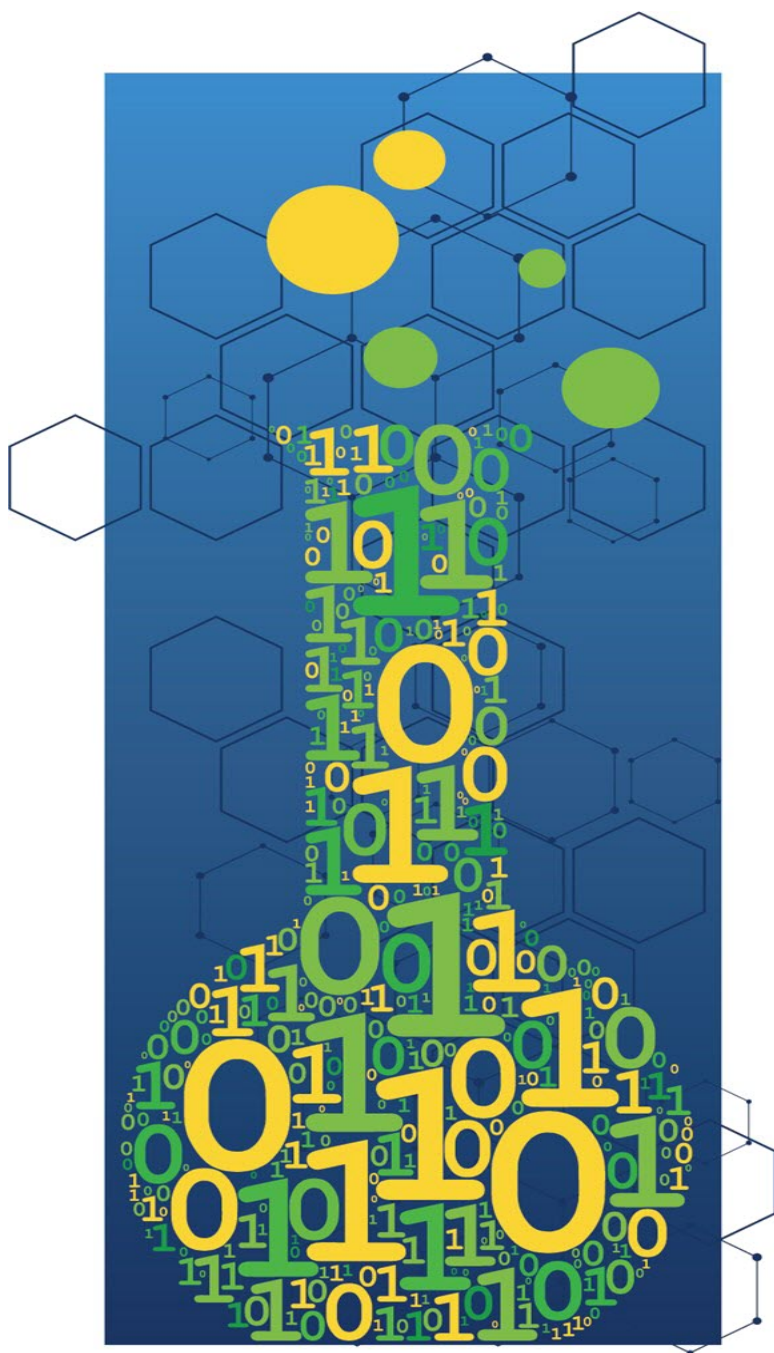




Overlooked Inherent Hazards of Commonly Used Pool and Water Treatment Chemicals



An **ioMosaic®** Publication

G. A. Melhem, Ph.D., FAICChE, E. Shaaban, Ph.D., and A. Iskandar, Ph.D.

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Overlooked Inherent Hazards of Commonly Used Pool and Water Treatment Chemicals

Process Safety and Risk Management Practices

authored by

G. A. Melhem, Ph.D., FAIChE, E. Shaaban, Ph.D., and A. Iskandar, Ph.D.

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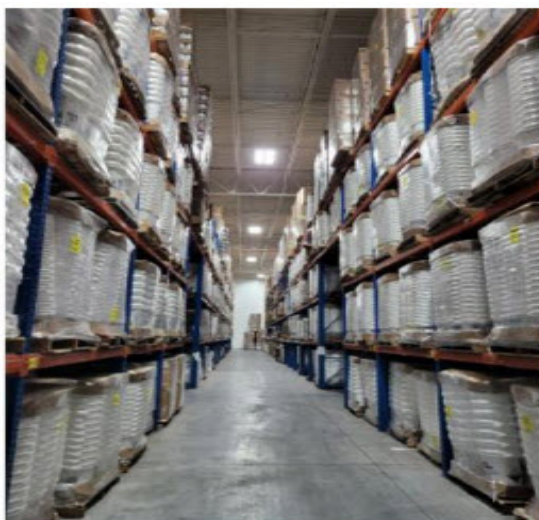
1 Introduction

Common pool chemicals are not classified as water reactive chemicals and are not considered by the general public to be hazardous. Why should they be? They are widely used to treat and disinfect pools and spas all over the world. When used to disinfect large quantities of water (dissolved in large amounts of water) and/or when stored or transported dry and without confinement, their reactivity hazards are negligible.

This paper will show that when common pool chemicals are confined and heated ¹ they decompose violently and generate large quantities of gaseous products. Decomposition may also initiate without added heat for some formulations under certain conditions. Adiabatic calorimetry measurements show that decomposition rates are exceedingly fast and rival the decomposition of propellants and some explosives. The decomposition products can be both flammable and/or toxic.

When partially wet and confined, for example during processing, storage, or transportation, the same water reaction that is intended to disinfect large amounts of water can trigger the decomposition of these materials, potentially leading to severe fires and explosions.

Figure 1: Warehouse storage racks



Source: CSB [1]

Confinement can be exhibited when wet pool chemicals (small granules and/or powder) are stored in a sealed container or when stored in bulk in large quantities [2]. A three to four feet of powder over a crusted wet cake of pool chemicals can form a sufficient sealant to permit the formation of highly unstable nitrogen trichloride (NCl_3) or nitrogen tribromide (NBr_3). If the concentration of NCl_3 or NBr_3 gets high enough, the spontaneous decomposition of these unstable chemicals acts as a trigger for the decomposition of the pool chemical itself, which can lead to severe fires and explosions. It is important to note that pool chemicals powders are also poor conductors of heat.

This paper provides irrefutable evidence and learnings from more than forty measured calorimetry and analytical tests data sets as well as thermochemical evaluations that demonstrate the mechanism of how

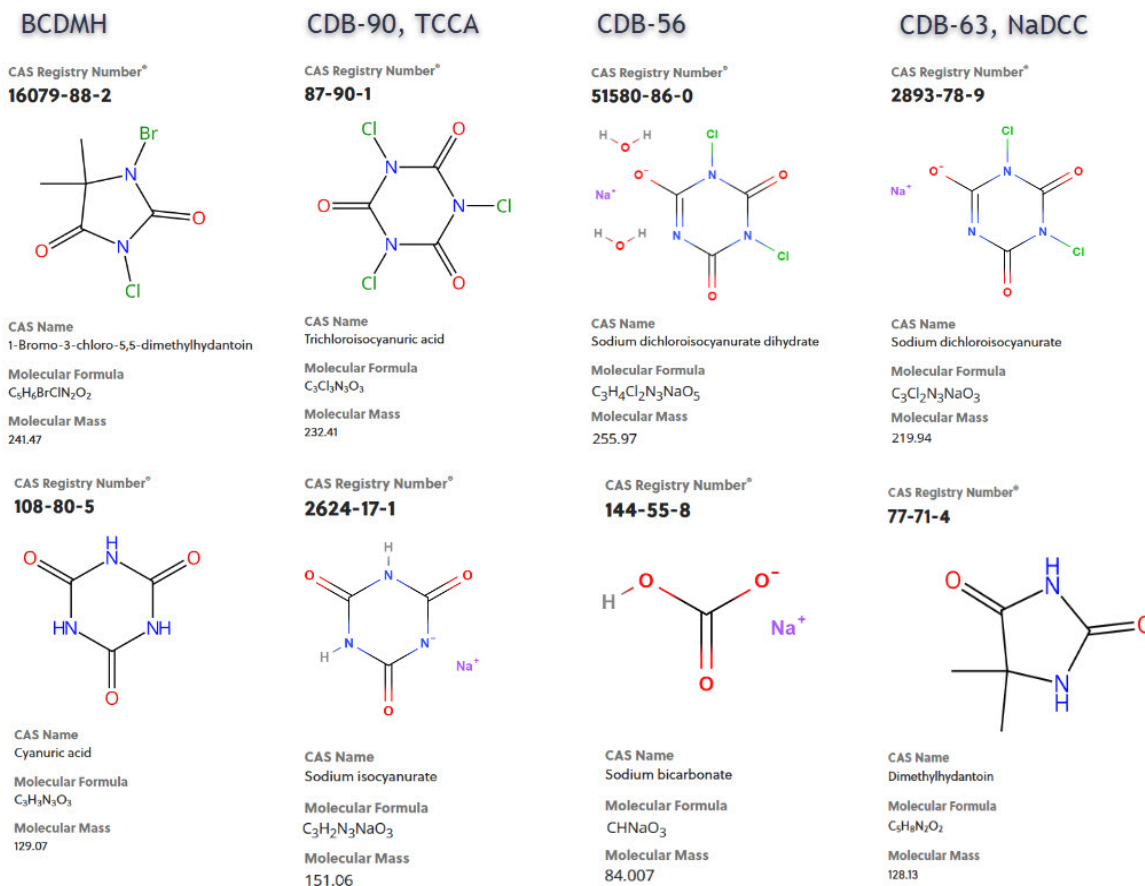
partially wet and confined pool chemicals can cause severe fires and explosions.

Pool chemicals ² considered in this study (see Figure 2) included trichloroisocyanuric acid (CDB-90 or TCCA), sodium dichloroisocyanurate (CDB-63, NaDCC), sodium dichloroisocyanurate dihydrate (CDB-56, $NaDCC \cdot 2H_2O$), bromochlorodimethylhydantoin (BCDMH), and related compounds.

¹Heating can occur due to reaction with water or with other materials as pool chemicals are strong oxidizers. Heating can also occur due to an external fire, or use of heating jackets, or use of heating elements.

²CDB-90/63/56 are “Chlorinated Dry Bleach” where the numbers denote percent by weight of available chlorine (as Cl_2): $\simeq 90\%$ for TCCA, $\simeq 63\%$ for anhydrous NaDCC, and $\simeq 56\%$ for $NaDCC \cdot 2H_2O$.

Figure 2: Chemical structures of common pool chemicals and related compounds

Source: [ioMosaic®](#)

Different ratios of water to pool chemical were tested using adiabatic and differential scanning calorimetry highlighting the critical water to chemical ratio required to cause the most severe decomposition outcomes. Reaction products were identified and quantified by Gas Chromatography and Mass Spectrometry (GC/MS) and Fourier Transform Infrared Spectroscopy (FTIR). Additional properties such as thermal effusivities and heats of combustion were also measured and are provided in this paper.

2 Recent Incidents

Some selected recent incidents highlight several overlooked inherent hazards of common pool chemicals during processing and storage.

2.1 Bio-Lab, 2024

On September 29, 2024, the Bio-Lab, Inc. (BioLab) facility located in Conyers, Georgia, experienced multiple fires, extensive off-gassing, and a massive plume of potentially toxic smoke [1, 3].

As a result of the incident, local officials reported that about 17,000 people were evacuated. The facility stored TCCA, BCDMH, CDB-56, and CDB-63 in a warehouse in large quantities (see Figure 1).

Due to heavy rain fall ³ from hurricane Helene and warehouse roof leaks some stored materials may have been exposed to rain and became partially wet. However, the Chemical Safety Board [3] considered this rain scenario as well as other scenarios that could have led to the partial wetting of some stored materials and concluded that the water leaks were caused by corrosion of sprinkler system components that started leaking shortly after the facility began storing chlorinated isocyanurates in 2019. Employees assigned to fire watch heard popping sounds. These popping sounds were most likely attributed to the formation of highly unstable nitrogen trichloride and/or nitrogen tribromide from wet materials.

2.2 Optima Belle, 2020

At approximately 10:00 PM on December 8, 2020, a pressure rated rotary double cone dryer containing CDB-56 exploded, causing a subsequent fire and toxic release at the Optima Belle LLC. facility (Optima) in Belle, West Virginia. In addition to shelter in place impacts on the surrounding communities, Optima experienced significant property damage, and one Optima employee was fatally injured ⁴.

The explosion occurred while Optima, a toll manufacturer [4, 5], was drying CDB-56 to remove water and to make CDB-63 on behalf of Clearon Corporation (Clearon). Optima's estimated property damage from the incident was in excess of thirty million dollars. A violent decomposition of partially wet CBD-56 occurred and caused the vessel failure [6, 7]. The partially wet CDB-56 caused the formation of nitrogen trichloride which accumulated in the dryer. The nitrogen trichloride spontaneously decomposed and caused the violent decomposition of the NaDCC.

