of the reactor."

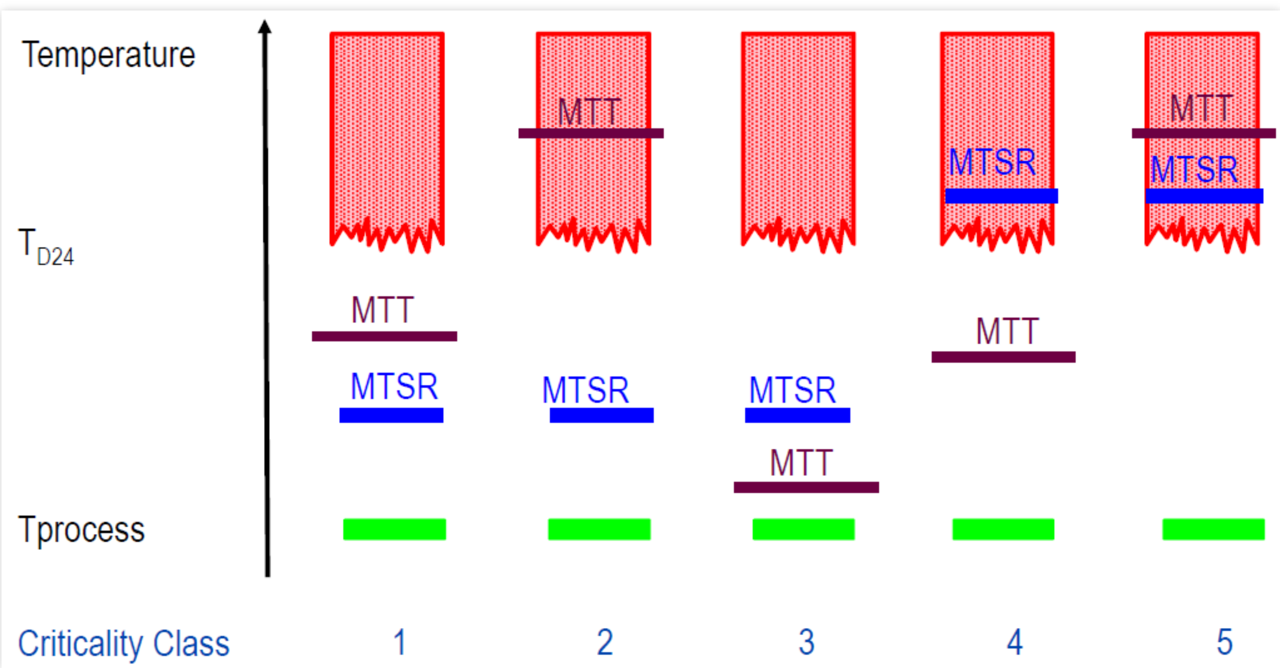


Figure E.3. Stoessel Criticality Classes. (Credit: Stoessel [54, p. 13])