A technology transfer package (TTP) ⁵ was provided by Clearon to Optima. The TTP contained adequate and critical information about the potential reaction hazards of NaDCC with water and the impact of confinement. Unfortunately, Optima personnel did not possess the necessary skills and chemical reactivity experience required to properly use the TTP information for equipment selection, process hazards analysis, and the development of safe operating limits.

Selected excerpts from the TTP ⁵ provide insight into the hydrolysis chemistry and dangers of partial wetting of TCCA and NaDCC. These excerpts are just but a few examples of some of the important and relevant process safety information (PSI) provided by the TTP.

In this excerpt, FMC points out with clarity that “inertial or mass or overburden confinement” can

³Approximately 10 inches of rain fell between September 26 and 27

⁴Employee was critically injured and died later due to intoxication from inhaled fumes

⁵FMC Corporation, Thermal Decomposition Studies of CDB-63, FMC-RR-68-5251-R, December, 1968.

prevent NCl_3 vapors from escaping and cause the NCl_3 vapors to accumulate as if the system was a closed system⁶. Stopping the dryer rotation can create the type of confinement the Clearon TTP warned about: *“The thermal decomposition of sodium dichloroisocyanurate (CDB-63) was initiated at temperatures as low as 60 to 90 °C by the presence of water in sufficient quantity to form a wet cake of the material. The CDB's must be in a container which will hold the NCl_3 vapors, produced by the hydrolysis reaction, until an explosive concentration is reached. The spontaneous decomposition of NCl_3 generates sufficient heat to initiate decomposition in the CDB mass. A 3 to 4 ft height of CDB powder over a crusted wet cake is sufficient sealant to permit this concentration build up. In a tightly sealed system NCl_3 build up is rapid enough to cause a detonation.”*

In the following excerpt, the TTP draws a clear distinction between **open** and **closed** systems: *“The effect of water on the decomposition of CDB-63 was studied in **open and closed systems** with the amount of CDB-63 ranging from test tube samples to 4 foot columns in 2-inch pipes.”* The operating limits provided by the TTP were for an open system and have been verified as accurate and representative by ioMosaic®. When dryer rotation is stopped for long periods of time, the bottom contents of the dryer become inertially confined by the mass on top or overburden of the CDB material.

This excerpt describes the equivalence of CDB-63 and CDB-56: *“CDB-63 forms a dihydrate at ambient temperature which becomes a monohydrate at 80 °C, and an anhydrous salt at 110 °C”*. CDB-56 is CDB-63 with two water molecules (a dihydrate). CDB-56 becomes a CDB-63 monohydrate at 80 °C and an anhydrous CDB-63 at 110 °C, well below the 140 °C upper temperature drying limit provided by Clearon. CDB-56 did not have to be called out specifically by the TTP⁵ as it is a CDB-63 dihydrate. Water did not have to be added to the CDB-56 to cause a self-sustaining runaway decomposition, the CDB-63 dihydrate (CDB-56) has its own stoichiometric water content which is released when heated and needed to be continuously removed by having an open and rotating double cone dryer system that is under vacuum and/or nitrogen purge.

The TTP warns about the potential hazards in a closed system: *“In the presence of sufficient water to give a wet of CDB-63, spontaneous decomposition will take place with detonation at 55-60 °C in a completely enclosed system. In a system closed only by a column of CDB-63 powder, the detonation occurs at 90 to 100 °C”*. Pulling a vacuum on the dryer and/or continuous purging with nitrogen, as long as the dryer is rotating, ensures that the dryer is behaving like an open system. Stopping the dryer for long periods of time turns it into a closed system by inertial or mass or overburden confinement.

3 Hydrolysis and Decomposition Reactions

Pool chemicals such as TCCA, Anhydrous NaDCC, NaDCC dihydrate, and BCDMH possess dual hazards as they are Class 2 Oxidizers and contain an organic fuel source (their ring structure) within the same molecule. This makes pool chemicals susceptible to self-accelerating decomposition and combustion without the need for air, similar to organic peroxides.

⁶The terms “closed”, “sealed”, and/or “confined” are used interchangeably

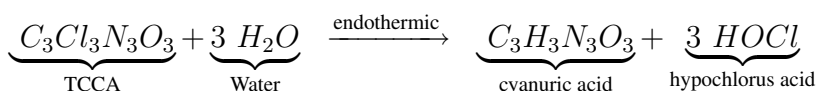
However, due to their apparent stability under ambient conditions in dry forms and when added to a large open body of water, their water reactivity is typically overlooked. Test data and multiple incidents indicate that wetting the powder under confinement (in a closed vessel or under self-confinement by bulk mass) causes reactions that initiate energetic decomposition and self-combustion reactions.

In such types of pool chemicals, the organic ring structure (e.g., isocyanuric acid or dimethylhydantoin) is engineered to ensure the controlled, sustained release of the active sanitizers, hypochlorous acid (HOCl) or hypobromous acid (HOBr), into the pool water. This slow release mechanism in a large body of water maintains a consistent residual sanitizer level over time, allowing the chemical to effectively decompose pathogens without requiring constant reapplication or reaching overly high concentrations that could irritate swimmers.

The opposite scenario, adding a small amount of water to a large amount of pool chemicals under confinement, however, can initiate the decomposition and combustion under a far lower onset temperature, in comparison to pure form, causing a serious chemical hazard. As these chemicals normally hydrolyze to form HOCl or HOBr or both, the wetted area of the powder becomes concentrated enough in HOCl or HOBr or both to initiate the exothermic decomposition and combustion of the organics in the material. Such decomposition can form hazardous gases, including the explosive NCI_3 and/or NBr_3 , and a hot spot that can initiate self-accelerating decomposition and combustion of the rest of the powder, leading to thermal runaway, overpressure/explosion, and toxic-gas release.

3.1 Trichlorocyanuric Acid (TCCA, CDB-90)

The TCCA hydrolysis reaction leads to the formation of cyanuric acid (CA) and hypochlorous acid (HOCl):



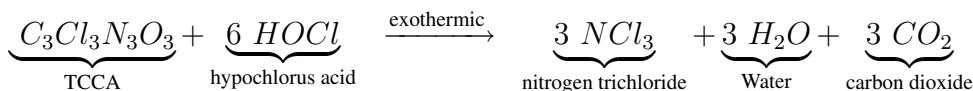
When water is well in excess of TCCA, HOCl will react in the water and there will be no free HOCl for further reaction with the TCCA or CA. HOCl will react with pathogens and disinfect the water, but will be too diluted for further reaction with TCCA or CA.

However, when TCCA is well in excess of water, water becomes highly concentrated with HOCl and the following reaction leads to the formation of nitrogen trichloride:

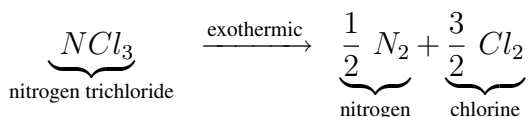
Figure 3: Nitrogen trichloride thermochemistry

** Melhem Index					
Hazard Rating	Heat of reaction	CART	Effective CART		
High	-456.63 cal/g	3371.86 K	4248.27 K		
		-54.96 kcal/gmol; 1 gmol basis			
Chemical Name	Formula	Phase	Initial Moles	Change	Final Moles
NITROGEN TRICHLORIDE	Cl3N	Vapor	1.0000	-1.0000	0.0000
NITROGEN	N2	Vapor	0.0000	0.5000	0.5000
CHLORINE	Cl2	Vapor	0.0000	1.5000	1.5000
Other. < 0.0001 moles			0.0000	0.0000	0.0000
Totals			1.0000	1.0000	2.0000

Source: SuperChem[®] Expert

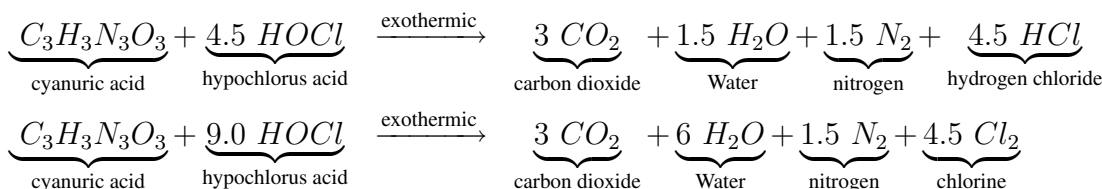


Nitrogen trichloride, which can also be formed by the decomposition of TCCA, is highly unstable and can spontaneously decompose exothermically if it is allowed to accumulate:



The nitrogen trichloride calculated adiabatic reaction (decomposition) temperature (CART [8, 9, 10, 11]) is very high (see Figure 3) which is why it serves as a strong trigger for the decomposition of TCCA. Nitrogen trichloride formation is favored by acidic conditions [12] or a low water to TCCA mass ratio. Under acidic conditions (low pH < 4), nitrogen trichloride formation is favored. Under alkaline conditions (pH > 7), monochloramine formation is favored.

Cyanuric acid will also react with HOCl exothermically via one of the following stoichiometries:

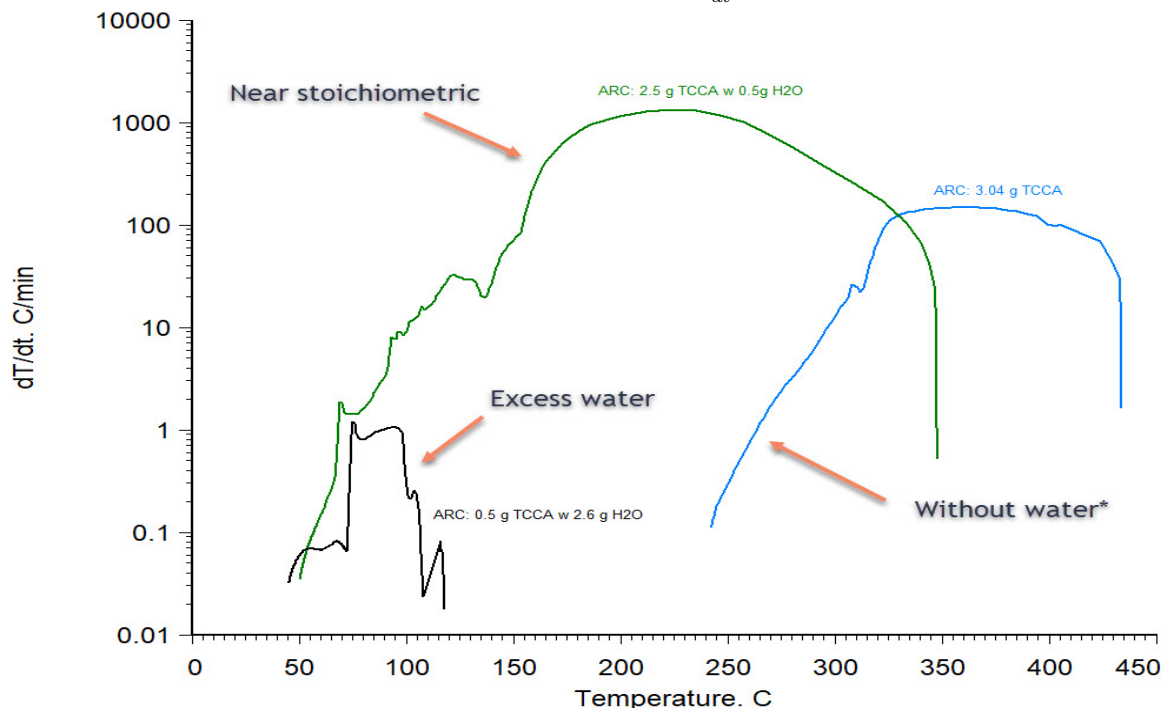


The worst case water to TCCA molar ratio, is 3 to 1 (or 18.86 % water mass fraction or 23.23 % water to TCCA mass ratio), or stoichiometric. Numerous calorimetry tests were conducted with varying water to TCCA mass fractions ranging from 0 % water (100 %TCCA) to 91.5 % water (141.9 to 1 water to TCCA molar ratio).

Differential scanning calorimetry tests were also conducted using sealed high pressure test cells and also open test cells. The measured heat of fusion by DSC ranged from 54 to 88 J/g while the measured heat of decomposition ranged from -1050 to -1060 J/g TCCA or -251 to -253 cal/g of TCCA.

Heat of combustion testing for TCCA results ranged from -1487 BTU/lb (-3459 kJ/kg) to -1572 BTU/lb (-3654 kJ/kg). The combustion tests resulted in a solid white-yellow residue remaining after the tests, which indicated that the TCCA was not fully combusted. The remaining TCCA powder was approximately 45 % of the initial amount of TCCA powder. The heat of combustion of TCCA may also include contributions from the decomposition of TCCA.

Figures 4 and 5 show the impact of water to TCCA ratio on the stability and reaction rates of TCCA and TCCA with water. When water is well in excess of TCCA, the overall rates of reactions (dissolution, mixing, and decomposition) are low and would be what is expected when treating large volumes of water with small amounts of TCCA. When TCCA is heated without water, its decomposition temperature is well in excess of 200 °C. The data shown in Figures 4

Figure 4: ARC Measured TCCA decomposition rate $\frac{dT}{dt}$ using different water to TCCA ratios

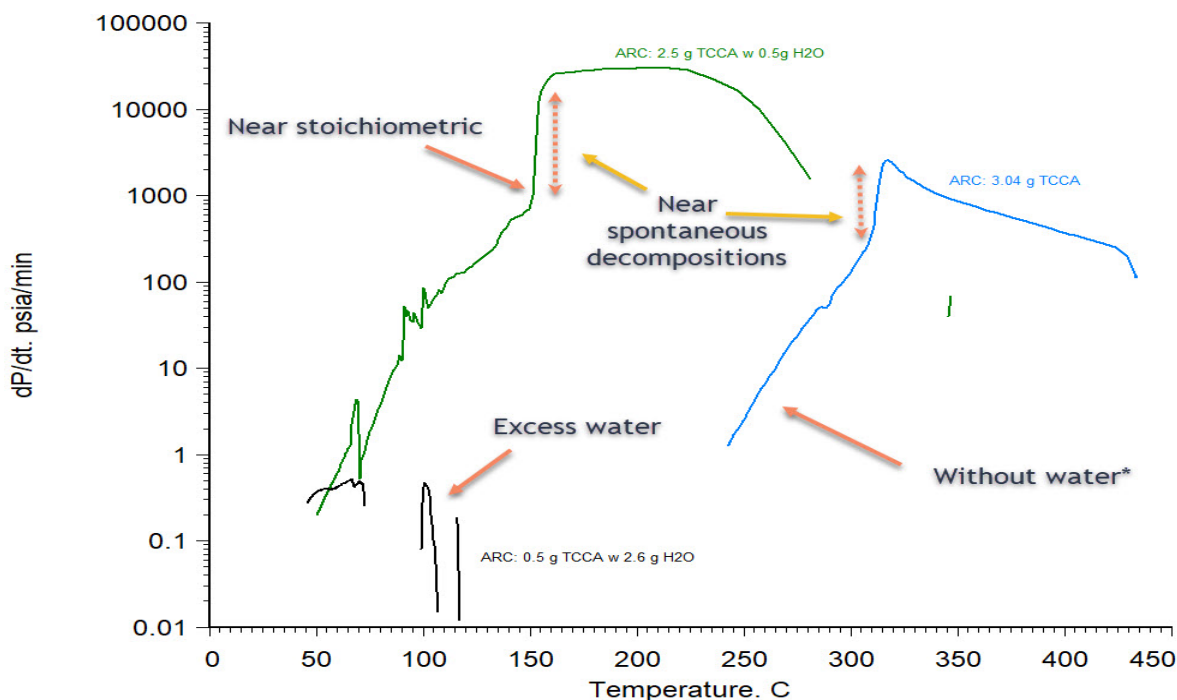
Source: ioMosaic®; *: Test terminated due to instrument temperature limit

and 5 does not capture the entire decomposition exotherm of TCCA because the decomposition reaction temperature either exceeded the temperature limit or the pressure rise rate tracking limit of the ARC. The estimated partial heat of decomposition of TCCA ranges from -175 to -218 cal/g TCCA. The decomposition of TCCA can form nitrogen trichloride which in turn can decompose spontaneously and exothermically to chlorine and nitrogen.

The near stoichiometric test shows a low detected onset temperature of approximately 50 °C. We also note the magnitude of the exotherm and the measured heat of reaction ranging from -420 to -520 cal/g of TCCA. As mentioned earlier [2], when TCCA is wet and stored in a sealed container or when stored in bulk in large quantities, severe fires and/or explosions can occur. A three to four feet of TCCA powder over a crusted wet cake of TCCA can form a sufficient sealant to permit the formation and accumulation of highly unstable nitrogen trichloride (NCl_3). If the concentration of NCl_3 gets high enough, the spontaneous decomposition of NCl_3 acts as a trigger for the decomposition of TCCA which can lead to severe fires and/or explosions. It is important to note that TCCA powders are also poor conductors of heat.

When confined, the formation and accumulation of nitrogen trichloride or the formation of hypochlorous acid (followed by formation and accumulation of nitrogen trichloride) have a profound impact on the hazard potential of TCCA (CDB-90). This is shown in Figure 6. As Figure 6 shows, when heated in an open system and decomposition products are allowed to escape, the hazard potential of TCCA is much less than when it is confined.

Figure 5: ARC Measured TCCA decomposition rate $\frac{dP}{dt}$ using different water to TCCA ratios



Source: ioMosaic®; *: Test terminated due to instrument temperature limit

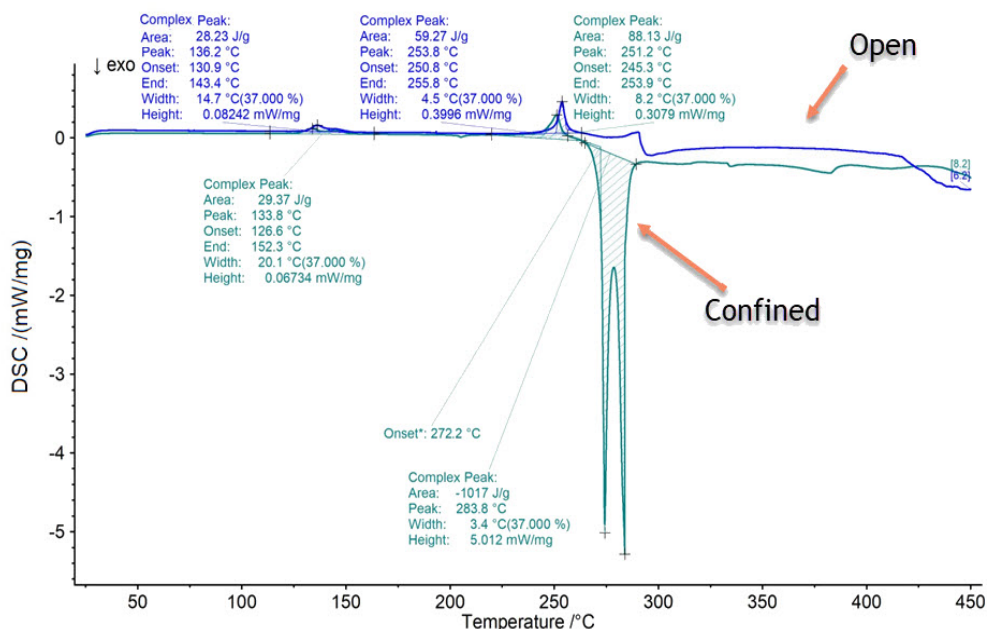
3.2 Sodium Dichloroisocyanate (NaDCC)

Anhydrous NaDCC (Dichlor-60 or CDB-63) and NaDCC dihydrate (Dichlor-56 or CDB-56) are essentially the same molecule. The $\approx 14\%$ by mass water of crystallization in the dihydrate ($\text{NaDCC} \cdot 2\text{H}_2\text{O}$) can be released by two endothermic reaction steps (see section 3.2.2) starting at 47°C and 86°C respectively. Although the release of water from NaDCC dihydrate crystal is endothermic, once the water is free, it initiates a hydrolysis reaction to form HOCl , which in turn starts an energetic isocyanurate ring exothermic decomposition ($\approx 75^\circ\text{C}$ as observed from adiabatic calorimetry tests as described later in this document) to produce NCl_3 . Calorimetry tests also show that increasing water beyond the stoichiometric amount in NaDCC systems, by injecting water, lowered the detected decomposition onset temperature, reaching $\approx 46^\circ\text{C}$ at 50% water by mass.

Anhydrous NaDCC does not contain crystallization water. Adiabatic calorimetry testing shows that the detected onset temperature for decomposition, without added water, was $\approx 111^\circ\text{C}$. However, once anhydrous NaDCC contacts water, it exothermically rehydrates to the NaDCC dihydrate or completely dissolves. In ARC testing, injecting 0.5 g of water into 2.5 g of anhydrous NaDCC at 30°C produced a rapid hydration heat release (exotherm), with the temperature rise rate reaching $\approx 80^\circ\text{C}/\text{min}$ four minutes after the water addition, and the released heat was estimated to be ≈ 44 calories per gram of mixture. The exotherm persisted and ultimately initiated the explosive decomposition.

The NaDCC dihydrate effectively carries its own trigger, two molecules of water bound to the

Figure 6: TCCA/CDB-90 measured runaway decomposition behavior using DSC under open and confined conditions



Source: [ioKinetic®](#)

NaDCC molecule and held in the lattice. When the bound water molecules are released and re-wet the solid, local hot spots are created, accelerate hydrolysis, and drive decomposition. Although heat is required to release the lattice water, adding a small amount of external water can lower the onset temperature to $\simeq 46$ °C. Anhydrous NaDCC requires external water. However, once the right amount of water is added, the exothermic hydration can drive the hydrolysis, and the decomposition proceeds more readily starting at room temperature.

To fully understand the hazard and risks for any process involving anhydrous or NaDCC dihydrate, three main reactions should be evaluated:

1. Hydration and dehydration dynamics (reversible conversion between dihydrate and anhydrous) with heat release on contact of anhydrous NaDCC with liquid water and heat absorption on thermal dehydration.
2. Hydrolysis to release HOCl in the presence of free water (small amount, added or liberated from the crystal). Hydrolysis is endothermic but it generates HOCl that can be concentrated enough to initiate an energetic exothermic decomposition.
3. The explosive decomposition of the isocyanurate ring; based on the two above reactions and the conditions that control them, the onset temperature of the exothermic explosive decomposition of the isocyanurate ring becomes a moving target.

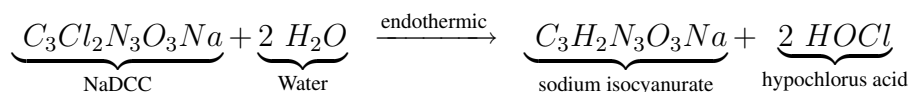
The Optima Belle double cone dryer explosion [6] occurred during drying of CDB-56 to CDB-63. The CSB concluded that the explosion was due to self accelerating decomposition of heated NaDCC dihydrate. The CSB attributed the incident to the unsafe setup, the repeated unplanned

dryer rotation pauses, and the disregard of shutdown instructions that left the dryer without rotation, nitrogen purge, or jacket cooling, which trapped heat, caused vapor to condense and re-wet the solids, lowered the decomposition onset temperature, and ultimately triggered the runaway decomposition reaction. The CSB findings are summarized in the Conclusion Section 5.1 of the published investigation final report [6]. These findings cover 1) process knowledge management, 2) thermal hazard assessment, 3) equipment selection and process design, 4) tolling of hazardous materials, and 5) regulatory coverage of reactive hazards.

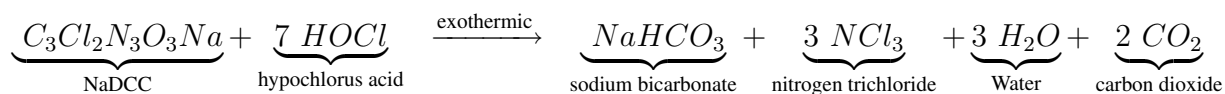
Another subtle factor that has not been considered in the CSB investigation is that the rewetting of some of the dried powder (once the recondensation happens during the operation pauses on the day of the incident) will cause fast exothermic rehydration. Local hot spots from the hydration exotherm formed wherever water touches the dried powder, will increase the likelihood of decomposition. To put this into perspective, about 125 gallons of water must be removed from 8,820 lb of the CDB-56⁷, so assuming a 10-hour run, that is 12.5 gal per hour. If 1 % of the total water condenses back when the dryer rotation is stopped without cooling and nitrogen purge, $\simeq 1.25$ gallons could recondense into the CDB powder to reform the dihydrate. For this 1.25 gallons of water, $\simeq 63.7$ lb of CDB-63 powder would become CDB-56. This will cause a fast increase in the temperature in this area by $\simeq 125$ °C above the operating temperature⁸.