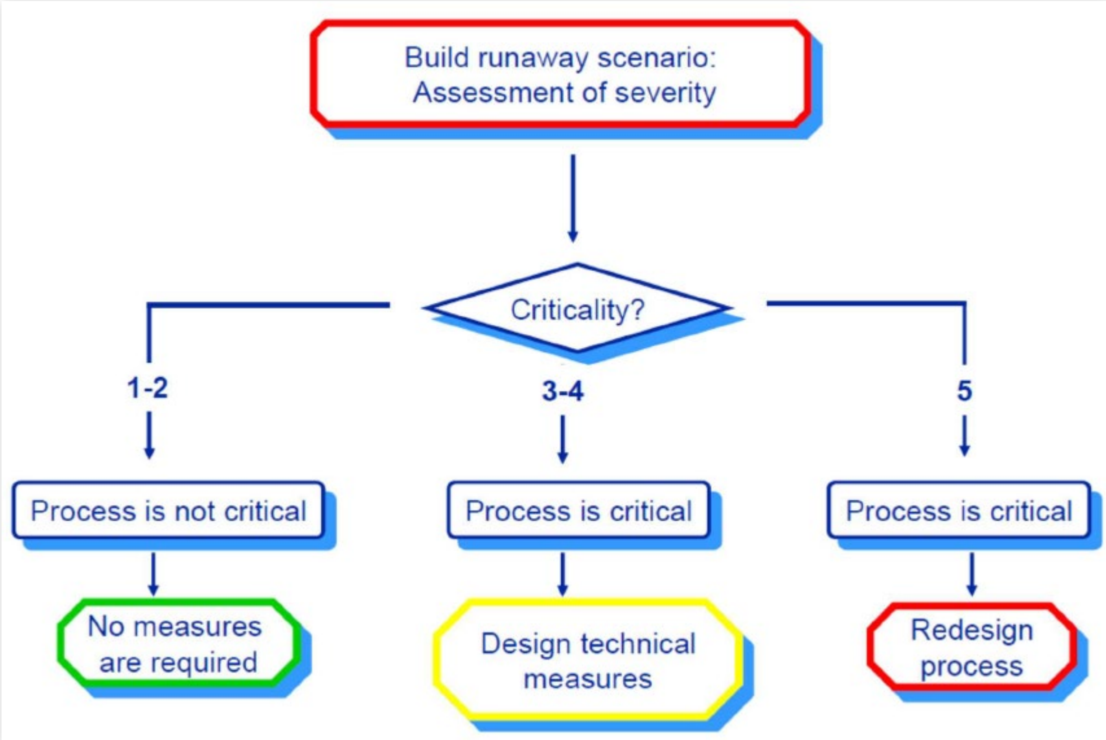


Figure E.4. Design Guidance for Stoessel Criticality Classes. (Credit: Stoessel, annotations by Salim and Sharratt [54, p. 16])

The CSB used the following key parameters for the assessment of NaDCC dihydrate using Stoessel's Criticality classes:

Key Parameter	Value (°C)	Source
T_p	120.0	Target dryer temperature stated in the Optima Belle dehydration procedure
MTT	134	Optima Belle's expected dryer temperature based on design of steam system used to heat the dryer
Adiabatic Temperature, ΔT_{ad}	116.84	Post-Incident ARC test result for NaDCC dihydrate
T_{D24}	49.3	Post-Incident result from ARC test data for NaDCC dihydrate
Q	>1000 Joule/gram	Post-Incident NaDCC dihydrate thermal testing heat of reaction results
Initial Temperature, T_0	120.0	Target dryer temperature stated in the Optima Belle dehydration procedure

Calculate MTSR using the below equation as published by Stoessel [66, p. 127].

Conclusion:

For the NaDCC dihydrate dehydration process at Optima Belle using its double cone dryer, it was determined that $T_p > T_{D24}$ (i.e., 120°C > 49.3°C) and MTSR > T_{D24} (i.e., 236.84°C > 49.3°C), indicating that a decomposition may be triggered during a runaway of a secondary reaction and suggesting further thermal evaluations be considered beyond the Stoessel Criticality Classes. For example:

- The heat release of the MTT (134°C) may be too high, resulting in a critical pressure increase.
- Should an alternate process design other than a rotary pressure vessel (double cone dryer) be considered?

In addition, a 2020 industry presentation on *Thermal Process Safety Criticality Classes as a Tool for Assessment and Design* states:

> "A decomposition reaction with a specific energy of 500 J/g releases 10 W/kg at a temperature of 15°C.
>
> A decomposition, able to raise the temperature by 250°C, leads to a severe thermal explosion within less than one hour, starting from 150°C." [67, p. 14]

VII. Evaluation of whether NaDCC Dihydrate is an energetic material using the SEMI S30 Standard

SEMI introduced and published evaluation tools (flowcharts) to determine whether a process chemical is "energetic" and whether a material is "hazardously exothermic" in its SEMI S30 *Safety Guideline for Use of Energetic Materials in Semiconductor R&D and Manufacturing Processes* standard [68].[a] The CSB used these flowcharts, as depicted below in **Figure E.5**, **Figure E.6**, and **Figure E.7**, to evaluate whether NaDCC dihydrate would be considered energetic or water-reactive.

Key Parameters used for NaDCC dihydrate (measurements observed during post-incident DSC test)

- 1077.93 Joule/gram (energy)
- 114.10°C (exotherm start temperature)

The CSB concluded that NaDCC dihydrate is hazardously exothermic and an energetic process chemical material according to the SEMI S30 standard. NaDCC dihydrate was also concluded to be water reactive using the SEMI S30 standard.