3.2.1 Anhydrous Sodium Dichloroisocyanurate (NaDCC, CDB-63)

The NaDCC hydrolysis reaction leads to the formation of sodium isocyanurate (NaCA) and hypochlorous acid (HOCl):



When water is well in excess of NaDCC, HOCl will react in the water and there will be no free HOCl for further reaction with the NaDCC or NaCA. HOCl will react with pathogens to disinfect the water, but will be too diluted for further reaction with NaDCC and NaCA. However, when NaDCC is well in excess of water, water becomes highly concentrated with HOCl and the following reaction leads to the formation of nitrogen trichloride:

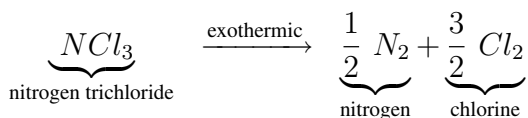


As mentioned earlier, nitrogen trichloride is highly unstable. When enough nitrogen trichloride is accumulated, its exothermic spontaneous decomposition (see Figure 3) acts as a trigger and causes

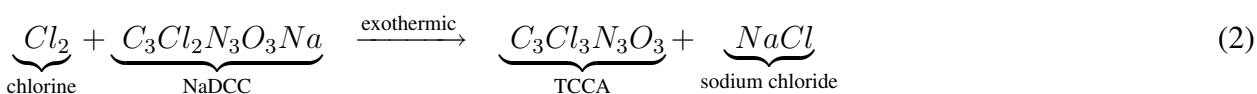
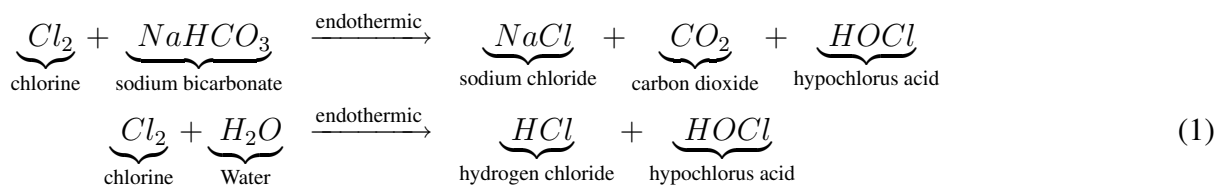
⁷The CSB published report [6] does not state 125 gallons of water must be removed. The CSB performed a theoretical calculation and the report states, “The CSB calculated that approximately 125 gallons of water could be removed from 8,820 lbs of CDB-56 during dehydration”. The CSB report also states the dehydration process was capable of releasing approximately 125 gallon of water.

⁸Assuming a heat capacity of water of 1.0 cal/g/K, a heat capacity of NaDCC of 0.25 cal/g/K, and that hydration or dissolution releases 44 cal per gram of mixture.

the decomposition of NaDCC.



Even when the concentration of nitrogen trichloride is not high enough to trigger a decomposition of NaDCC, the chlorine that is formed further reacts with sodium bicarbonate and also with water to make additional HOCl:



Any TCCA that is formed as a reaction product will also react with water as outlined in section 3.1. The worst case water to NaDCC molar ratio, is 2 to 1 (or 14 % water mass fraction or 16.3 % water to NaDCC mass ratio), or stoichiometric. Numerous calorimetry tests were conducted with varying water to NaDCC mass fractions ranging from 0 % water (100 % NaDCC) to 96 % water (61 to 1 water to NaDCC molar ratio).

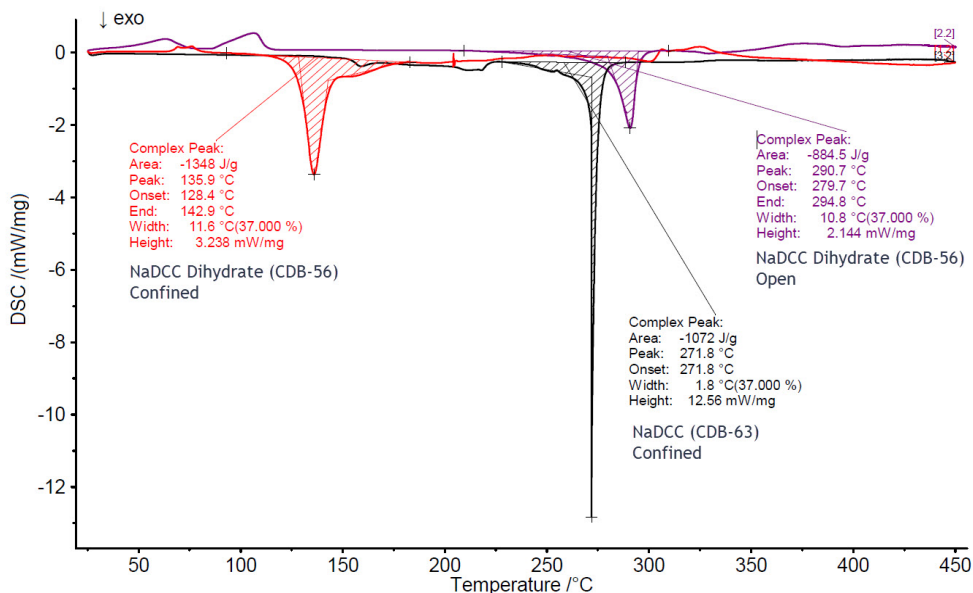
Differential scanning calorimetry tests were also conducted using sealed high pressure test cells and also open test cell for and anhydrous NaDCC and NaDCC dihydare. The measured heat of decomposition under confinement by DSC is -1072 J/g NaDCC (-256 cal/g NaDCC) (see Figure 7).

When confined, the formation and accumulation of nitrogen trichloride or the formation of hypochlorous acid (followed by formation and accumulation of nitrogen trichloride) have a profound impact on the hazard potential of NaDCC. This is shown in Figure 7. As Figure 7 shows, when heated in an open system and decomposition products are allowed to escape, the hazard potential of NaDCC is much less than when it is confined.

Heat of combustion testing for NaDCC (CDB-63) results ranged from -1642 BTU/lb (-3816 kJ/kg) to -1700 BTU/lb (-3952 kJ/kg). The combustion tests resulted in a solid white-yellow residue remaining after the tests, which indicated that the NaDCC was not fully combusted and/or formation of solid ionic combustion products such as sodium salts. The heat of combustion measurement may also include contributions from the decomposition of NaDCC.

Figures 8 and 9 show the impact of water to NaDCC ratio on the stability and reaction rates of NaDCC and NaDCC with water. When water is well in excess of NaDCC, the overall rates of reactions (dissolution, mixing, and decomposition) are low and would be what is expected when treating large volumes of water with small amounts of NaDCC. When NaDCC is heated without water, its ARC detected decomposition temperature is approximately 100 °C. The data shown

Figure 7: NaDCC measured runaway decomposition behavior using DSC under open and confined conditions



Source: [ioKinetic®](#)

in Figures 8 and 9 does not capture the entire decomposition exotherm of NaDCC because the decomposition reaction pressure rise rate exceeded the pressure limit of the [ARC](#). The estimated partial heat of decomposition of NaDCC is -263 cal/g NaDCC. The decomposition of NaDCC can form nitrogen trichloride which in turn can decompose spontaneously and exothermically to chlorine and nitrogen.

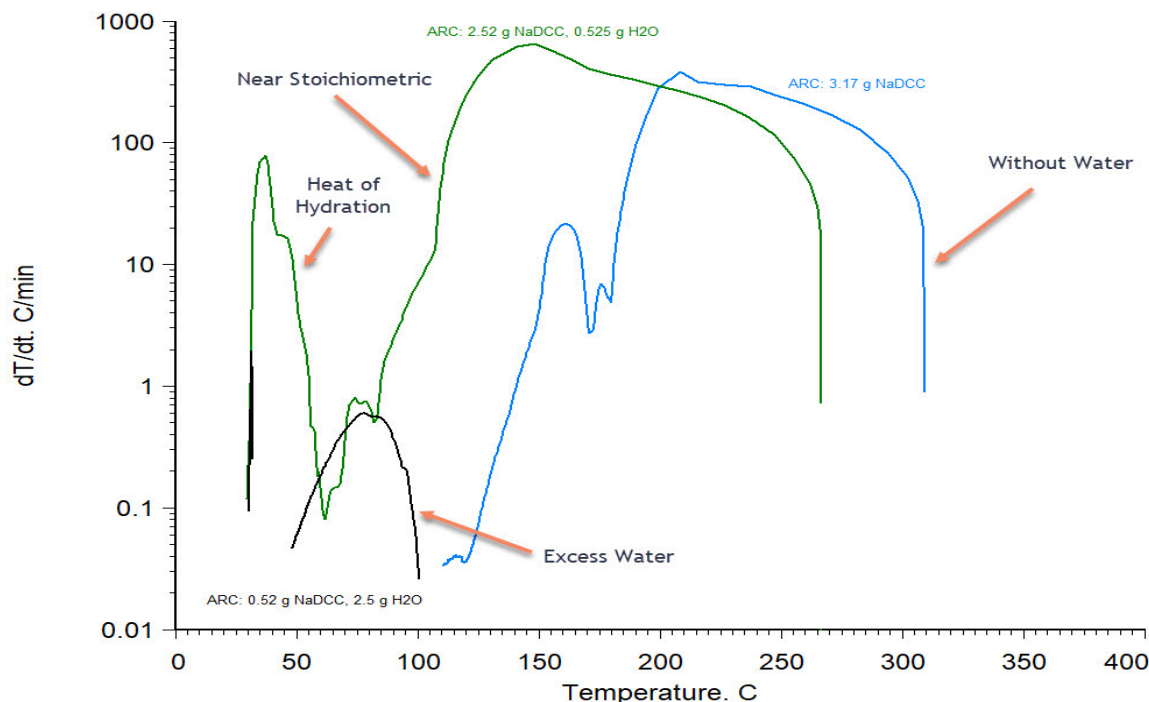
The near stoichiometric test shows that the exothermic reaction starts once the water is injected into the NaDCC at 30 °C. We also note the magnitude of the exotherm and the measured partial heat of reaction of -730 cal/g of NaDCC. The entire exotherm was not captured as the pressure rise rate exceeded the limit of the [ARC](#).

As mentioned earlier [2], when NaDCC is wet and stored in a sealed container or when stored in bulk in large quantities, severe fires and/or explosions can occur. A three to four feet of NaDCC powder over a crusted wet cake of NaDCC can form a sufficient sealant to permit the formation and accumulation of highly unstable nitrogen trichloride (NCl_3). If the concentration of NCl_3 gets high enough, the spontaneous decomposition of NCl_3 acts as a trigger for the decomposition of NaDCC which can lead to severe fires and/or explosions.

The confinement impact on water reactivity of NaDCC is often ignored or discounted because water is added to NaDCC in an open system [13]. Carpenter and Ogle [13] conducted moisture testing in the open to determine the cause of an industrial accident involving NaDCC. They also conducted [ARC](#) testing and their results are consistent with our findings for dry NaDCC under confinement. However, their water testing with 4 g of water added to 30 grams of NaDCC product mixture only caused a momentary temperature rise⁹ to 115 °C but failed to initiate an NaDCC

⁹Most likely due to heat of hydration

Figure 8: ARC Measured NaDCC decomposition rate $\frac{dT}{dt}$ using different water to NaDCC ratios



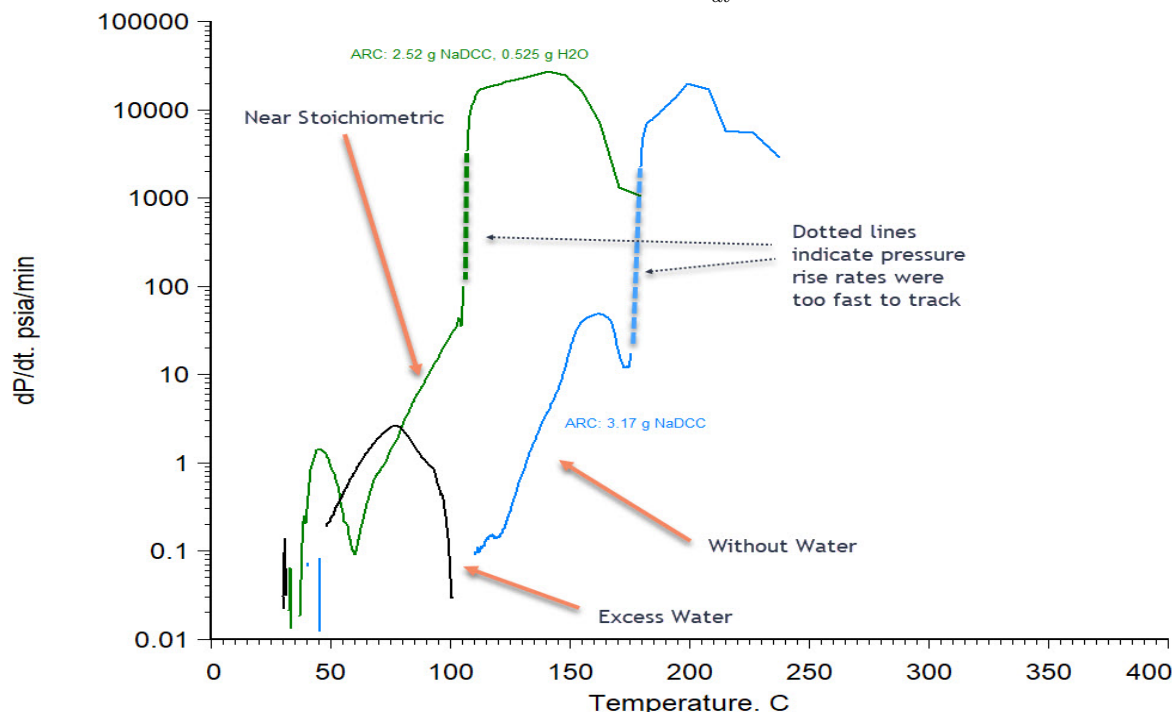
Source: ioMosaic®; Tests of dry near stoichiometric NaDCC terminated before completion due to ARC maximum temperature and/or pressure rise rate limits.

decomposition because the system was open. Had they injected water to NaDCC using the ARC, they would have come to similar findings regarding the profound impact of small amounts of water on potential NaDCC decomposition hazards. Because of this oversight, their incident investigation finding (that friction caused the decomposition of 500 kg of material in a ribbon blender) was most likely in error and may not have been the actual cause of the incident.

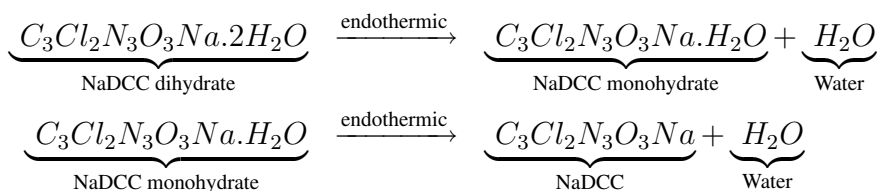
It is important to note that NaDCC powders are also poor conductors of heat. FMC [2] reports a heat capacity of 0.24 cal/g NaDCC, a bulk density of 801 kg/m³, and a thermal conductivity of 0.072 W/m/K.

3.2.2 NaDCC Dihydrate, CDB-56

The NaDCC Dihydrate (NaDCC.2H₂O) is the same as NaDCC but it has two molecules of water chemically bound to it. These two water molecules can react with NaDCC at elevated temperatures if they are freed by heating the NaDCC dihydrate by either oxidizing other materials or contaminants, using an external heating source, or by adding more water. The dehydration of NaDCC dihydrate proceeds via two reactions, the formation of NaDCC monohydrate, and the formation of dry NaDCC.

Figure 9: ARC Measured NaDCC decomposition rate $\frac{dP}{dt}$ using different water to NaDCC ratios

Source: ioMosaic®; Tests of dry near stoichiometric NaDCC terminated before completion due to ARC maximum temperature and/or pressure rise rate limits.

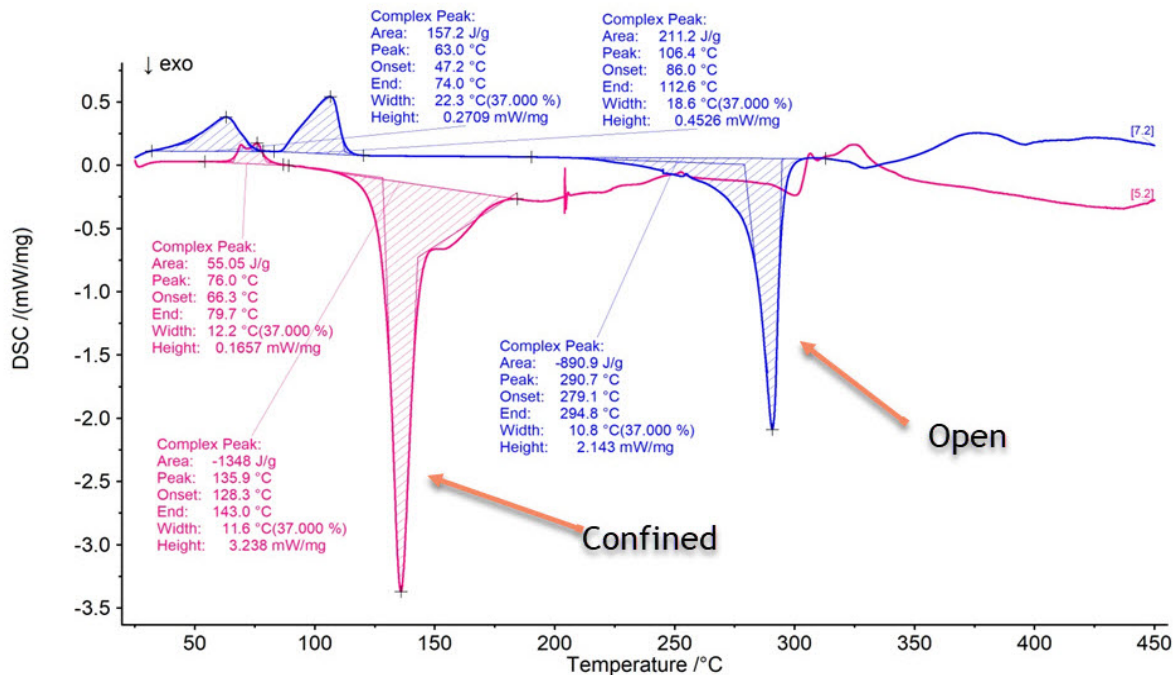


Both reactions are endothermic based on DSC measurements as shown in Figure 10. The production of NaDCC monohydrate starts at 47 °C and is endothermic with a heat of reaction of 157 J/g (37.5 cal/g) of NaDCC Dihydrate. The production of dry NaDCC from the monohydrate is also endothermic. It starts at 86 °C with a heat of reaction of 211 J/g (50 cal/g) of NaDCC monohydrate.

We also note from Figure 10 that the decomposition of NaDCC Dihydrate is more energetic and occurs at lower temperatures when confined. The heat of reaction when confined is -1348 J/g (-322 cal/g) of NaDCC Dihydrate. The heat of reaction for an open system is -890 J/g (-212 cal/g) of NaDCC Dihydrate.

Figures 11 and 12 show the impact of water to NaDCC dihydrate water ratio on the stability and reaction rates of NaDCC dihydrate and NaDCC dihydrate with water. When water is well in excess of NaDCC dihydrate, the overall rates of reactions (dissolution, mixing, and decomposition) are low and would be what is expected when treating large volumes of water with small amounts of

Figure 10: CDB-56 measured runaway decomposition behavior using DSC under open and confined conditions



Source: [ioMosaic®](#).

NaDCC dihydrate.

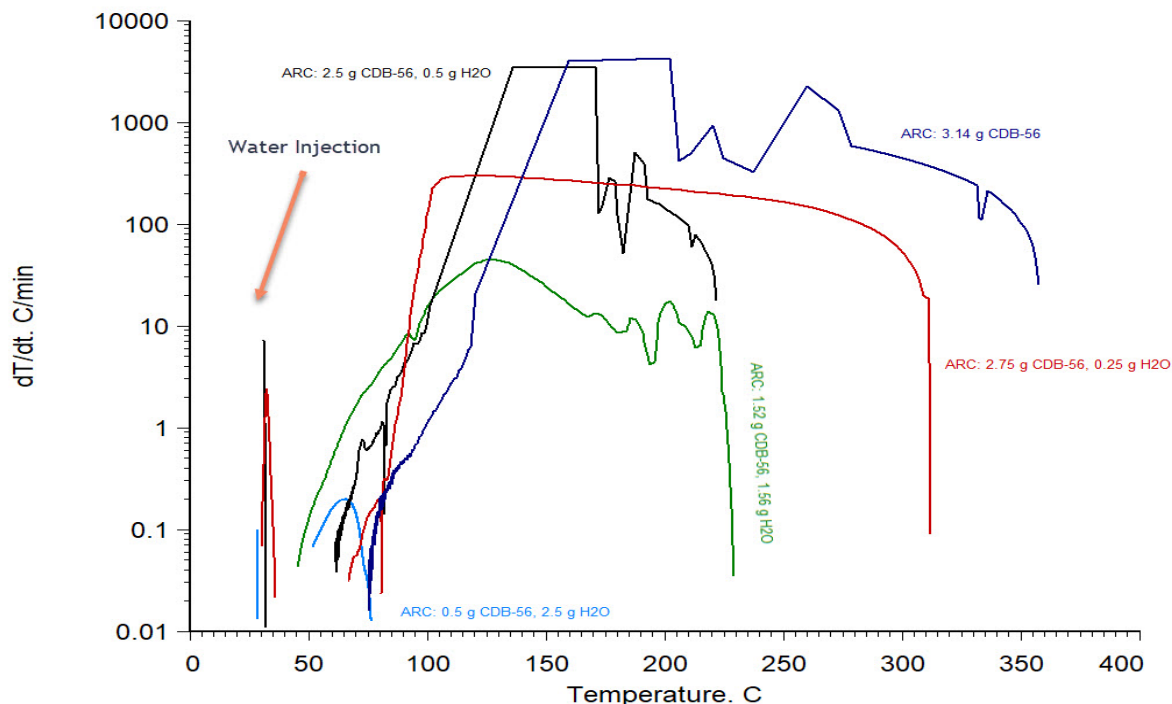
When NaDCC dihydrate is heated without water, its [ARC](#) detected decomposition temperature is approximately 75 °C. The data shown in Figures 11 and 12 does not capture the entire decomposition exotherm of NaDCC dihydrate because the decomposition reaction temperature rise rate exceeded the preset limit of the [ARC](#). The estimated partial heat of decomposition of NaDCC dihydrate ranges from -300 to -373 cal/g NaDCC dihydrate (vs. a [DSC](#) value of -322 cal/g). When mixed with water, the detected onset temperature is approximately 45 °C¹⁰. However, an exotherm due to mixing is detected at 30 °C as soon as water is injected into the test cells. The decomposition of NaDCC dihydrate can form nitrogen trichloride which in turn can decompose spontaneously and exothermically to chlorine and nitrogen.

Heat of combustion testing for NaDCC dihydrate (CDB-56) results ranged from -1581 BTU/lb (-3675 kJ/kg) to -1735 BTU/lb (-4033 kJ/kg). The combustion tests resulted in a solid white-yellow residue remaining after the tests, which indicated that the NaDCC dihydrate was not fully combusted. The heat of combustion measurement may also include contributions from the decomposition of NaDCC dihydrate.

It is important to note that NaDCC dihydrate powders are also poor conductors of heat. [ioKinetic®](#) measured a thermal conductivity of 0.0946 W/m/K and an average thermal effusivity of 300

¹⁰When corrected for the thermal inertia of the [ARC](#) (Φ), the corrected onset temperature, $T_{d,c}$, can be 5 to 10 degrees lower than the detected/measured onset temperature, $T_{d,m}$: $\frac{1}{T_{d,c}} = \frac{1}{T_{d,m}} + \frac{R_g}{E} \ln(\Phi)$ where R_g is the universal gas constant, E is the activation energy, and T is absolute temperature.

Figure 11: ARC Measured NaDCC dihydrate decomposition rate $\frac{dT}{dt}$ using different water to NaDCC dihydrate ratios

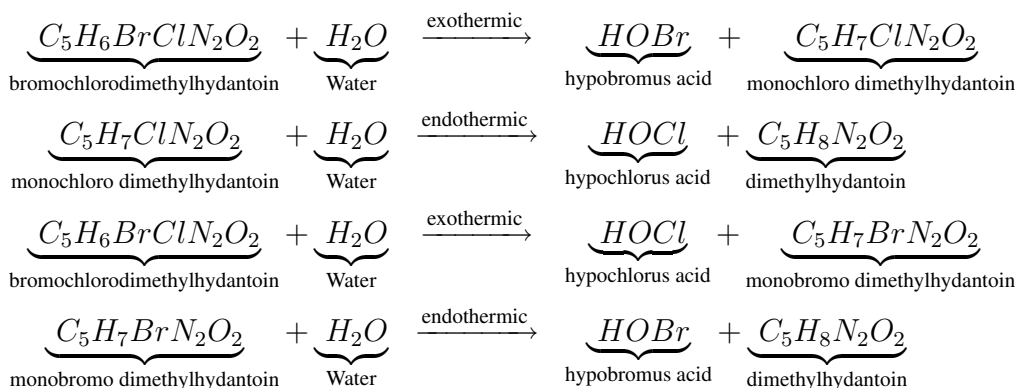


Source: [ioMosaic®](#); All tests were terminated before completion due to ARC preset limits

$Ws^{0.5}/K/m^2$ at room temperature.