[a] The SEMI S30 standard was technically approved by the Environmental, Health & Safety Global Technical Committee. The standard was originally published in 2019 and editorially modified in 2021. SEMI standards are voluntary technical agreements for the semiconductor industry and others covering many topics related to electronics manufacturing, including process chemicals, facilities, and equipment automation.

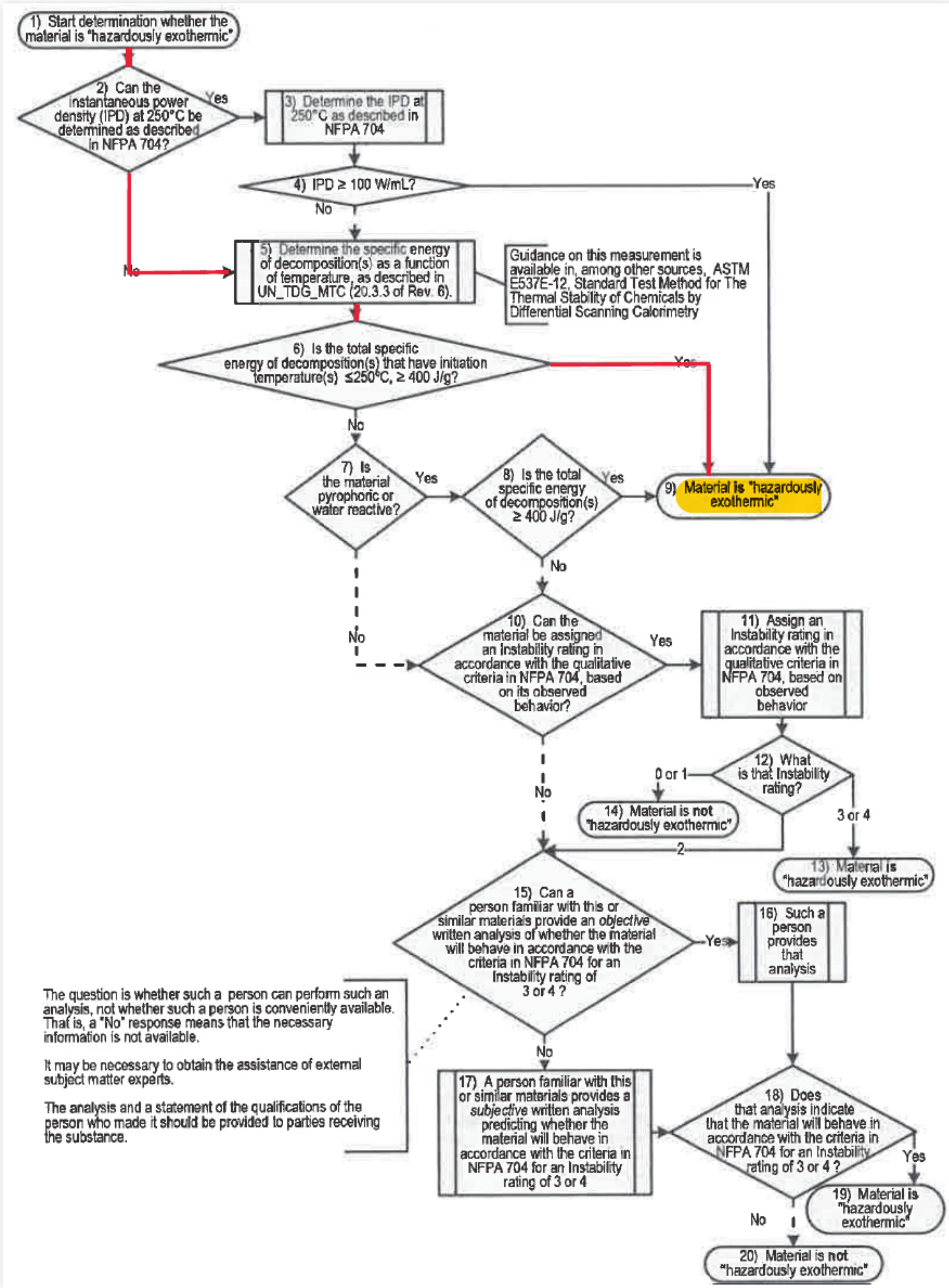


Figure E.5. Flowchart for the determining whether a material is hazardously exothermic [68, p. 11] highlighting the path of a hazardous exothermic material. (Credit: SEMI, annotations by CSB)

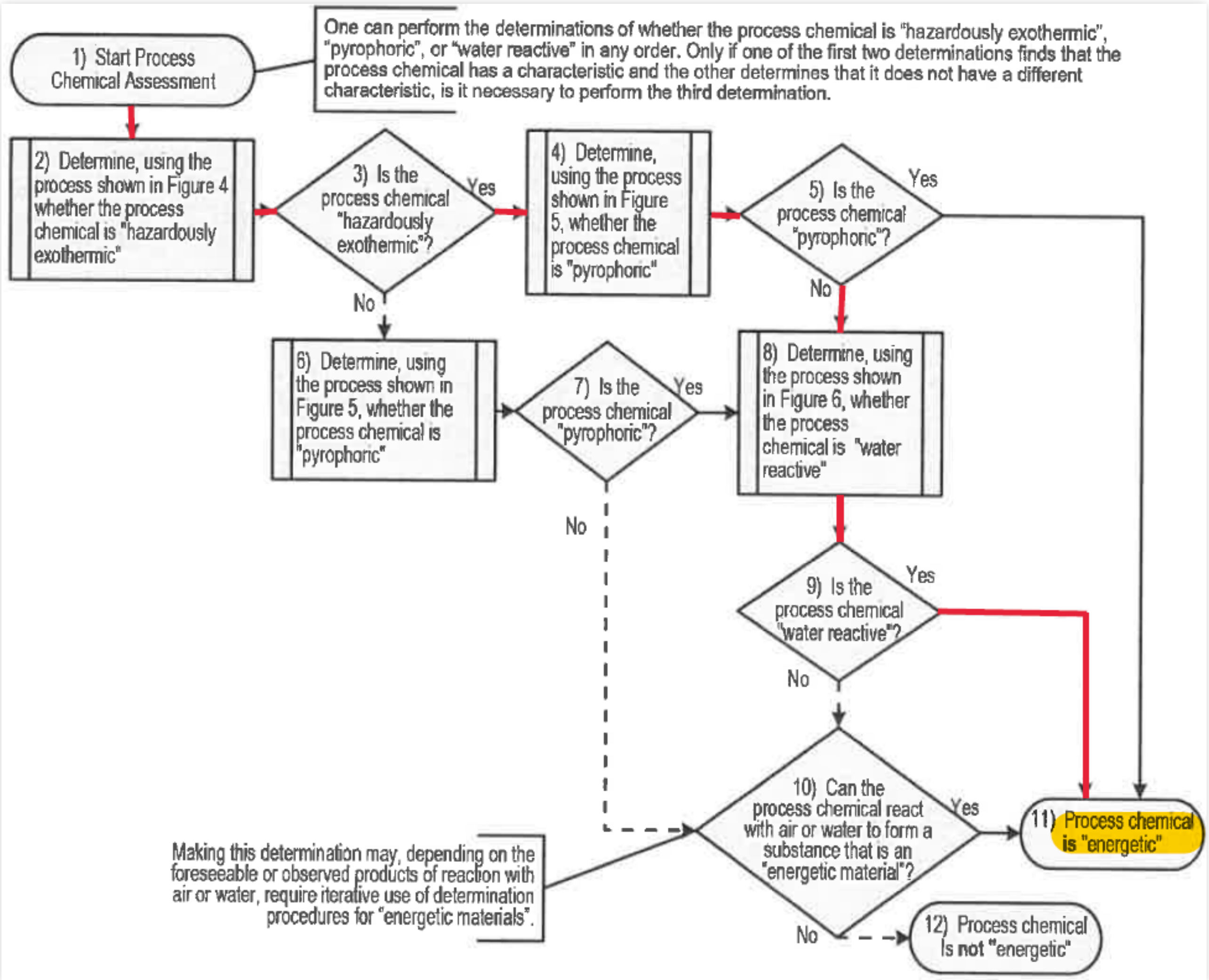


Figure E.6. Flowchart for the determining whether a process chemical is energetic [68, p. 9] highlighting the path of a hazardous exothermic material. (Credit: SEMI, annotations by CSB)