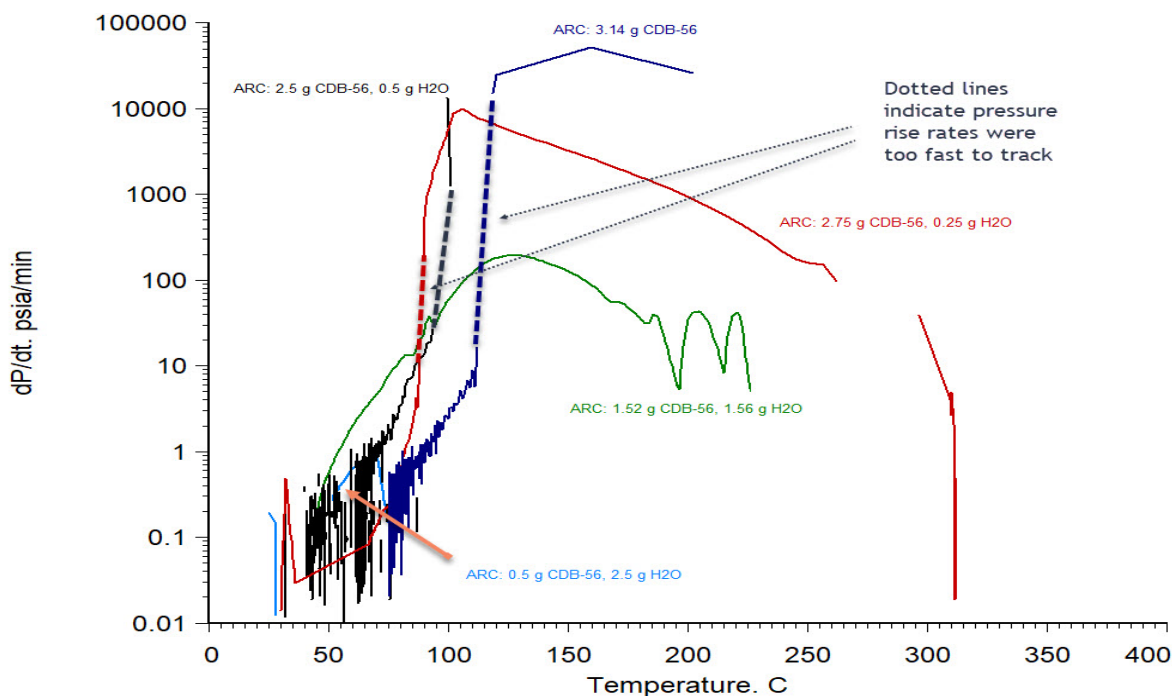
3.3 Bromochlorodimethylhydantoin, BCDMH

The hydrolysis of BCDMH releases bromine and chlorine as hypobromous acid (HOBr) and hypochlorous acid (HOCl). The bromine is released rapidly while the chlorine is released slowly. Analysis of the hydrolysis reactions indicates that HOBr formation is thermodynamically favored:

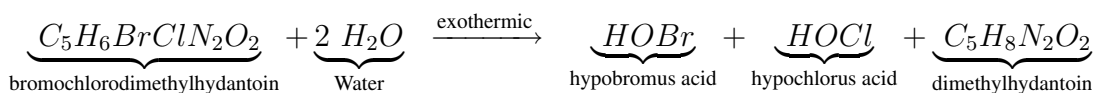


This leads to the following overall hydrolysis reaction:

Figure 12: ARC Measured NaDCC dihydrate decomposition rate $\frac{dP}{dt}$ using different water to NaDCC dihydrate ratios



Source: ioMosaic®; All tests were terminated before completion due to ARC preset limits



When water is well in excess of BCDMH, HOCl and HOBr will react in the water and there will be no free HOCl or HOBr for further reaction with the BCDMH or dimethylhydantoin (DMH). HOCl and HOBr will react with pathogens and disinfect the water, but will be too diluted for further reaction with BCDMH or DMH. ioKinetic® testing for the excess water reaction with BCDMH (67 to 1 water to BCDMH molar ratio) using the ARC, yields a heat of reaction of -27 cal/g of mixture or -162 cal/g of BCDMH. This value is also confirmed by thermochemical estimates using SuperChems® Expert with formation energies independently calculated using quantum chemistry and heat of combustion measurements. Thermochemical estimates in the ideal gas phase using SuperChems® Expert

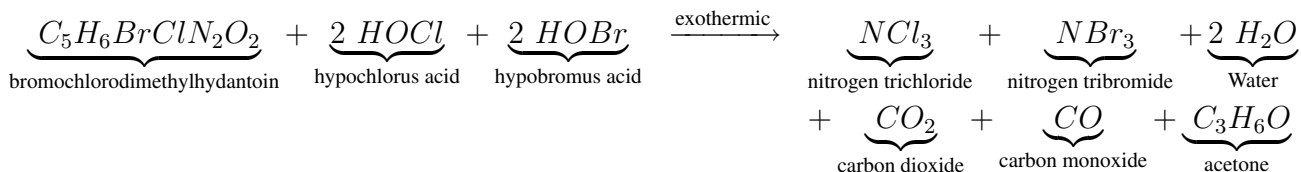
Figure 13: Nitrogen tribromide thermochemistry

** Melhem Index					
Hazard Rating		Heat of reaction		CART	Effective CART
High		-216.66 cal/g		3310.59 K	4171.08 K
		-54.97 kcal/gmol; 1 gmol basis			
Chemical Name		Formula	Phase	Initial Moles	Change
					Final Moles
NITROGEN TRIBROMIDE		NBr3	Vapor	1.0000	-1.0000
NITROGEN		N2	Vapor	0.0000	0.5000
BROMINE-REF		Br2	Vapor	0.0000	1.5000
					1.5000
Other, < 0.0001 moles				0.0000	0.0000
					0.0000
Totals				1.0000	1.0000
					2.0000

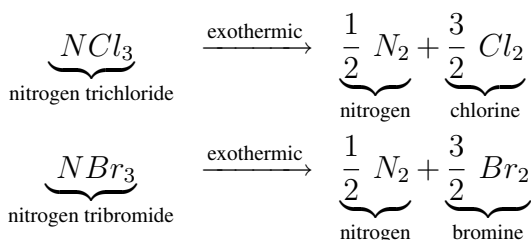
Source: SuperChems® Expert

show a heat of reaction of -51 cal/g of mixture. We note that the ideal gas estimate does not include heat of mixing and/or solution effects. The hydantoin ring in BCDMH and DMH is less stable than the triazine ring in TCCA and cyanuric acid, as confirmed by quantum chemical and heat of combustion estimates of the formation energies.

When BCDMH is well in excess of water, water becomes highly concentrated with HOCl and HOBr and the following reaction leads to the formation of nitrogen trichloride and nitrogen tribromide:



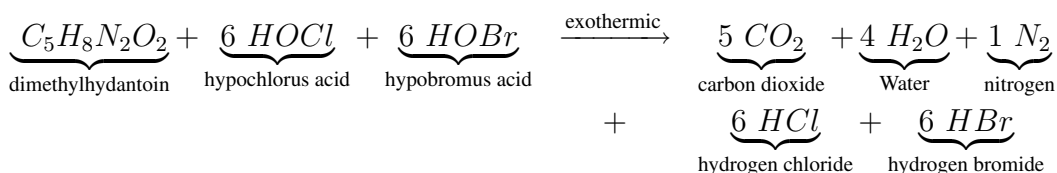
Nitrogen tribromide and nitrogen trichloride, that can also be formed by the decomposition of BCDMH, are highly unstable and can spontaneously decompose exothermically if allowed to accumulate:



Nitrogen trichloride (and possibly nitrogen tribromide) formation is favored by acidic conditions [12] or a low water to BCDMH mass ratio. Under acidic conditions (low pH < 4), nitrogen trichloride (and possibly nitrogen tribromide) formation is favored. Under alkaline conditions (pH > 7), monochloramine formation (or monobromoamine) is favored.

The Calculated Adiabatic Reaction (decomposition) Temperatures (CART) [8, 9, 10, 11] for nitrogen trichloride and nitrogen tribromide are very high (see Figures 3 and 13 which is why they are strong reaction triggers for the decomposition of BCDMH).

DMH will also react with HOCl and HOBr exothermically via one of many potential reaction stoichiometries or pathways. A thermodynamically favorable stoichiometry leading to maximum energy release and minimum Gibbs free energy (equilibrium state) using ideal gas formation energies is:

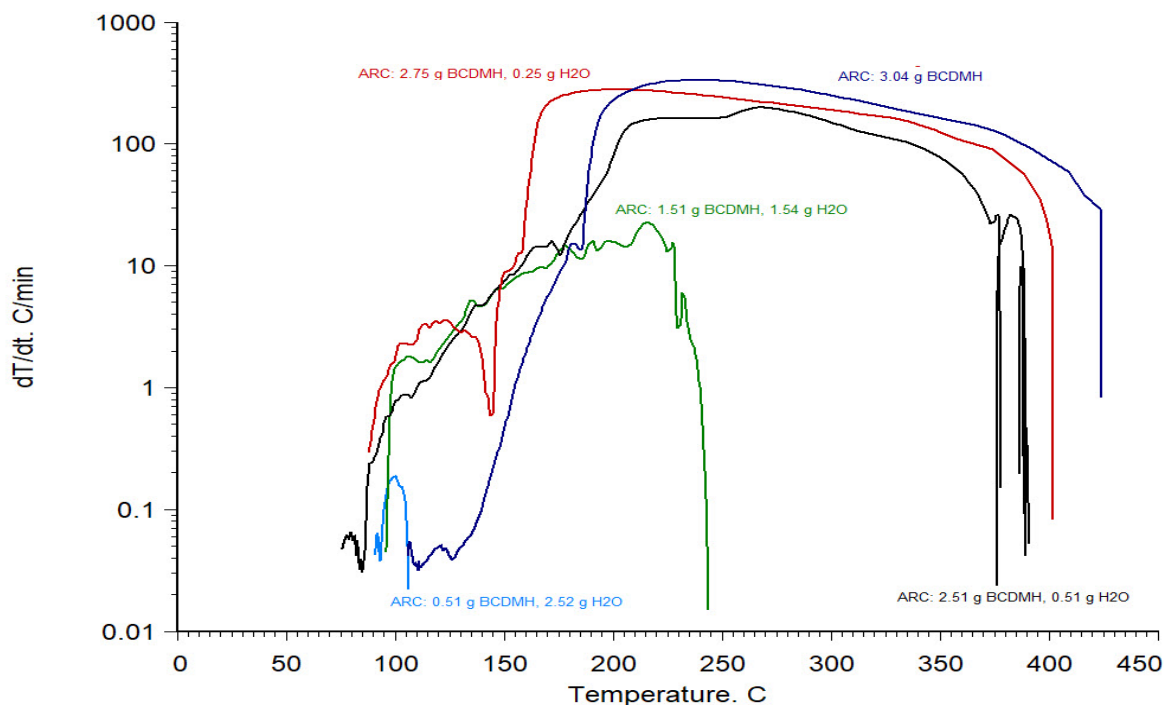


The worst case water to BCDMH molar ratio, is 2 to 1 (or 13 % water mass fraction or 15 %

water to BCDMH mass ratio), or stoichiometric. Numerous calorimetry tests were conducted with varying water to BCDMH mass fractions ranging from 0 % water (100 %BCDMH) to 98.5 % water (67 to 1 water to BCDMH molar ratio).

Heat of combustion testing for BCDMH results ranged from -5042 BTU/lb (-11720 kJ/kg) to -5100 BTU/lb (-11855 kJ/kg). These values are considerably higher than measured heat of combustion values of TCCA and NaDCC. The BCDMH combustion tests resulted in an oily residue. The heat of combustion of BCDMH may also include contributions from the decomposition of BCDMH.

Figure 14: ARC Measured BCDMH decomposition rate $\frac{dT}{dt}$ using different water to BCDMH ratios



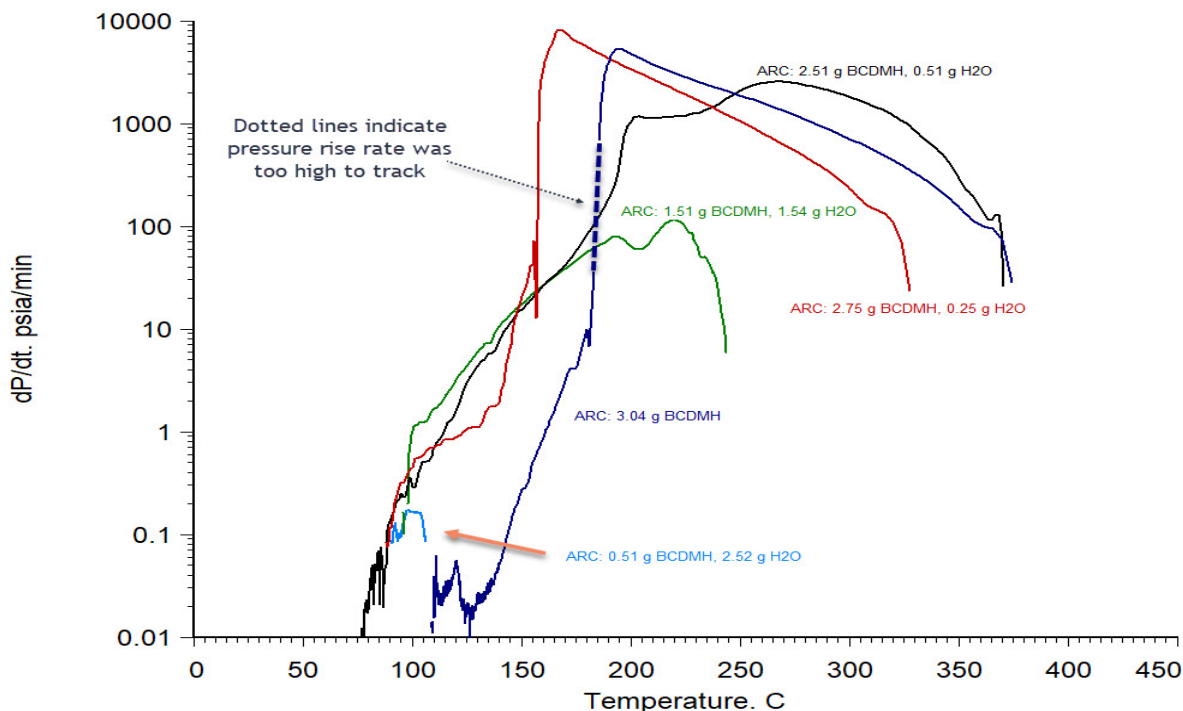
Source: ioMosaic®; Tests terminated due to instrument preset temperature and/or pressure limits

Figures 14 and 15 show the impact of water to BCDMH ratio on the stability and reaction rates of BCDMH and BCDMH with water. When water is well in excess of BCDMH, the overall rates of reactions (dissolution, mixing, and decomposition) are low and would be what is expected when treating large volumes of water with small amounts of BCDMH.