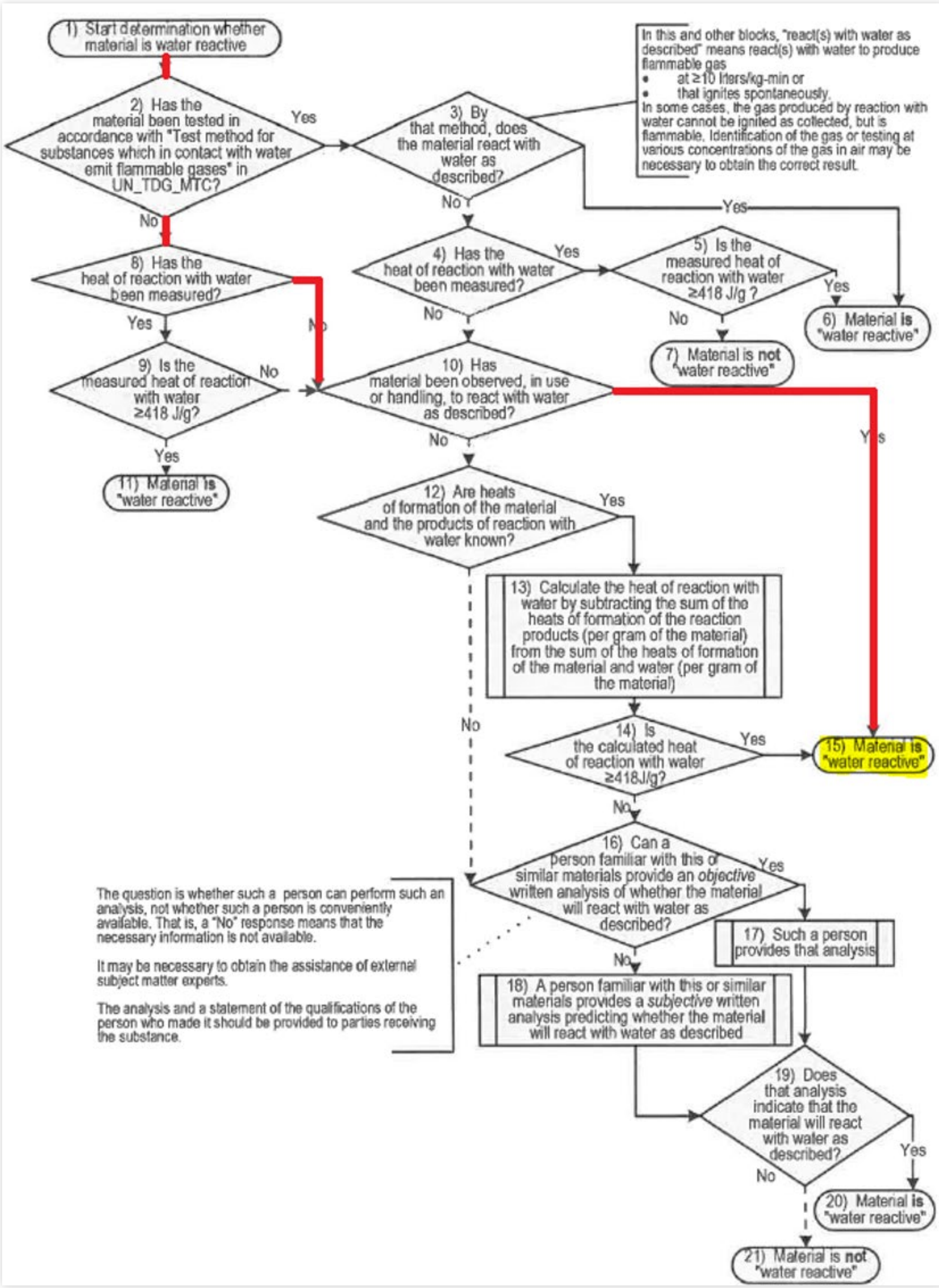


Figure E.7. Flowchart for the determining whether a material is water reactive [68, p. 16] highlighting the path of a hazardous exothermic material. (Credit: SEMI, annotations by CSB)

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