When BCDMH is heated without water, its decomposition temperature is in excess of 100 °C. The data shown in Figures 14 and 15 does not capture the entire decomposition exotherm of BCDMH because the decomposition reaction temperature exceeded the preset ARC temperature limit. The estimated partial heat of decomposition of BCDMH is approximately -191 cal/g BCDMH using a BCDMH heat capacity of 0.25 cal/g. The decomposition of BCDMH can form nitrogen trichloride and nitrogen tribromide that in turn can decompose spontaneously and exothermically to chlorine, bromine, and nitrogen. The heat of decomposition of BCDMH was also measured using DSC (as shown in Figure 16) to be -948 J/g of BCDMH or -227 cal/g of BCDMH.

The near stoichiometric test shows a low detected onset temperature of approximately 76 °C. When

Figure 15: ARC Measured BCDMH decomposition rate $\frac{dP}{dt}$ using different water to BCDMH ratios



Source: ioMosaic®; Tests terminated due to instrument preset temperature and/or pressure limits

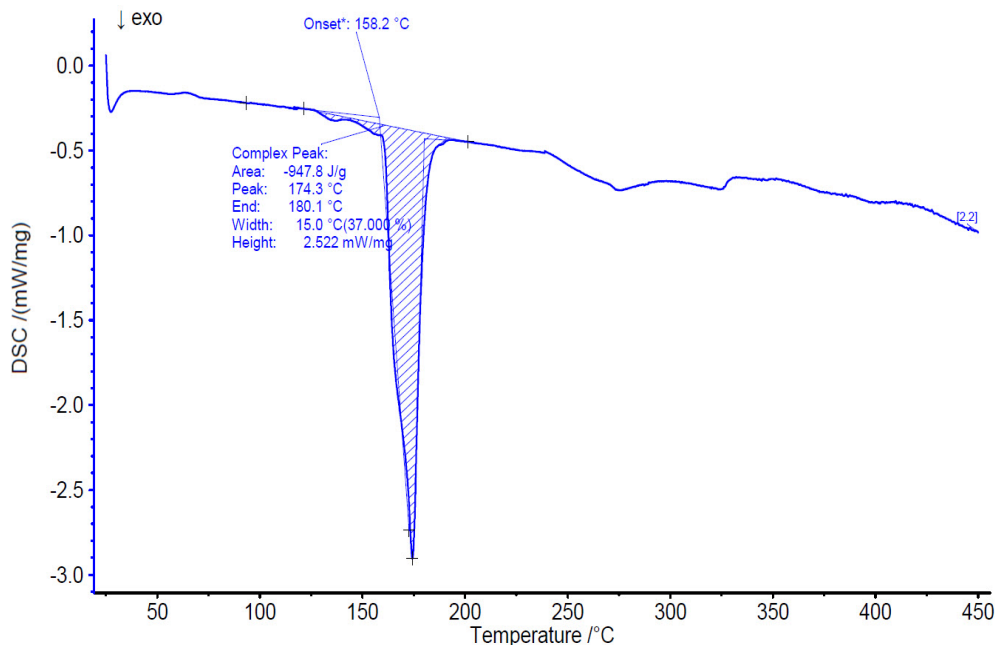
BCDMH is wet and stored in a sealed container, or when stored in bulk in large quantities, severe fires and/or explosions can occur. A three to four feet of BCDMH powder over a crusted wet cake of BCDMH can form [2] a sufficient sealant to permit the formation and accumulation of highly unstable nitrogen trichloride (NCl_3) and nitrogen tribromide (NBr_3). If the concentrations of NCl_3 and/or (NBr_3) get high enough, the spontaneous decomposition of NCl_3 and/or NBr_3 acts as a trigger for the decomposition of BCDMH which can lead to severe fires and/or explosions. It is important to note that BCDMH powders may also be poor conductors of heat.

When confined, the formation and accumulation of nitrogen trichloride or nitrogen tribromide, or the formation of hypochlorous acid or hypobromous acid (followed by formation and accumulation of nitrogen trichloride or nitrogen tribromide) have a profound impact on the hazard potential of BCDMH.

This finding was also reported by Arthur D. Little Inc. (ADL) internal studies ¹¹ on the stability of BCDMH and BCDMH with water in the mid 1990s. The ADL study used the ARC as well as additional testing using heated copper blocks and glass tubes to not only demonstrate the confinement impact on BCDMH potential decomposition/explosion hazards, but also to demonstrate and to visually confirm the impact of having an open system to show the substantial reduction of such hazards.

¹¹These studies were conducted by G. A. Melhem and E. Shanley

Figure 16: BCDMH measured runaway decomposition behavior using DSC under confined conditions



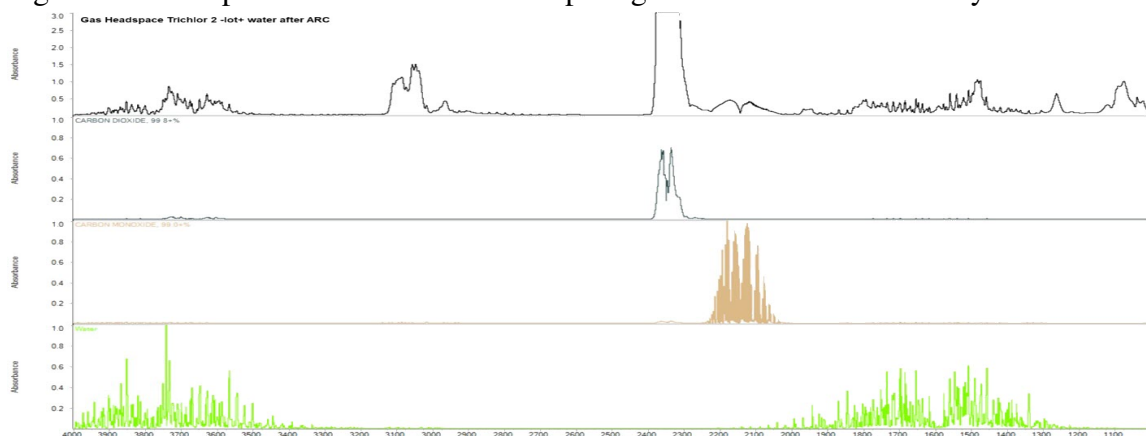
Source: [ioKinetic®](#)

4 GC-MS and FTIR Gas Analysis After The Runaway

Gas Chromatography-Mass Spectrometry (GC-MS) and Fourier Transform Infrared Spectroscopy (FTIR) gas analysis was performed for the headspace gases following [ARC](#) testing. Testing was conducted to evaluate the chemical reactivity of TCCA, Anhydrous NaDCC, NaDCC dihydrate, and BCDMH samples with water. The gas analysis was performed after the [ARC](#) test (near stoichiometric ratio of water to pool chemical) was completed. It should be noted that the headspace gas was sampled after the [ARC](#) run (up to 400 °C) and after cooling, so some reactive species that evolved earlier as the reaction progressed may have already been transformed. Also, the GC-MS can under-report heavier or highly reactive gases due to column retention or surface reactions. The gases were collected in a 500 ml Swagelok® stainless steel sample cylinder.

For the GC-MS analysis, a sample from the cylinder was injected into the GC-MS using a 250 μ l gas-tight syringe. The analysis was performed using a GC-MS system (Agilent 6890N coupled with 5973 MS) equipped with a PLOT column (Agilent J&W PoraBOND Q for volatile solvents and hydrocarbons, 25 m x 0.25 mm x 3 μ m, -100 °C to 300/320 °C). Helium was used as the carrier gas at a 1.5 ml/min flow rate. The oven temperature program started at 40 °C (held for 10 minutes), increased at 10 °C/min to 200 °C, and was then held at the final temperature for 5 minutes. The injector was operated in splitless mode at 200 °C.

For the FTIR analysis, the gas cell was first evacuated, and a background spectrum was recorded. A spectrum of the empty gas cell was then measured to confirm the absence of any residual peaks. Subsequently, the sample cylinder was briefly opened to fill the FTIR gas cell, and the sample

Figure 17: Example of FTIR of **ARC** headspace gases after thermal runaway of TCCA with waterSource: [ioKinetic®](#)

spectrum was acquired.

4.1 TCCA

The headspace after thermal runaway of TCCA with water is dominated by hydrogen chloride, carbon dioxide, and carbon monoxide. All three species are confirmed by FTIR (see Figure 17). HCl shows a band near 2600-3100 cm^{-1} , CO_2 has bands near 2400-2200 and 3740-3540 cm^{-1} , and CO appears near 2250-2050 cm^{-1} . Water is detected by FTIR (broad bands at 4000-3500 and 2000-1250 cm^{-1}).

Other compounds observed by GC-MS (see Figure 18) at lower relative abundance include nitrous oxide and several chlorinated $\text{C}_1 - \text{C}_3$ species and related oxygenates, such as chloromethane, chloroacetic acid, chloroacetaldehyde, 2-chloro-2-nitropropane, chloroform, dichloromethane, chloroacetyl chloride, and 1,2-dichloro-2-methylpropane.

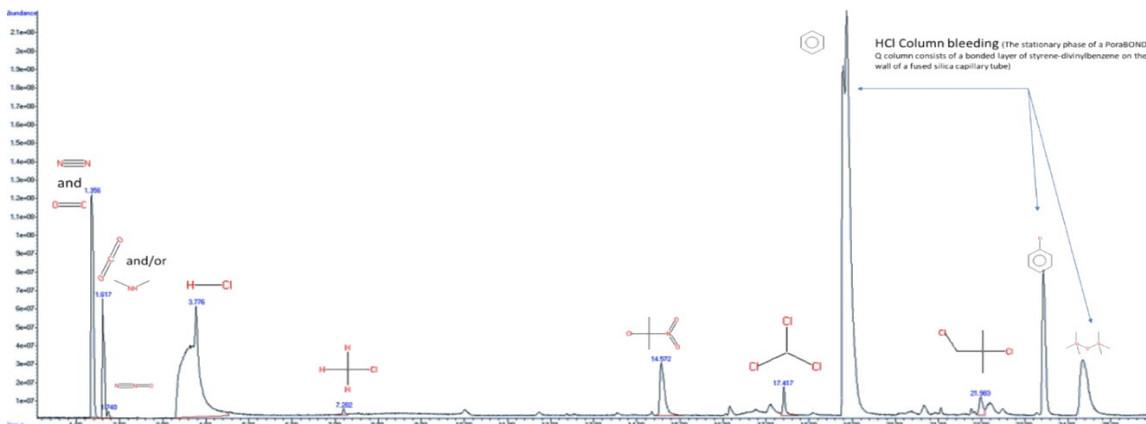
Several GC-MS peaks in the analysis reflected simultaneous elution of two or more compounds, causing mixed spectra and reduced match factors. For example, at 1.4 min the peak contains nitrogen, carbon monoxide, and/or ethylene; at 1.6 min the peak contains carbon dioxide with minor amounts of 2-hydroxy-propanamide and dimethylamine; at 17.4 min the peak comprises chloroform, with co-eluting dichloronitromethane and dichloroacetyl chloride.

4.2 Anhydrous NaDCC

The headspace after thermal runaway of anhydrous NaDCC with water is dominated by carbon dioxide and carbon monoxide. FTIR confirms CO_2 (2400-2200, 3740-3540 cm^{-1}) and CO (2250-2050 cm^{-1}), and also detects water (4000-3500, 2000-1250 cm^{-1}) and hydrogen chloride (2600-3100 cm^{-1}).

Lower-abundance GC-MS species include cyanogen chloride (3.2% at 9.2 min) and acetone (2.5% at 14.6 min). Several GC-MS peaks show co-elution that can depress match factors: at 1.4 min

Figure 18: Example of GC-MS peaks versus retention time of **ARC** headspace gases after thermal runaway of TCCA with water



Source: **ioKinetic**® Agilent MS5973N GC 6890

carbon monoxide co-elutes with nitrogen and/or ethylene; at 1.6 min carbon dioxide overlaps with ethanolamine and methylhydrazine.

4.3 NaDCC dihydrate

The headspace after thermal runaway of NaDCC dihydrate with water is dominated by carbon dioxide, carbon monoxide, and nitrous oxide, with acetone also present at notable levels. FTIR confirms CO_2 (2400-2200, 3740-3540 cm^{-1}) and CO (2250-2050 cm^{-1}), and also detects methane (2850-3170, 1350-1200 cm^{-1}), water (4000-3500, 2000-1250 cm^{-1}), acetone (1250-1150, 1450-1350, 1700-1800, 3100-2850 cm^{-1}), and ethylene (3200-2900 cm^{-1}).

Other GC-MS components at lower abundance include nitrogen, methylhydrazine, cyanogen chloride, acetonitrile, methyl isocyanide, methylene chloride (dichloromethane), and trichloromethane (chloroform). Several GC-MS peaks show simultaneous elution, at 1.4 min: nitrogen, carbon monoxide, and ethylene co-elute; at 1.6 min nitrous oxide, carbon dioxide, and methylhydrazine overlap; at 13.1 min acetonitrile and methyl isocyanide co-elute.

4.4 BCDMH

The headspace after thermal runaway of BCDMH with water is dominated by both propane and acetone, each approximately 28% by area in the GC-MS results, followed by significant carbon dioxide at around 9.6%. FTIR confirms carbon dioxide (2400-2200, 3740-3540 cm^{-1}) and carbon monoxide (2250-2050 cm^{-1}), and also detects methane (2850-3170, 1350-1200 cm^{-1}), water (4000-3500, 2000-1250 cm^{-1}), acetone (1250-1150, 1450-1350, 1700-1800, 3100-2850 cm^{-1}), and propane (3000-2850, 1550-1425, 1425-1300 cm^{-1}).

Lower-abundance GC-MS species include isobutane, cyclopropane, butane, several C_3-C_4 alkenes (including 2-methylpropene (isobutene) and 2-butene), acetonitrile, and traces of halogenated com-

pounds such as chloroform and dichloromethane/bromodichloromethane.

Multiple GC-MS peaks reflect co-elution, leading to mixed spectra and sometimes lower match factors. For instance, at 1.6 minutes, the carbon dioxide peak overlaps with 2-hydroxy-propanamide, methylhydrazine, and dimethylamine. At 2.4 minutes, acetonitrile co-elutes with ethane/ethylene, and at 7.4 minutes, propane overlaps with cyclopropylcarbinol and pentanal.

5 NFPA Water Reactivity Classification

The National Fire Protection Association (NFPA) addresses water reactivity in two standards: NFPA-704 and NFPA-400. The purpose of water-reactivity classification in NFPA-704 is to warn of situations where using water in non-flooding quantities during emergency response could increase or change the hazard posed by a chemical, whereas NFPA-400 sets general facility controls for water-reactive materials.

NFPA 704 Annex F classifies water reactivity by how much heat a material releases on contact with water and whether that reaction drives hazardous gas evolution. When the expected heat release is substantial (Class W2 for heat of mixing between 100 and 600 cal/g and Class W3 for more than 600 cal/g), the barred “W” is required to warn responders against using water in non-flooding quantities. According to Annex F, in fires involving class W2 materials, water “should be used only where it can be applied in flooding quantities (which can be impractical for large piles of solids)” so that water can absorb the heat, quench the reaction, and help control any gases produced. The standard calls for considerable judgment when applying the W because even with low measured heat release, conditions that produce toxic gas or localized boiling when small amounts of water contact large piles can justify assigning W2 to enforce a flooding-only response.

Water reactivity classification also warrants regulations for storage controls per NFPA 400. Class 1 materials are treated more leniently through managing lower maximum allowable quantities (MAQs) and general incompatibility segregation without costly structural modifications. Class 2 and 3 materials, however, trigger prescriptive building exclusions-water-resistant (waterproof) rooms ¹², no floor drains, and no non-fire-protection water piping routed over/through the area unless isolated.

6 Pool Chemicals Water Reactivity Classification

ARC tests showed that partial wetting of TCCA, NaDCC (as dihydrate or anhydrous), or BCDMH in closed systems causes the violent decompositions to start at far less temperature (in some cases at ambient temperature) compared to the dry powder. In all cases, the heat of reactions exceeded the 100 cal/g threshold for W2 classification and was accompanied by rapid pressure build-up from toxic gases.

Except in the case of anhydrous NaDCC, it should be noted that the amount of heat released is

¹²NFPA does not distinguish “water-resistant” from “waterproof”. “water-resistant” and “waterproof” may have different meanings for some specific industrial applications.

not instantaneous or rapid upon contact with water; in fact, the initial contact of these chemicals with water causes an endothermic hydrolysis reaction to produce HOCl and/or HOBr. High concentrations of these acids in small amounts of water and confinement are necessary to trigger the dangerous exothermic decomposition reactions that will follow.

As demonstrated by calorimetry testing earlier, lack of confinement will slow the decomposition or shifts it to higher temperatures as the Cl_2 (gaseous form of HOCl in water) and NCl_3 gases escape the reaction mixture. On this basis, it can be argued that the W2 classification may be overstating the risk and thereby unnecessarily restricting the use of water (the most effective and readily available firefighting agent), which could actually dissipate heat, dilute HOCl, and dissolve toxic gases such as HCl. However, it should be noted that W is a precautionary warning, not an absolute ban on water. It mandates that emergency responders avoid using non-flooding quantities (like hose streams or fog) because limited water could initiate a violent, dangerous reaction.

Water reactivity classification also warrants regulations for storage controls per NFPA 400. Given the severity of the exothermic decomposition and its probable initiation upon wetting, TCCA, NaDCC (as dihydrate or anhydrous), or BCDMH should be classified as W2. As mentioned earlier, W triggers prescriptive building exclusions to prevent unintended water contact and keep spills/runoff out of plumbing and the environment. It should be noted that the CSB investigation updates on the 2024 Bio-Lab (Conyers, GA) fire note recurrent corrosion in the facility fire-protection system, including corroded sprinkler components; investigators also observed corrosion on a sprinkler pipe near the suspected incident origin area. The evidence points to chlorine-driven corrosion of sprinkler pipes, which can breach the system, introduce water, and escalate toward catastrophic outcomes.

7 Should Pool Chemicals be Designated as Water Reactive ?

As mentioned earlier, NFPA-704 proposes a thermal stability indicator for water reactivity, W, in Appendix F [14, 15] for informational purposes only. Where a material shows unusual reactivity with water, the symbol W is to be displayed on the NFPA hazard rating diamond. NFPA-704 water reactivity ratings are shown in Table 1.

The heat of reaction with water is best determined using an adiabatic calorimeter such as the ARC or other screening tools such as the two drop calorimeter [16] using an equal mass ratio of chemical to water (1:1).

NFPA-704 indicates that considerable judgment is required when classifying the water reactivity of chemicals and also warns of cases where use of water in non-flooding quantities during emergency response can increase the hazard. We have demonstrated through calorimetry testing that the most severe water reactivity hazard occurs at stoichiometric water to pool chemical ratios, significantly less than 1:1 water to chemical ratio by weight.

Furthermore, NFPA-704 does not consider the impact of mass confinement on water reactivity classification. As indicated earlier, confinement can be exhibited when wet pool chemicals (small granules and/or powder) are stored in a sealed container or when stored in bulk in large quantities [2] where three to four feet of powder over a crusted wet cake of pool chemicals can form

Table 1: NFPA 704 Rating for degree of water reactivity hazards

Rating	ΔH_{rxn} , cal/g	Description
0	< 30	Non-reactive, below 30 cal/g. Does not require a W to be displayed in the special hazards quadrant.
1	$\geq 30 \ \& \ < 100$	Materials that react vigorously with water, but not violently [†] . Materials whose heat of mixing is at or above 30 cal/g and less than 100 cal/g. Materials that react with water, producing either heat or gas leading to pressurization or toxic or flammable gas hazards.
2	$\geq 100 \ \& \ < 600$	Materials that react violently with water, including the ability to boil water, or that evolve flammable or toxic gas at a sufficient rate to create hazards under emergency response conditions ^{††} . Materials whose heat of mixing is at or above 100 cal/g and less than 600 cal/g.
3	≥ 600	Materials that react explosively with water without requiring heat or confinement ^{††} . Materials whose heat of mixing is greater or equal to 600 cal/g.
4		Not Applicable

†: Criterion most applicable when assigning water reactivity rating to solids because the heat of mixing is determined by physical characteristics and the degree to which the material has dissolved).

††: Qualitative description most applicable when assigning water reactivity ratings to solids because the heat of mixing is determined by physical characteristics and the degree to which the material has dissolved)

a sufficient sealant to permit the formation of highly unstable nitrogen trichloride (NCl_3) and/or nitrogen tribromide (NBr_3). If the concentration of NCl_3 or NBr_3 gets high enough, the spontaneous decomposition of these unstable chemicals acts as a trigger for the decomposition of the pool chemical itself which can lead to severe fires and explosions hazards. As also noted earlier, pool chemicals powders are also poor conductors of heat.

As a result, pool chemicals shipped, stored, or processed in bulk, should carry the NFPA classification of W2. Pool chemicals shipped in sealed containers where sufficient pressure can be built up, regardless of quantity, should also carry the NFPA classification of W2.

8 NFPA-704 vs. NFPA-400, Tactics vs. Prevention

NFPA-704 and NFPA-400 use essentially the same qualitative criteria for water reactivity, but focus on different stages of hazard management. NFPA-704 provides firefighters with information on whether water in use in non-flooding amounts will make a fire worse. NFPA-400 focuses on preventive measures (storage design, separations, MAQs, and operating safeguards).

The case of pool chemicals shows how we should separate firefighters needs (NFPA 704), which tend to be more effective in choosing between two bad scenarios, while NFPA 400 is focused on

risk prevention. For example, relinquishing the W symbol and classifying the material as water-reactive class 1 might aid early fire suppression, but it would also relax NFPA 400 safeguards, likely increasing the frequency of incidents.

9 Should Pool Chemicals be Designated as Class 1 Explosives ?

Pool chemicals are not manufactured to have a pyrotechnic or explosive affects. However, numerous ARC tests (under confinement) show exceedingly high decomposition rates at elevated temperatures for dry pool chemicals and for partially wet pool chemicals. The pressure rise rates are shown in Figures 5, 9, 12, and 15. These pressure rise rates are high enough to be fast deflagration rates and will most likely fail the UN Series Test 2(c)(i) Time/Pressure Test criteria [17] of an overpressure rise from 100 psig to 300 psig in less than 30 ms.

We believe these ARC test results strongly indicate that it is also highly likely that pool chemicals will fail UN Series Test 2(b) Koenen test. The UN Series Test 2(b) Koenen test determines the sensitivity of solid and liquid substances to intense heat under high confinement where the confinement is a steel tube with a specified orifice plate size. The substance is heated within this tube, and the size of the orifice controls the pressure build-up. The violence of the reaction is assessed based on the resulting damage.

The goal of UN Series 2 testing is to determine if a substance is too insensitive to be classified as a Class 1 explosive (see [17] Section 25 and Figures 20.1 (a), 10.2 and 10.3). The use of “defined confinement” ensures the test results are repeatable and provides a standardized method for assessing the substance’s hazardous properties. According to UN Series 2 testing, “defined confinement” is the condition of testing a substance within a specific, rigid enclosure to determine its explosive behavior when subjected to shock, heat, or ignition under pressure. The specific test equipment and conditions define the level of confinement. The tests in this series are designed to evaluate if a substance is too insensitive to be included in the UN Class 1 for explosives. If pool chemicals are designated as Class 1 explosives, there maybe limits on packaging weight or sizes for transportation.

10 Conclusions

This paper conclusively demonstrates that pool chemicals can decompose at elevated temperatures when dry, and can violently decompose when partially wet and confined, or dry and confined. Confinement may be provided by the vessel or by the inertial loading of pool chemical powders/solids overburden or mass.

Pool chemicals fire and explosion hazards are exacerbated when pool chemicals are partially wetted (see Figures 4, 8, 11, and 14), and/or confined as shown by the test data presented in this paper.

The onset of decomposition for partially wet and confined pool chemicals can be as low as ambient temperature. We have provided conclusive measurements indicating that pool chemicals (when confined and/or partially wetted) should be classified as water reactive (W2) and possibly as Class 1 explosives¹³.

¹³Further testing is needed to confirm or refute this proposed classification

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